

Journal of Organometallic Chemistry, 388 (1990) 169–174
 Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
 JOM 20684

**Synthesis of $\text{Fe}_2(\text{CO})_6(\mu\text{-CRCR}'\text{COEtH})$ complexes
 ($\text{R} = \text{R}' = \text{Ph}$; $\text{R} = \text{Ph}$, $\text{R}' = \text{Me}$). New products resulting
 from the action of $[\text{Et}_3\text{O}][\text{BF}_4]$ on a mixture
 of di- and tri-nuclear anionic iron complexes
 containing a bridging ethene or alkyne ligand**

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(Received December 7th, 1989)

Abstract

The action of $[\text{Et}_3\text{O}][\text{BF}_4]$ with the mixture resulting from the reaction of the $\text{RC}\equiv\text{CR}'$ alkynes ($\text{R} = \text{R}' = \text{Ph}$; $\text{R} = \text{Ph}$, $\text{R}' = \text{Me}$) with $[\text{PPh}_4][\text{HFe}_3(\text{CO})_{11}]$ in boiling THF or acetone leads to the formation of $\text{Fe}_2(\text{CO})_6(\mu\text{-CRCR}'\text{C}(\text{OEt})\text{H})$ complexes as the main products. For the complex with $\text{R}' = \text{Me}$, the X-ray structure of the complex shows that the $\text{Fe}_2(\text{CO})_6$ unit is bridged by the organic fragment, which is $\eta^1\eta^3$ -bonded through the carbons of the chain to the two iron atoms and also bonded to an iron atom through the oxygen of the ethoxy group.

Introduction

During a study of the reactions of the $\text{Fe}_2(\text{CO})_6(\mu\text{-COEt})(\mu\text{-CRCR}'\text{H})$ complexes [1] (**1a**: $\text{R} = \text{R}' = \text{Ph}$, **1b**: $\text{R} = \text{Ph}$, $\text{R}' = \text{Me}$) we thought that a more convenient route to such complexes might be provided by treatment with triethyloxonium salts of the mixture obtained by reaction of $[\text{PPh}_4][\text{HFe}_3(\text{CO})_{11}]$ with alkynes in

boiling acetone [2] with subsequent chromatographic purification. This would avoid the sometimes difficult step of isolating the $[\text{PPh}_4][\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CRCR}'\text{H})]$ (**2a** and **2b**) complexes from the $[\text{PPh}_4][\text{HFe}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{RC}\equiv\text{CR}')]$ compounds. The new procedure was formed not to give **1a** or **1b**, but instead the isomers **3a** and **3b**. An X-ray diffraction study of **3b** showed that it consists of a $\text{Fe}_2(\text{CO})_6$ unit bridged by a CPhCMeC(OEt)H unit, the ethoxy group being *O*-bonded to an iron centre.

Results and discussion

Addition of triethyloxonium tetrafluoroborate to the mixture of **2a** or **2b** and $[\text{PPh}_4][\text{Fe}_3(\text{CO})_9(\mu\text{-H})(\mu^3\text{-}\eta^2\text{RC}\equiv\text{CR}')]$ (**4a** or **4b**) in acetone, followed by purification of the products by chromatography gave $\text{Fe}_3(\text{CO})_9(\mu^3\text{-}\eta^2)(\text{RC}\equiv\text{CR}')$ (**5a** and **5b**) and **3a** or **3b**. The formation of **5a** and **5b** was observed during the study of the reaction of triethyloxonium tetrafluoroborate with **4a** or **4b** in dichloromethane [3]. The outcome is the same when the procedure is carried out in THF solution, but purification of the products is sometimes complicated by polymerization of the solvent.

