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Preliminary communication

A NEW SYNTHESIS OF C-FUNCTIONAL FERROLE COMPLEXES*

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Summary

The reaction of 1-methoxyallenyllithium with $Fe_3(CO)_{12}$, followed by addition of benzoyl chloride, resulted in the formation of a ferrole in which there is a benzoate substituent on the α-carbon atom of the ferracyclopentadiene ring and a methoxy group on the β carbon atom. The structure of the product was determined by X-ray crystallography.

The first preparation of a ferrole was reported in 1953 [1] and since then many other members of this class of organoiron compounds have been reported [2]. In these complexes a 1,1,1-tricarbonyl-1-ferracyclopentadiene ring is bonded to a second $Fe(CO)_3$ group. In all the ferroles which have been examined by X-ray crystallography there is an Fe—Fe bond and in most, but not all, there is also a semi-bridging CO ligand between the two iron atoms. The structure of the simplest member of the ferrole series, $C_4H_4Fe_2(CO)_6$, determined by Dettlaf and Weiss [3], is shown in Fig. 1. The generally applicable methods for the preparation of ferroles involve reactions of alkynes with $Fe_3(CO)_{12}$ or benzalacetonetricarbonyliron, or of thiophenes with $Fe_3(CO)_{12}$. Functionally substituted ferroles, e.g., 1, are obtained in reactions of alkynes with aqueous alkaline solutions of $[HFe(CO)_4]^-$ and further conversions of the reaction products [2]. We report here a new, potentially general route to novel functionally substituted ferroles.

During our ongoing investigations of the preparation and reactions of dinuclear iron carbonyl complexes containing organosulfur ligands [4] we had occasion to study the reaction of $Fe_3(CO)_{12}$ with an allenyllithium reagent, $CH_2=C=C(OCH_3)Li$. This reagent was prepared [5] by the reaction of n-butyllithium (2.34 mmol in hexane) with 2.34 mmol of methoxyallene in 5 ml of

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*Dedicated to an old friend, Professor Erwin Weiss, on the occasion of his 60th birthday, July 9, 1986.

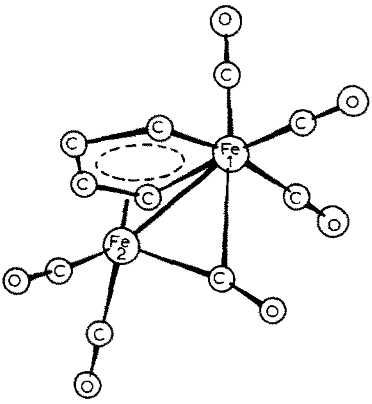
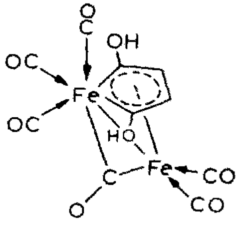


Fig. 1. Molecular structure of the ferrole $C_4H_4Fe_2(CO)_6$ [3].



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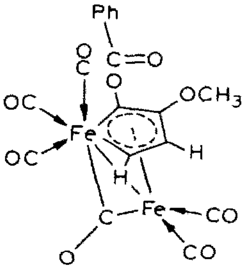

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THF at −78°C (These and all subsequent operations were carried out under nitrogen). The cold reagent solution was added to a solution of 1.98 mmol of $Fe_3(CO)_{12}$ in 40 ml of THF at −78°C. No color change was observed, but as the reaction mixture was allowed to warm to room temperature, a color change from green to dark red was noted. To the reaction mixture then was added 2.58 mmol of benzoyl chloride. After the mixture had been stirred overnight at room temperature, the volatiles were removed at reduced pressure and the residue was taken up in 30/70 by volume CH_2Cl_2/pentane and subjected to silicic acid filtration chromatography. Elution with pentane gave a minor yellow-orange band. Dichloromethane/pentane (1/1 by volume) eluted a yellow band from which 0.277 g of yellow crystals, m.p. 137—138°C (from pentane/ CH_2Cl_2), could be isolated. These represent a 29% yield, based on $Fe_3(CO)_{12}$, of the new ferrole 2. No other products were eluted using more polar solvent mixtures. The identity of the product as 2 was established by analysis (Found: C, 44.77; H, 2.17, $C_{18}H_{10}O_9Fe_2$ calcd.: C, 44.86; H, 2.09%), electron impact mass spectroscopy (ions, inter alia, corresponding to $[M - n\mathrm{CO}]^+$ (n = 1—6)), ^1H and ^{13}C NMR and IR spectroscopy and X-ray diffraction.

^1H NMR (90 MHz, CD_2Cl_2): δ 3.82 (s, 3H, OCH_3), 6.04 (d, J 6.0 Hz, 1H, C(3)H), 6.57 (d, J 6.0 Hz, C(2)H, 1H), 7.20—8.20 (m, 5H, Ph). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ(C) 58.9 (q, J 146.7 Hz, $O(CH_3)$), 91.6 (d, J 170.4 Hz, C(3)), 128.5, 129.9, 133.4 (Ph carbons), 129.2 (s, C(4)), 140.6 (d, J 162.6 Hz, C(2)), 152.1 (s, *ipso* Ph carbon), 164.1 (s, C(6), 205.1, 206.7, 209.1, 211.1 (all s, CO). IR

