

Preliminary communication

SYNTHESIS OF A VINYL CARBYNETETRAIRON COMPLEX. CRYSTAL AND MOLECULAR STRUCTURE OF $[(C_5H_5)_2(CO)_2Fe_2(\mu-CO)]_2 \cdot (\mu-C_5H_3)^+ BF_4^-$

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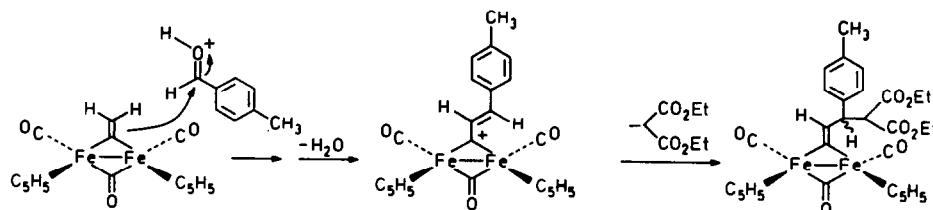
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Summary

The diiron vinyl ether carbyne complex $[(C_5H_5)(CO)Fe]_2(\mu-CO)-(\mu-CCH=CHOCH_2CH_3)^+ BF_4^-$ (1) reacted with the diiron ethenylidene complex $[(C_5H_5)(CO)Fe]_2(\mu-CO)(\mu-C=CH_2)$ (2) to yield the tetrairon complex $[(C_5H_5)_2(CO)_2Fe_2(\mu-CO)]_2(\mu-C_5H_3)^+ BF_4^-$ (3) which was characterized by spectroscopy and by single crystal X-ray diffraction.

Recently we reported the synthesis of vinylcarbynediiron complexes by the condensation of cationic μ -alkylidynediiron complexes with aldehydes, acetone, and orthoesters [1]. We believe that these reactions involve attack of a carbon electrophile (such as a protonated aldehyde) on the electron rich double bond of an intermediate diiron bridging alkenylidene complex. The driving force for the reaction is the formation of a new carbon-carbon bond and of a carbocation stabilized by two electron donor iron centers. We have also found that cationic vinylcarbyne complexes are readily attacked by nucleophiles such as PMe_3 [2] or $NaCH(CO_2CH_2CH_3)_2$ [3] at the remote vinyl carbon atom to generate new bridging alkenylidene complexes. Here we report the coupling of a μ -alkenylidenediiron complex with a cationic vinylcarbyne complex that combines these two types of reactivity to produce a complex in which two diiron groups are joined by a $\mu-C_5H_3$ bridge.



When a solution of $[(C_5H_5)(CO)Fe]_2(\mu-CO)(\mu-CCH=CHOCH_2CH_3)^+BF_4^-$ (1) [1] (200 mg, 0.40 mmol) and $[(C_5H_5)(CO)Fe]_2(\mu-CO)(\mu-C=CH_2)$ (2) [4] (258 mg, 0.76 mmol) were stirred in 40 ml of THF at ambient temperature under N_2 , a coupling reaction took place to generate $[(C_5H_5)_2(CO)_2Fe_2(\mu-CO)]_2(\mu-C_5H_3)^+BF_4^-$ (3). Concentration of the solvent to 10 ml and addition of 50 ml diethyl ether led to the isolation of 3 as pink-brown microcrystals (270 mg, 84%) slightly contaminated with solvent. Analytically pure 3 was obtained by recrystallization from CH_2Cl_2 .