Complexes **3a** and **3b**, which analyse satisfactorily for $\text{Fe}_2(\text{CO})_6(\text{COEt})(\text{CRCR}'\text{H})$, have quite different infrared spectra in the $\nu(\text{CO})$ stretching region from those of the expected $\text{Fe}_2(\text{CO})_6(\mu\text{-COEt})(\mu\text{-CRCR}'\text{H})$ [1] compounds and those of the product resulting from the coupling of the two bridging ligands [4]. The ^1H NMR data are also different, especially in respect of the resonance of the CH proton, which is shifted from 3.48 ppm for **1a** to 5.8 ppm for **3a**, and from 2.56 ppm for **1b** to 5.0 ppm for **3b**. Moreover in the latter case no coupling of the hydrogen with the Me group is observed. Confirmation of the changed nature of the organic fragments in **3a** and **3b** comes also from the ^{13}C NMR data. There is no evidence of a bridging carbyne ligand and the appearance of a signal at 173.8 ppm for **3a** suggests the presence of a bridging carbene group.

The precise nature of **3b** was established by an X-ray diffraction study. An Ortep view of **3b** is shown in Fig. 1, and values of significant distances and angles are listed in Table 1.

The structure of **3b** consists of a $\text{Fe}_2(\text{CO})_6$ unit, the two iron atoms being at a normal distance for a Fe–Fe single bond [15]. This dinuclear unit is bridged by the organic ligand 1-phenyl-2-methyl, 3-ethoxy-2-propene-1-ylidene, this ligand being bonded to the iron atoms through C(4), C(5), and C(6) and the oxygen atom O(3) of the ethoxy group. In this configuration each iron atom is surrounded by 18 valence electrons. The C(6) carbon atom is nearly equidistant from Fe(1) and Fe(2), and the distances are close to those found in μ -carbene complexes of iron [6]. The Fe(2)–C(4) bond is the shortest of the (C(4)–C(5)–C(6) Fe(2)) bonds.

The O(3)–Fe(1) dative bond has a normal length for this type of bonding [7], and this coordination results in a lengthening of the C(4)–O(3) bond. Moreover the Fe(1)–C(11) distance, as expected for a CO group *trans* to Fe(1)–O(3), is the shortest of the iron carbon distances with the carbonyl groups. The C(4)–C(5) and C(5)–C(6) bond lengths are almost equal, indicating electron delocalization in this fragment.

In summary the action of triethyloxonium tetrafluoroborate on the mixture of the reaction of $\text{PhC}\equiv\text{CPh}$ or $\text{PhC}\equiv\text{CMe}$ with $[\text{HFe}_3(\text{CO})_{11}]^-$ in boiling acetone or

Table 1

Bond lengths (Å) and angles (°) of interest for **3b** with e.s.d.s. in parentheses

Fe(2)...Fe(1)	2.561(1)	C(4)...O(3)	1.434(7)
O(3)...Fe(1)	2.057(3)	C(5)...C(4)	1.438(7)
C(4)...Fe(1)	2.720(5)	C(6)...C(5)	1.420(7)
C(6)...Fe(1)	1.991(5)	C(51)...C(5)	1.508(7)
C(11)...Fe(1)	1.752(6)	C(61)...C(6)	1.488(7)
C(12)...Fe(1)	1.846(6)	C(62)...C(61)	1.398(7)
C(13)...Fe(1)	1.806(6)	C(63)...C(62)	1.397(8)
C(4)...Fe(2)	2.047(5)	C(64)...C(63)	1.380(9)
C(5)...Fe(2)	2.087(5)	C(65)...C(64)	1.375(9)
C(6)...Fe(2)	2.105(5)	C(66)...C(65)	1.409(8)
C(21)...Fe(2)	1.771(6)	O(11)...C(11)	1.162(6)
C(22)...Fe(2)	1.799(6)	O(12)...C(12)	1.137(7)
C(23)...Fe(2)	1.792(6)	O(13)...C(13)	1.145(7)
C(2)...C(1)	1.514(10)	O(21)...C(21)	1.156(7)
O(3)...C(2)	1.488(7)	O(22)...C(22)	1.155(7)
		O(23)...C(23)	1.146(7)
C(11)-Fe(1)-Fe(2)	93.9(2)	O(11)-C(11)-Fe(1)	179.1(5)
C(12)-Fe(1)-Fe(2)	105.8(2)	O(12)-C(12)-Fe(1)	178.6(5)
C(13)-Fe(1)-Fe(2)	150.9(2)	O(13)-C(13)-Fe(1)	175.9(6)
C(21)-Fe(2)-Fe(1)	85.9(2)	O(21)-C(21)-Fe(2)	176.2(5)
C(22)-Fe(2)-Fe(1)	98.2(2)	O(22)-C(22)-Fe(2)	177.3(5)
C(23)-Fe(2)-Fe(1)	167.3(2)	O(23)-C(23)-Fe(2)	179.3(6)
C(23)-Fe(2)-C(21)	99.0(3)	C(5)-C(4)-O(3)	114.7(4)
C(23)-Fe(2)-C(22)	92.5(2)	C(6)-C(5)-C(4)	111.4(4)
O(3)-C(2)-C(1)	107.8(5)	C(51)-C(5)-Fe(2)	125.3(5)
C(2)-O(3)-Fe(1)	125.1(3)	C(51)-C(5)-C(4)	122.1(5)
C(4)-O(3)-Fe(1)	100.9(3)	C(51)-C(5)-C(6)	126.4(5)
C(4)-O(3)-C(2)	111.7(4)	C(61)-C(6)-Fe(2)	131.8(4)
		C(61)-C(6)-C(5)	119.2(4)

