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Synthesis of (μ_3,η^2-vinylidene)(μ-CO)nonacarbonyltriiron complexes

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Abstract

Trinuclear vinylidene complexes of the type (μ_3,η^2-C=CHR^1)(μ-CO)Fe$_3$(CO)$_9$ were prepared from the reactions of 1-bromoalkynes (R^{1}C≡CBr) with [Et$_3$NH][HFe$_3$(CO)$_{11}$]. Structural assignment by the standard analytical and spectroscopic techniques was confirmed by the X-ray crystal structure determination of the phenyl derivative. This molecule, (μ_3,η^2-C=CHPh)(μ-CO)Fe$_3$(CO)$_9$ crystallizes in the triclinic space group $P\bar{1}$ with a 9.254(2) Å, b 12.717(3) Å, c 9.114(1) Å, α 102.15(2)°, β 100.84(1)°, γ 75.45(2)°, V 1004.4 Å^3 and $Z = 2$. On the basis of 3147 unique observations and 280 parameters varied, the structure was refined by full-matrix, least-squares techniques to $R = 0.031$ and $R_w = 0.043$. The three iron atoms form a near equilateral triangle with the vinylidene α carbon atom bonded to all three iron centers by short Fe–C bonds (1.909(2), 1.917(2) and 2.009(2) Å) but with the β carbon bonded only to the apical iron by an unusually long Fe–C bond (2.288(2) Å). Presumably, formation of these products resulted from an intramolecular hydride migration to an initially formed acetylide intermediate.

Introduction

Transition-metal acetylide complexes have been prepared by a variety of methods including the reactions of acetylenes [1], acetylenic Grignard reagents, and sodium or lithium acetylides [2] with metal carbonyls or metal halides. In addition, mono- and bi-nuclear acetylide complexes themselves have been shown to be useful precursors for the synthesis of higher nuclearity and mixed metal acetylide clusters [3]. We recently reported a new method for metal-acetylide synthesis involving the reaction of 1-bromo-1-alkynes (R^{1}C≡CBr) with [(μ-CO)(μ-RS)Fe$_2$(CO)$_6$]$^-$ anions

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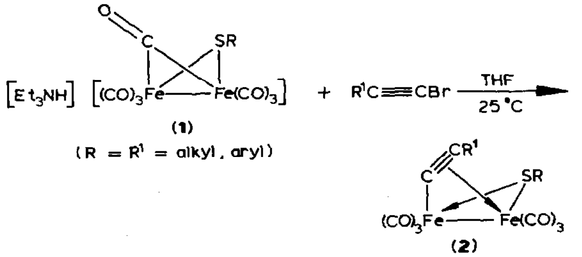
(eq. 1) [4], and in this paper we extend this method to include the reaction of α-bromoalkynes with other iron carbonyl anions. In the first experiments, reaction of phenylbromoacetylene with $Na_2[Fe_2(CO)_8]$ and $[PNN]_2[Fe_3(CO)_{11}]$, only intractable oils were obtained. However, in the subsequent reaction of phenylbromoacetylene with $[Et_3NH][HFe_3(CO)_{11}]$, a stable product was isolated. Since triply bridging acetylide clusters of the type $(\mu_3,\eta^2\text{-C}{\equiv}\text{CR}^1)(\mu\text{-H})Ru_3(CO)_9$ (3), have been reported [1e,1f,5], it was thought that reaction of $R^1C{\equiv}CBr$ with $[HFe_3(CO)_{11}]^-$ would generate analogous trinuclear iron species. Unexpectedly, however, these new iron-acetylide clusters were not formed, but instead, products derived from hydride migration to the acetylenic framework were isolated.