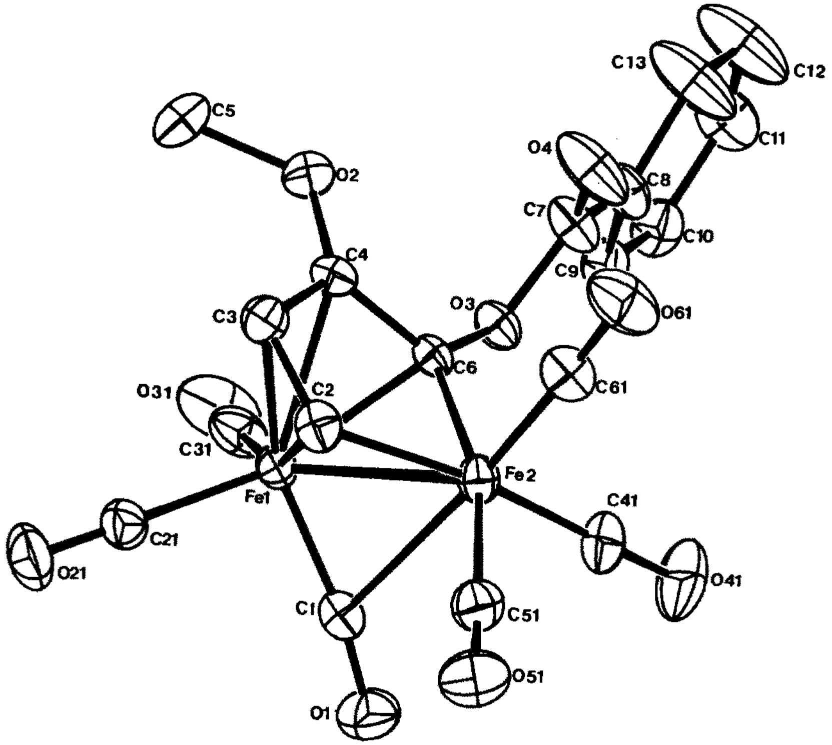


Fig. 2. ORTEP diagram of compound 2 showing the atom labeling scheme and 30% probability thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Fe(1)—Fe(2), 2.522(1); Fe(1)—C(1), 1.776(5); Fe(2)—C(1), 2.596(5); Fe(1)—C(2), 2.077(5); Fe(1)—C(6), 2.066(4); Fe(1)—C(3), 2.128(5); Fe(1)—C(4), 2.177(4); Fe(2)—C(2), 1.955(5); Fe(2)—C(6), 1.920(4); Fe(1)—C(1)—O(1), 169.6(5); Fe(1)—C(2)—Fe(2), 77.4(2); Fe(1)—C(6)—Fe(2), 78.4(1).

(THF, NaCl, cm^{-1}): $\nu(C{\equiv}O)$ 2079(s), 2040(vs), 2004(vs), 1960(m, broad); $\nu(C{=}O)$ 1739(m), 1720(s).

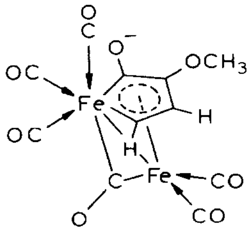
X-ray data were collected at +7°C on an Enraf—Nonius CAD4F-11 diffractometer equipped with a liquid-nitrogen low-temperature device and using Mo-K_α radiation. Data collection, reduction and refinement procedures have been detailed elsewhere [6]. A total of 4448 reflections ($+h$, $+k$, $+l$) were collected in the range $3° \leqslant 2\theta \leqslant 55°$ with 2931 having $F_0 > 4\sigma(F_0)$ being used in the structure refinement which was by full-matrix least-squares techniques (262 variables) using SHELX-76. Final $R_1 = 0.050$ and $R_2 = 0.058$. Hydrogen atoms were ignored; all other atoms were refined anisotropically. A final difference-Fourier map showed no significant features.

Crystal data are: a 12.444(2), b 8.837(2), c 18.429(3) Å, β 105.77(1)°, V 1950.3 $Å^3$, space group $P2_1/a$, $Z = 4$, mol. wt. 481.5 g, ρ (calcd) 1.641 g cm^{-3}, μ 15.0 cm^{-1}. A semi-empirical absorption correction was applied. The structure of 2 is shown in Fig. 2 which gives important bond distances and angles.

We will defer detailed discussion of the structural data until publication of the full paper on our studies in this area. The observed Fe—Fe distance of 2.522(1) Å is at the long end of the range for semi-bridged ferroles (~2.46—2.53 Å) [2]. The Fe(2)—C(1) iron-semi-bridging CO ligand distance of 2.596(5)

Å is longer than that observed in other ferroles of this type reported previously [2]. Also, the Fe(1)—C(1)—O(1) angle, 169.6(5)°, is large. The structure of 2 thus appears to be one intermediate between those few ferroles without and those with a definite semi-bridging CO ligand. This may be the result of the electronic effects of the two oxygen-containing substituents.

The mechanism of formation of 2 in the reaction of $CH_2{=}C{=}C(OCH_3)Li$ with $Fe_3(CO)_{12}$, followed by addition of benzoyl chloride, is a question of some interest since a CO insertion into an Fe—C bond and an apparent hydrogen shift from one carbon atom to the adjacent one are involved. Possible reaction courses can be written, but at this point they are only speculation. In any case, the species in solution at the time the benzoyl chloride was added must be 3, a reactive oxygen nucleophile. Thus introduction of functions other than the ester group is possible. It may be noted that unanticipated formation of ferroles in other kinds of organic ligand reactions in polynuclear iron carbonyl complexes have been encountered by other workers in recent years [7, 8]. However, the preparation reported here should be applicable to other allenyllithium reagents, so that diverse functional ferroles should be accessible*.



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**Supplementary material.* Tables S1 and S2 listing final positional parameters and thermal parameters, and final observed and calculated structure factors are available from D.S.