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Preliminary communication

THE STRUCTURES OF TWO REACTION PRODUCTS OF DITERTIARY-BUTYLACETYLENE WITH DIIRON NONACARBONYL. A NEW IRON—IRON DOUBLE BOND.

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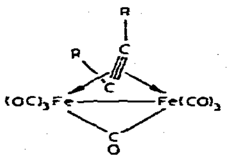
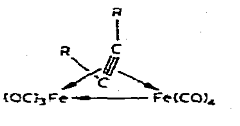
Summary

The reaction of a commercial sample of t-BuC≡C-t-Bu with $Fe_2(CO)_9$ gave two products. One is green $(OC)_3Fe(\mu\text{-t-BuC≡C-t-Bu})Fe(CO)_3$; it contains an Fe=Fe (double) bond with a length of 2.316(4) Å. The other, dark orange, product arises from reaction of $Fe_2(CO)_9$ with the impurity $CH_2{=}C(CH_3)C{\equiv}C\text{-t-Bu}$ (L) and has the formula $(LCO)Fe_2(CO)_6$. The structures of both compounds as obtained from isotropic refinement of X-ray data are reported.

Some years ago W. Hübel et al. explored a great deal of chemistry based on reactions of acetylenes with metal carbonyls, especially iron carbonyls [1]. Two of the more important compounds which are precursors to many of the final products were assigned the formulas $Fe_2(CO)_7(RC{\equiv}CR)$, R = Ph, t-Bu. Both were reported to be dark green and to have IR spectra in the CO stretching region consisting of five bands *in the terminal region only*. Thus, instead of the structure Ia, which would seem (to us at least) to be the "natural" one, structure Ib was suggested in order to reconcile the formula with the absence of a bridging CO band in the IR.



(Ia)



(Ib)

We considered this proposal unconvincing and undertook a reinvestigation. Equimolar amounts of $Fe_2(CO)_9$ and $(t\text{-Bu})_2C_2$ in hexane at 25 °C gave a dark green solution after 24 h. This was concentrated in vacuum and chromatographed on Florisil. The dark green band was evaporated to dryness in vacuum and the solid recrystallized from pentane at −40 °C to give a dark green crystalline product (IR in hexane: 2050, 2005, 1984, 1973(sh), 1968(sh) cm^{-1}). This compound must be the one described by Hübel as $Fe_2(CO)_7[(t\text{-}Bu)_2C_2]$, since its properties appear to be identical to those mentioned by Hübel and, more convincingly, the compound we have obtained by repeating as closely as possible Hübel's preparation is the same substance. However, crystallographic study of this compound shows that it has the formula $Fe_2(CO)_6[(t\text{-}Bu)_2C_2]$, and the structure shown schematically in Fig. 1. The structure, based on 1848 reflections having $|F_O|^2 > 3\sigma(F_O{}^2)$ collected with monochromatized Mo-K_α radiation, using a variable-scan θ—2θ collection procedure, is presently refined to convergence with isotropic temperature parameters for all atoms and the unit-weighted R value is 7.6%. The space group is $P2_1/n$, with $Z = 4$ and the following unit cell dimensions: $a = 13.824(4)$; $b = 9.776(3)$; $c = 13.826(5)$ Å; $\beta = 94.26(2)°$.

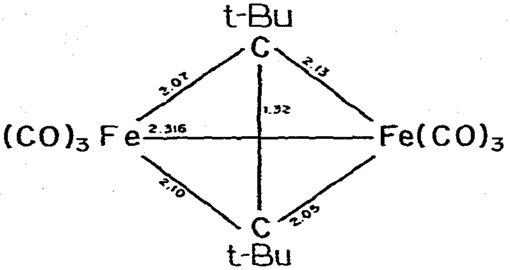


Fig. 1. The molecular structure of $[(t\text{-}Bu)_2C_2]Fe_2(CO)_6$ (I). The slight twist of the acetylenic C—C bond away from orthogonality to the Fe=Fe bond appears to be real, since ESD's on Fe—C bonds are currently about 0.02 Å.