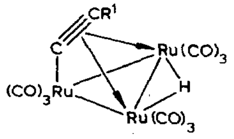


(1)

(R = R¹ = alkyl, aryl)

(2)

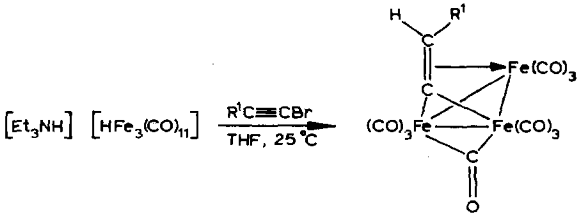
(1)



(3)

Results and discussion

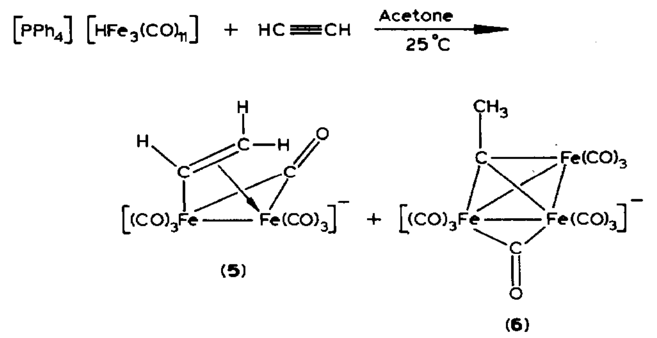
Reaction of $[Et_3NH][HFe_3(CO)_{11}]$ with α-bromoacetylenes, $R^1C{\equiv}CBr$ (R^1 = alkyl, aryl) yielded new trinuclear vinylidene complexes of the type $(\mu_3,\eta^2\text{-C}{=}\text{CHR}^1)(\omega\text{-CO})Fe_3(CO)_9$ (4) (eq. 2). Although initially formed acetylide species may be implicated as transient reaction intermediates, it is likely that intramolecular rearrangement involving the hydride and acetylide ligands occurs, ultimately producing the new vinylidene clusters in moderate yields. Mathieu has observed hydride migration/insertion in the related reaction of acetylene with $[PPh_4][HFe_3(CO)_{11}]$



(2)

(4)

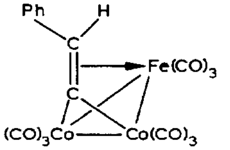
a : R^1 = Ph, 51 %
b : R^1 = CH_3OCH_2, 39 %
c : R^1 = Me_3Si, 17 %
d : R^1 = Et, 47 %
e : R^1 = ^nPr, 48 %
f : R^1 = ^nBu, 44 %



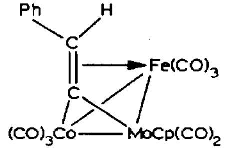
(3)

(5)

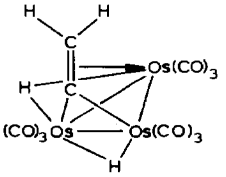
(6)



(7) [7b]



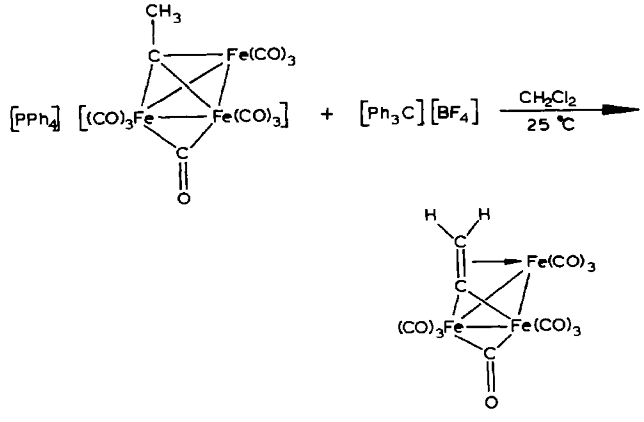
(8) [7b]



(9)[7c]

which yielded anionic μ-vinyl and μ-ethylidyne complexes (eq. 3) [6]. Furthermore, triply bridging vinylidene clusters of the general type **4**, e.g., **7**, **8** and **9** are known [7], in fact, concurrent with this research, Mathieu reported the synthesis of the parent complex of this class, **4g** ($R^1 = H$), by the reaction of $[PPh_4][(\mu_3,\eta^3\text{-}CCH_3)(\mu\text{-}CO)Fe_3(CO)_9]$ with $[Ph_3C][BF_4]$ (eq. 4) [8].