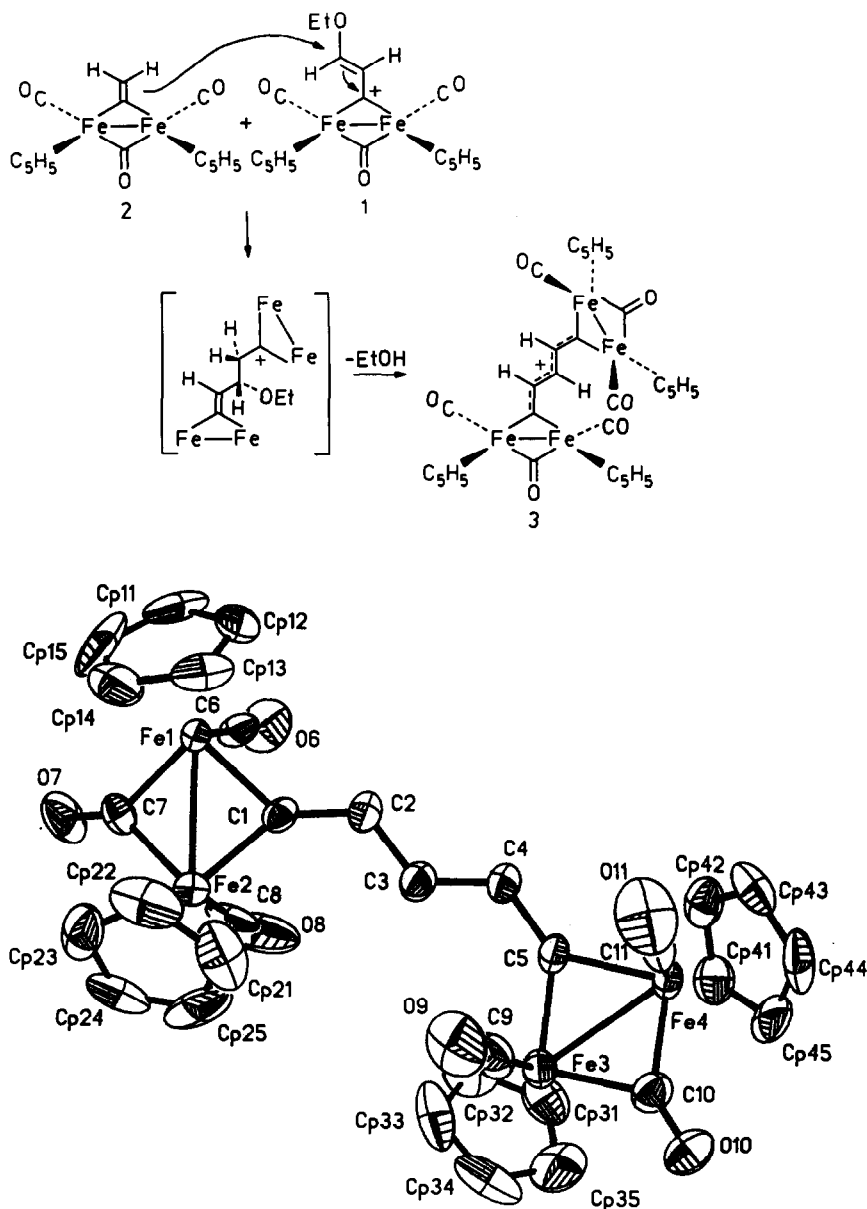


Fig. 1. Structure of 3 with BF_4^- and hydrogens omitted.

3 was readily identified by ^1H NMR. The distinguishing features of 3 in the ^1H NMR are the presence of a two proton doublet at δ 9.10 ppm (J 12.6 Hz, $\mu\text{-C-CH}$) and a one proton triplet at δ 7.73 ppm (J 12.6 Hz, $\mu\text{-C-CH-CH}$). The four C_5H_5 rings give rise to a twenty proton singlet at δ 5.44 ppm at 30°C . Since the X-ray structure of 3 has two different types of C_5H_5 rings, the observation of a single room temperature C_5H_5 resonance implies a fluxional process that interchanges the environment of the C_5H_5 rings [3]. The ^{13}C NMR, IR, and elemental analysis are also consistent with the proposed structure [5].

In order to more closely define the bonding within the five carbon bridge and to determine the stereochemistry at opposite ends of the molecule, we

TABLE 1

SELECTED BOND LENGTHS AND BOND ANGLES FOR 3

Bond Lengths, Å		Bond Lengths, Å		Bond Angles, deg	
Fe(1)—Fe(2)	2.498(5)	Fe(4)—C(5)	1.855(8)	Fe(1)—C(1)—C(2)	134.3(6)
Fe(3)—Fe(4)	2.507(5)	C(1)—C(2)	1.355(11)	Fe(2)—C(1)—C(2)	141.7(6)
Fe(1)—C(1)	1.894(8)	C(2)—C(3)	1.382(11)	Fe(3)—C(5)—C(4)	138.3(6)
Fe(2)—C(1)	1.859(8)	C(3)—C(4)	1.372(11)	Fe(4)—C(5)—C(4)	136.8(6)
Fe(3)—C(5)	1.884(8)	C(4)—C(5)	1.373(11)	C(1)—C(2)—C(3)	124.8(7)
				C(2)—C(3)—C(4)	127.5(7)
				C(3)—C(4)—C(5)	125.0(7)