The structure has mirror symmetry though no crystallographic symmetry is imposed; the appearance of only five rather than six terminal CO stretching bands in the IR must be due to overlap or to unusual weakness of one band. Before considering any contribution due to sharing of electrons in Fe to Fe bonding, each iron atom should have six electrons from its three CO groups, two from the acetylene and thus a total, counting its own eight electrons, of 16. The attainment of 18-electron configurations on the iron atoms would therefore require formation of a double bond. The short Fe—Fe distance, 2.316(4) Å, is in accord with this assumption. Another argument leading to the postulation of an Fe—Fe double bond begins by noting the similarity of this compound to $Ph_2C_2Co_2(CO)_6$ [2], in which there is a Co—Co single bond. Since each iron atom has one less electron than a cobalt atom, a double bond is required in the iron compound.

There have been three previous reports of compounds containing doubly bonded iron atoms. The first such compound [3], $Fe_2(t\text{-}BuC{\equiv}C\text{-}t\text{-}Bu)_2(CO)_4$, is related to the one described here in the sense that two terminal CO ligands are replaced by a bridging t-BuC≡C-t-Bu group; the Fe=Fe distance is 2.215 Å. Another $Fe_2(\text{acetylene})_2(CO)_4$ type compound [4], with $\overline{SCH_2CMe_2C{\equiv}CCMe_2CH_2}$ as the acetylene, has Fe=Fe = 2.225 Å. In $(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}NO)_2$ [5], the Fe=Fe distance is 2.326 Å. Two compounds containing Fe≡Fe triple bonds have also been structurally characterized [6, 7]; the metal—metal distances are 2.177 Å and 2.34 Å. It is thus beginning to appear that the formation of multiple bonds between iron atoms may be a phenomenon of some generality.

In the course of preparing compound I very small quantities of a dark orange product, II, were also obtained and separated chromatographically. This compound arises from reaction of $Fe_2(CO)_9$ with about 1% of 2,5,5-trimethylhex-1-ene-3-yne, $CH_2{=}C(CH_3)C{\equiv}CC(CH_3)_3$, present as an impurity in the $(t\text{-}Bu)_2C_2$. The mass spectrum did not exhibit the parent ion peak, M^+, for $C_9H_{14}Fe_2(CO)_7$ but did exhibit peaks for $[M-n(CO)]^+$, with $n = 1\text{-}7$.

The structure of II has also been determined crystallographically using 1930 reflections (Syntex $P\bar{1}$; Mo-K_α). The space group is again $P2_1/n$ with $Z = 4$. Unit cell dimensions are $a = 10.025(4)$; $b = 11.167(4)$; $c = 16.482(8)$ Å, $\beta = 101.94(3)°$. The structure, which has been refined isotropically to a unit weight R of 6.6%, is shown in Fig. 2.

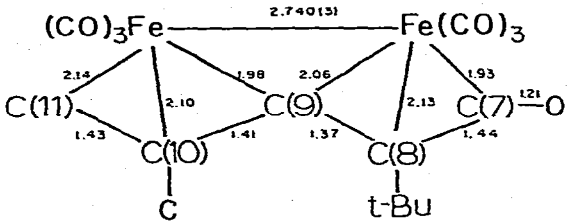


Fig. 2. The molecular structure of $(C_{10}H_{14}O)Fe_2(CO)_6$ (II).

The elements contained in this structure are all conventional, but their juxaposition has some interesting and unusual features. The coordination of a double bond [C(8)—C(9)] β to the Fe(1)—C(7) bond is, to say the least, uncommon. It is possible that the actual electron distribution here is described at least partly by an allylic contribution, i.e., by representing the C(9)—C(8)—C(7)—O portion as C═C═C=O. Another remarkable feature is the presence of a coordinated allyl, C(9)—C(10)—C(11), which has an atom in common with a coordinated olefin, C(9)—C(8), so that C(9) has no hydrogen atom and is bonded to both metal atoms.

A complete report on both these compounds will be published after completion of anisotropic refinements and some chemical studies.

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