Despite their unexpected formation, characterization of these new μ-vinylidene complexes by the standard spectroscopic and analytical techniques was straightforward. While the carbon/hydrogen combustion analyses and the electron impact mass spectrum of **4a** were useful in ascertaining the chemical composition of these molecules, the coordination of the bridging ligands was determined primarily from the infrared and ^{13}C NMR data (Table 1). Although shifted somewhat to higher frequency than typically expected for μ-CO ligands [12], very strong bands assignable to the bridging carbonyl ligands were observed in the infrared spectra in the region of 1880 cm^{-1}. For most of the complexes, a second bridging carbonyl band also was observed as a shoulder or weak absorption around 1850 cm^{-1}. The appearance of this lower frequency band is puzzling although it may be a solution phenomenon indicative of a relatively slow (at least on the IR time scale) fluxional process equilibrating two or more bridging carbonyl ligands at room temperature. This conclusion is supported by the ^{13}C NMR spectra of **4a–4f**. In all cases, rapid



(4)

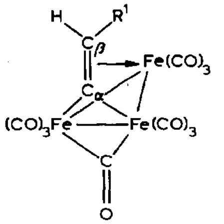
(4g) 50%

exchange of the carbonyl ligands at room temperature is inferred since only one signal is observed in the CO region (δ(C) ~ 211).

As expected, the α-carbon resonances of the bridging carbene ligand are observed as singlets far downfield (δ(C) ~ 288) in the ^{13}C NMR spectra. In comparison, the β-carbon atoms of the vinylidene ligand appear as higher field doublets, δ(C) ~ 100. Furthermore, although the β-vinylidene protons are observed in the corresponding ^{1}H NMR spectra in the region typical for olefinic protons [9], an absorption for a carbon–carbon double bond is not observed in the infrared spectra [9]. Likely, this band is shifted well into the range of carbon–carbon single bonds due to coordination of the vinylidene double bond to the third iron center.

Table 1

IR, ^{1}H NMR, and ^{13}C NMR data for **4**



	R^1	$\nu(\mu$-CO)	δ(H(C$_\beta$))	δ(C$_\alpha$)	δ(C$_\beta$)
4a	Ph	1878vs		274.14(s)	102.73(d)
4b	MeOCH$_2$	1885vs 1850sh	6.06(t)	288.16(s)	95.24(d)
4c	Me$_3$Si	1880s 1842w	5.36(s)	291.95(s)	96.72(d)
4d	Et	1880vs 1850sh	5.69(t)	287.78(s)	105.05(d)
4e	^{n}Pr	1882vs 1850sh	5.74(t)	285.78(s)	101.93(d)
4f	^{n}Bu	1885vs 1860sh	6.04(t)	285.55(s)	102.28(d)

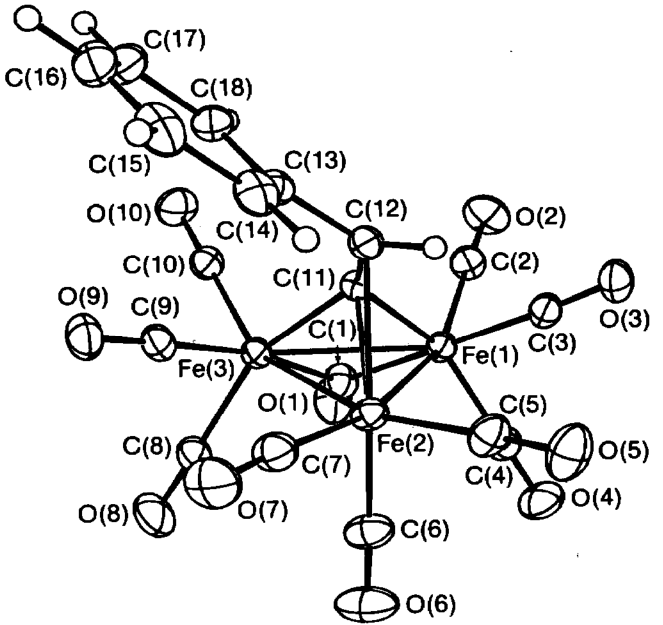


Fig. 1. ORTEP plot of **4a**. Thermal ellipsoids are shown at the 20% level except for hydrogens which are shown artificially small.