tetrahydrofuran gives, as the main product, dinuclear complexes in which the $\text{Fe}_2(\text{CO})_6$ unit is bridged by an organic fragment formed by coupling of the alkyne with a $\text{C}(\text{OEt})\text{H}$ group. The outcome is totally different to that of the action of triethyloxonium salts on **2a** or **2b**.

Experiments designed provide insight into the origin of this change in the nature of the reaction led to the following observations:

(a) Refluxing of a solution of **1a** in acetone or tetrahydrofuran led only to the formation of $\text{Fe}_2(\text{CO})_6(\mu\text{-C}(\text{OEt})\text{C}(\text{Ph})\text{C}(\text{Ph})\text{H})$, the product resulting from the coupling of the carbyne and ethenyl bridges [4].

(b) Ethylation of **2a** in acetone or tetrahydrofuran led to the formation of " $\text{Fe}_2(\text{CO})_6\text{C}(\text{Ph})\text{C}(\text{Ph})$ ", a complex with a ferraindene ring system [3].

(c) Ethylation in dichloromethane of the mixture obtained by refluxing $[\text{PPh}_4][\text{HFe}_3(\text{CO})_{11}]^-$ with the alkyne in THF gave a mixture of **1a** and $\text{Fe}_3(\text{CO})_9(\text{RC}\equiv\text{CR})$.

The results do not reveal the origin of the complexes of type **3** but they are evidently formed only during the alkylation of the mixture generated in acetone or tetrahydrofuran. They may be formed in a complex reaction involving the di- and

tri-nuclear anionic compounds and a coordinating solvent such as acetone or tetrahydrofuran.

Experimental

All reactions were performed under nitrogen by standard Schlenk tube techniques. Infrared spectra were recorded with a Perkin Elmer 225 spectrometer in hexane solution. The ^1H NMR spectra were recorded on a Bruker WH90 spectrometer, and ^{13}C NMR spectra on a Bruker WM250 instrument.

$[\text{PPh}_4][\text{HFe}_3(\text{CO})_{11}]$ was made by a published procedure [8].