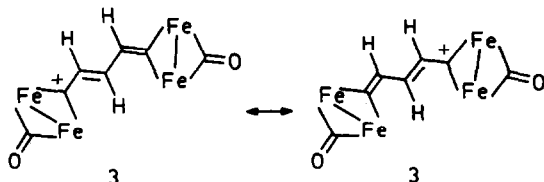
TABLE 2

SUMMARY OF CRYSTAL DATA AND INTENSITY COLLECTION

Empirical formula	$\text{C}_{31}\text{H}_{23}\text{BF}_4\text{Fe}_4\text{O}_6$
Formula weight	801.713
Crystal dimensions, mm	$0.05 \times 0.30 \times 0.80$
Temperature, K	297
Cell parameters, a , Å	8.712 (2)
b , Å	27.598 (9)
c , Å	13.000 (3)
β , deg	98.13 (2)
Space group	$P2_1/c$
Z	4
Density, calcd, g/cm^3	1.72
Absorption correction	Psi-scan method
Absorption coeff. μ , cm^{-1}	18.1
Diffractometer	Nicolet P3/F
Radiation	Graphite-monochromated Mo- K_{α} (λ 0.71073 nm)
Scan range	1 deg below 2θ Mo- $K_{\alpha 1}$ to 1 deg above 2θ Mo- $K_{\alpha 2}$
Scan speed, deg/min	3.5—29.3
Scan type	θ — 2θ
2θ limits, deg	3.00—50.87
$\sin \theta / \lambda_{\text{max}}$, Å^{-1}	0.602
Unique data, theoretical	7092
$F_o > 3\sigma(F_o)$	3716
R	0.068
R_w	0.057
Goodness of fit	1.51
Number of variables	412
Largest peak, final difference map	0.83 e/Å ³

undertook a single crystal X-ray diffraction study [6]. **3** crystallizes as light purple plates in the monoclinic space group $P2_1/c$, a 8.712(2) Å, b 27.598(9), c 13.000(3) Å, β 98.13(2)°, V 3094(1) Å³, and $Z = 4$. The structure of **3** is shown in Fig. 1. Bond lengths and angles for the Fe_4C_5 core are given in Table 1, the crystal data and reference collection is given in Table 2. The remaining bond lengths and angles are similar to those of related structures [1,7,8] and are available as supplementary material [9]. The four iron atoms and the five carbons of the bridging C_5H_3 group lie nearly in the same plane. The maximum deviation from planarity is for Fe(4), 0.22 Å. The *cis*- C_5H_5 ligands of one diiron unit are above the Fe_4C_5 plane and the *cis*- C_5H_5 ligands of the other diiron unit are below the Fe_4C_5 plane. While **3** possesses no crystallographically imposed symmetry, this tetrairon cation possesses a pseudo C_2 axis passing through the center carbon of the μ - C_5H_3 group and lying in the Fe_4C_5 plane.

There are no significant differences between the carbon-carbon bond lengths (1.37 ± 0.01 Å) of the μ - C_5H_3 unit. The similarity of the bond lengths is readily understood in terms of the two equivalent resonance forms for this planar, delocalized π -system.



We believe that the formation of **3** is initiated by attack of the electron rich double bond of ethenylidene complex **2** on the remote vinyl carbon of the cationic vinyl ether carbyne complex **1**. Subsequent loss of ethanol produces **3**.

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References

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- 5 ¹³C {¹H} NMR (50.10 MHz, acetone-*d*₆, 0.07 M Cr(acac)₃) δ 379.1 (μ -C), 259.4 (μ -CO), 210.4 (CO), 156.2 (μ -C-CH-CH), 148.5 (μ -C-CH), 91.2 (C₅H₃). IR (CH₂Cl₂) ν (CO) 2010 (s), 1990 (sh), 1830 (m), 1822 (m) cm⁻¹. Anal. Found: C, 46.30; H, 2.79. C₃₁H₂₃BF₄Fe₄O₆ calcd.: C, 46.44; H, 2.89%.
- 6 Single crystals of **3**, approximate dimensions 0.05 × 0.30 × 0.80 mm³ were obtained by vapor diffusion of diethyl ether into a concentrated solution of **3** in CH₂Cl₂ under N₂ at -15°C. The crystal was attached to the walls of a capillary with grease and sealed under N₂. Data reduction, solution, and refinement of the structure were performed with the SHELXTL structure determination package (Nicolet XRD Corp., Madison, WI).
- 7 C.P. Casey, S.R. Marder and A.L. Rheingold, *Organometallics*, 4 (1985) 762.
- 8 C.P. Casey, P.J. Fagan, and V.W. Day, *J. Am. Chem. Soc.*, 104 (1982) 7360.
- 9 Tables of bond lengths and angles, atomic coordinates, anisotropic thermal parameters, and hydrogen atom coordinates and isotropic thermal parameters. are available as supplementary material from the authors.