The structure of derivative **4a** has been confirmed by X-ray crystallography. An ORTEP plot showing the atom labeling scheme is displayed in Fig. 1 while pertinent bond distances and angles are summarized in Tables 2 and 3, respectively. Fe(1), Fe(2), and Fe(3) define a trinuclear core which is a near equilateral triangle (Fe(1)–Fe(2) 2.5969(5), Fe(1)–Fe(3) 2.5616(5) and Fe(2)–Fe(3) 2.5840(5) Å). Fe(1) and Fe(3) are linked by the symmetrical carbonyl bridge with Fe(1)–C(1) and Fe(3)–C(1) distances of 1.992(3) and 2.014(3) Å, respectively. In addition, the α-carbon atom of the vinylidene ligand (C(11)) bridges Fe(1) and Fe(3) symmetrically with very short "carbene-like" distances of 1.917(2) and 1.909(2) Å, respectively [13]. C(11) is bonded further to the third iron atom, Fe(2), although this

Table 2

Relevant bond distances (Å) for compound **4a**

Fe(1)–Fe(2)	2.5969(5)	Fe(2)–C(12)	2.288(2)	O(7)–C(7)	1.133(3)
Fe(1)–Fe(3)	2.5616(5)	Fe(3)–C(1)	2.014(3)	O(8)–C(8)	1.140(3)
Fe(2)–Fe(3)	2.5840(5)	Fe(3)–C(8)	1.825(3)	O(9)–C(9)	1.142(3)
Fe(1)–C(1)	1.992(3)	Fe(3)–C(9)	1.800(3)	O(10)–C(10)	1.135(3)
Fe(1)–C(2)	1.802(3)	Fe(3)–C(10)	1.801(3)	C(11)–C(12)	1.378(3)
Fe(1)–C(3)	1.788(3)	Fe(3)–C(11)	1.909(2)	C(12)–C(13)	1.485(3)
Fe(1)–C(4)	1.838(3)	O(1)–C(1)	1.154(3)	C(13)–C(14)	1.398(4)
Fe(1)–C(11)	1.917(2)	O(2)–C(2)	1.132(3)	C(13)–C(18)	1.380(4)
Fe(2)–C(5)	1.801(3)	O(3)–C(3)	1.137(3)	C(14)–C(15)	1.399(4)
Fe(2)–C(6)	1.788(3)	O(4)–C(4)	1.128(3)	C(15)–C(16)	1.370(5)
Fe(2)–C(7)	1.794(3)	O(5)–C(5)	1.141(4)	C(16)–C(17)	1.369(5)
Fe(2)–C(11)	2.009(2)	O(6)–C(6)	1.140(4)	C(17)–C(18)	1.387(4)