Synthesis of **3a**

A mixture of 2 g of $[\text{PPh}_4][\text{HFe}_3(\text{CO})_{11}]$ (2.4 mmol) and 0.43 g of diphenylacetylene (2.4 mmol) in 25 ml of tetrahydrofuran was refluxed for 5 h. The solution was cooled and $[\text{Et}_3\text{O}][\text{BF}_4]$ (0.3 g, 1.6 mmol) was added and the solution was stirred for 2 h. Evaporation of the solvent and chromatography of the residue on a silica gel column gave 0.12 g of **3a** as the main product (20% yield). Anal. Found: C, 53.52; H, 2.91. $\text{C}_{23}\text{H}_{16}\text{Fe}_2\text{O}_7$ calcd.: C, 53.49; H, 3.10%. IR ($\nu(\text{CO})$): 2070 m, 2020 s, 2000 m, 1984 m, 1972 w, 1967 sh cm^{-1} . ^1H NMR (CDCl_3): 7.2 (10 H, Ph), 5.80 (1 H), 3.45 (m, OCH_2), 1.10 (t, J 7 Hz, CH_3) ppm. ^{13}C NMR (CD_2Cl_2) (except phenyl

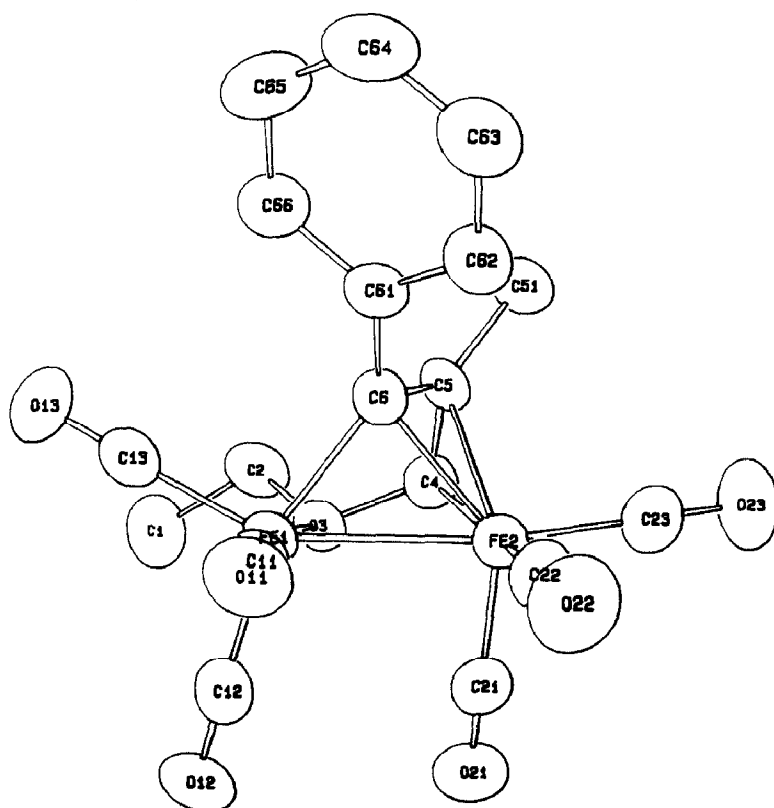


Fig. 1. Ortep view of **3b** showing the atomic numbering scheme.

resonances): 215.4, 213.3, 211.7, 211.3, 206.8, 204, 173.8, 98.6, 95.4 (d, J 186 Hz), 81.9 (t, J 147 Hz), 13.4 (q, J 128 Hz).

Synthesis of **3b**

A THF solution of 2 g of $[\text{PPh}_4][\text{HFe}_3(\text{CO})_{11}]$ (2.4 mmol) and 0.3 ml of $\text{PhC}\equiv\text{CCH}_3$ (3.6 mmol) was refluxed for 5 h. The solution was cooled and $[\text{Et}_3\text{O}][\text{BF}_4]$ (0.3 g, 1.6 mmol) was added and the mixture was stirred for 3 h. Evaporation of the solvent and chromatography of the residue on a silica gel column with benzene as eluant gave 0.16 g of **3b** (30%) as orange crystals after recrystallisation from hexane at -20°C . Anal. Found: C, 47.59; H, 3.02. $\text{C}_8\text{H}_{14}\text{Fe}_2\text{O}_7$ calcd.: C, 47.58; H, 3.08%. IR ($\nu(\text{CO})$): 2065 m, 2017 s, 1997 m, 1988 m, 1965 w, 1960 sh cm^{-1} . ^1H NMR: 7.2 (m, Ph), 5.0 (1 H), 3.0 (m, OCH_2), 1.91 (CH_3), 1.12 (t, J 7.1 Hz, CH_3).