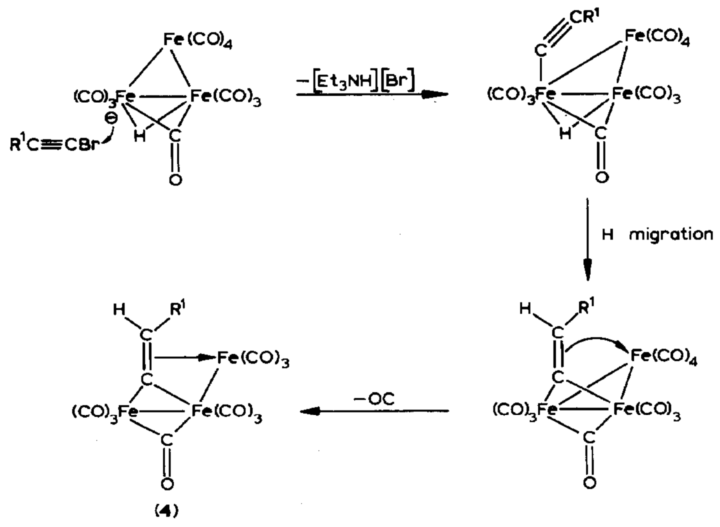
Table 3

Relevant bond angles (°) for compound **4a**

Fe(2)–Fe(1)–Fe(3)	60.12(1)	Fe(3)–Fe(2)–C(12)	77.11(7)	C(10)–Fe(3)–C(11)	100.7(1)
Fe(2)–Fe(1)–C(1)	101.23(9)	C(5)–Fe(2)–C(6)	97.7(2)	Fe(1)–C(1)–Fe(3)	79.5(1)
Fe(2)–Fe(1)–C(2)	154.8(1)	C(5)–Fe–C(7)	92.6(1)	Fe(1)–C(1)–O(1)	141.1(3)
Fe(2)–Fe(1)–C(3)	83.23(8)	C(5)–Fe(2)–C(11)	117.3(1)	Fe(3)–C(1)–O(1)	139.3(3)
Fe(2)–Fe(1)–C(4)	104.13(9)	C(5)–Fe(2)–C(12)	93.6(1)	Fe(1)–C(2)–O(2)	177.6(3)
Fe(2)–Fe(1)–C(11)	50.14(7)	C(6)–Fe(2)–C(7)	95.9(1)	Fe(1)–C(3)–O(3)	176.1(2)
Fe(3)–Fe(1)–C(1)	50.63(8)	C(6)–Fe(2)–C(11)	125.8(1)	Fe(1)–C(4)–O(4)	179.4(3)
Fe(3)–Fe(1)–C(2)	110.38(9)	C(6)–Fe(2)–C(12)	162.5(1)	Fe(2)–C(5)–O(5)	177.6(3)
Fe(3)–Fe(1)–C(3)	133.42(8)	C(7)–Fe(2)–C(11)	120.5(1)	Fe(2)–C(6)–O(6)	177.2(3)
Fe(3)–Fe(2)–C(4)	120.78(9)	C(7)–Fe(2)–C(12)	97.0(1)	Fe(2)–C(7)–O(7)	176.4(3)
Fe(3)–Fe(1)–C(11)	47.83(7)	C(11)–Fe(2)–C(12)	36.66(9)	Fe(3)–C(3)–O(8)	178.5(3)
C(1)–Fe(1)–C(2)	85.9(1)	Fe(1)–Fe(3)–Fe(2)	60.62(1)	Fe(3)–C(9)–O(9)	174.0(3)
C(1)–Fe(1)–C(3)	175.5(1)	Fe(1)–Fe(3)–C(1)	49.85(9)	Fe(3)–C(10)–O(10)	176.8(3)
C(1)–Fe(1)–C(4)	84.4(1)	Fe(1)–Fe(3)–C(8)	118.89(9)	Fe(1)–C(11)–Fe(2)	82.77(9)
C(1)–Fe(1)–C(11)	96.2(1)	Fe(1)–Fe(3)–C(9)	138.35(9)	Fe(1)–C(11)–Fe(3)	84.1(1)
C(2)–Fe(1)–C(3)	90.4(1)	Fe(1)–Fe(3)–C(10)	109.35(9)	Fe(1)–C(11)–C(12)	135.1(2)
C(2)–Fe(1)–C(4)	100.6(1)	Fe(1)–Fe(3)–C(11)	48.11(7)	Fe(2)–C(11)–Fe(3)	82.48(9)
C(2)–Fe(1)–C(11)	105.3(1)	Fe(2)–Fe(3)–C(1)	101.02(9)	Fe(1)–C(11)–C(12)	82.7(2)
C(3)–Fe(1)–C(4)	93.9(1)	Fe(2)–Fe(3)–C(8)	105.6(1)	Fe(3)–C(11)–C(12)	135.2(2)
C(3)–Fe(1)–C(11)	87.2(1)	Fe(2)–Fe(3)–C(9)	82.71(9)	Fe(2)–C(12)–C(11)	60.6(1)
C(4)–Fe(1)–C(11)	154.0(1)	Fe(2)–Fe(3)–C(10)	149.81(9)	Fe(2)–C(12)–C(13)	122.0(2)
Fe(1)–Fe(2)–Fe(3)	59.26(1)	Fe(2)–Fe(3)–C(11)	50.44(7)	C(11)–C(12)–C(13)	124.6(2)
Fe(1)–Fe(2)–C(5)	103.21(9)	C(1)–Fe(3)–C(8)	81.8(1)	C(12)–C(13)–C(14)	121.4(3)
Fe(1)–Fe(2)–C(6)	87.19(9)	C(1)–Fe(3)–C(9)	169.7(1)	C(12)–C(13)–C(18)	119.8(2)
Fe(1)–Fe(2)–C(7)	163.3(1)	C(1)–Fe(3)–C(10)	89.4(1)	C(14)–C(13)–C(18)	118.9(3)
Fe(1)–Fe(2)–C(11)	47.09(7)	C(1)–Fe(3)–C(11)	95.7(1)	C(13)–C(14)–C(15)	119.2(3)
Fe(1)–Fe(2)–C(12)	77.05(6)	C(8)–Fe(3)–C(9)	87.9(1)	C(14)–C(15)–C(16)	120.8(3)
Fe(3)–Fe(2)–C(5)	161.40(9)	C(8)–Fe(3)–C(10)	104.0(1)	C(15)–C(16)–C(17)	120.1(3)
Fe(3)–Fe(2)–C(6)	88.2(1)	C(8)–Fe(3)–C(11)	155.2(1)	C(16)–C(17)–C(18)	119.8(3)
Fe(3)–Fe(2)–C(7)	104.4(1)	C(9)–Fe(3)–C(10)	92.2(1)	C(13)–C(18)–C(17)	121.3(3)
Fe(3)–Fe(2)–C(11)	47.08(7)	C(9)–Fe(3)–C(11)	94.0(1)		