Crystal data for **3b**

$\text{C}_{18}\text{H}_{14}\text{Fe}_2\text{O}_7$: $M = 453.996$, monoclinic, a 14.796(3), b 14.636(3), c 9.234(2) Å, β 105.02(2)°, V 1931 Å³, space group $P2_1/a$, D_c 1.557 g cm⁻³, $Z = 4$, $F(000) = 920$, (Mo- K_α) 0.70169 Å, $\mu(\text{Mo-}K_\alpha)$ 10.79 cm⁻¹.

Table 2

Atomic coordinates ($\times 10^4$) with e.s.d's in parentheses for **3b**

	x	y	z
Fe(1)	1821(1)	6299(1)	901(1)
Fe(2)	899(1)	7216(1)	-1365(1)
C(1)	3165(7)	7700(7)	3883(9)
C(2)	3085(5)	7984(6)	2277(8)
O(3)	2169(3)	7650(3)	1343(4)
C(4)	1961(4)	8016(4)	-147(7)
C(5)	2308(4)	7483(4)	-1195(6)
C(6)	2192(4)	6533(4)	-991(7)
C(51)	2687(5)	7919(5)	-2397(8)
C(61)	2558(4)	5869(4)	-1919(7)
C(62)	2090(5)	5654(5)	-3399(7)
C(63)	2502(6)	5094(5)	-4275(9)
C(64)	3382(6)	4735(6)	-3679(10)
C(65)	3852(5)	4897(5)	-2211(9)
C(66)	3445(4)	5476(5)	-1337(8)
C(11)	1313(4)	5254(5)	200(7)
O(11)	987(4)	4558(3)	-265(6)
C(12)	1134(5)	6364(5)	2304(7)
O(12)	710(4)	6423(4)	3167(6)
C(13)	2885(5)	5750(5)	1941(7)
O(13)	3547(4)	5359(5)	2540(7)
C(21)	192(4)	7573(4)	-188(8)
O(21)	-241(4)	7851(4)	592(6)
C(22)	199(4)	6298(5)	-2364(8)
O(22)	-282(4)	5728(4)	-3006(7)
C(23)	489(5)	8000(5)	-2883(9)
O(23)	232(4)	8499(4)	-3861(7)

Data collection and processing

A tabular crystal ($0.1 \times 0.1 \times 0.15$) was mounted on a Philips PW-1100 four circle diffractometer. Unit-cell parameters were determined from 25 reflections ($6 \geq \theta \geq 12^\circ$) and refined by the least-squares procedure. Intensities were collected with graphite monochromatized Mo- K_α radiation, by the ω -scan technique, with scan width 0.8° and scan speed $0.03^\circ \text{ s}^{-1}$. 2498 independent reflections were measured in the range $2 \leq \theta \leq 25^\circ$; 2419 of which were assumed as observed by applying the condition $I \geq 2.5\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity control and no significant intensity decay was observed. Lorentz-polarization, but not absorption, corrections were made.

Structure analysis and refinement

The structure was solved by direct methods, by use of the MULTAN 80 system of computer programs [9] and refined by full-matrix least-squares, using the SHELX 76 program [10]. The function minimized was $\sum w |F_o| - |F_c|^2$, where $w = (\sigma^2(F_o) + 0.0005 |F_o|^2)^{-1}$. f, f' and f'' were taken from International Tables of Crystallography [11]. H sites were calculated, they were refined with an overall isotropic temperature factor and the remaining atoms anisotropically. The final R was 0.050 ($R_w = 0.057$) for all observed reflections. Atomic coordinates are given in Table 2. Tables of thermal parameters, calculated H positions, and structure factors are available from the authors.

Acknowledgements

R.Y. and J.R. are very grateful to C.I.C.Y.T. of Spain for the financial support.

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