distance, 2.009(2) Å, is nearly 0.1 Å longer. The corresponding Fe(2)–C(12) bond is quite long (2.288(2) Å); however, this is consistent with the structures of other μ_3-vinylidene complexes [7b,d]. As expected, due to π-coordination of the vinylidene ligand, the C(11)–C(12) bond of 1.378(3) Å shows some lengthening from that of an uncoordinated double bond [14], although this effect is certainly not dramatic. Similarly, the C(12)–C(13) distance of 1.485(3) Å is essentially as expected [14] for a carbon–carbon single bond between one sp^2 carbon (C(13)) and one (C(12)) which is intermediate between sp^2 and sp^3. Finally, due to the symmetrical nature of both the carbonyl and vinylidene bridges with respect to the Fe(1)–Fe(3) bond, C(1), O(1), Fe(2), C(11) and C(12) all define a plane from which the largest deviation is only 0.009 Å for C(1). In addition, the dihedral angle between this plane and that defined by Fe(1), Fe(2), and Fe(3) is 89.98(4)°.

A possible mechanism that accounts for the formation of these unexpected vinylidene complexes is outlined in Scheme 1. In analogy to proposed mechanisms for nucleophilic substitution of α-bromoacetylenes [15], the initial step likely results from attack of an iron-centered anion on the bromine atom of the acetylene with eventual elimination of bromide ion and formation of [Et_3NH][Br] (which precipi-



Scheme 1

tates out of solution). Subsequent migration of the hydride ligand to the β-carbon atom of the resulting transient terminal acetylide ligand can lead to formation of a μ_2,η^1-vinylidene complex. Bridging of the vinylidene ligand through the π-electron cloud to the third iron atom then gives **4** with concurrent expulsion of carbon monoxide. In general, vinylidene complexes were isolated from both alkyl and aryl bromoacetylenes. Likely due to steric affects, however, reaction of the bulkier bromoacetylenes led to a diminished product yield in the case of $Me_3SiC{\equiv}CBr$ and no reaction for $^tBuC{\equiv}CBr$. In the reaction of $Me_2NCH_2C{\equiv}CBr$, the desired product was initially observed by TLC. However, this product appeared to be thermally unstable since after a reaction time of 24 h, none of the desired complex was observed.

Experimental

General comments

All reactions were carried out under an atmosphere of prepurified tank nitrogen. Tetrahydrofuran (THF) was distilled under nitrogen from sodium/benzophenone ketyl and purged with nitrogen prior to use. Phenylbromoacetylene ($PhC{\equiv}CBr$), methoxymethylbromoacetylene ($MeOCH_2C{\equiv}CBr$), trimethylsilylbromoacetylene ($Me_3SiC{\equiv}CBr$), ethylbromoacetylene ($EtC{\equiv}CBr$), n-propylbromoacetylene ($^nPrC{\equiv}CBr$), and n-butylbromoacetylene ($^nBuC{\equiv}CBr$) all were prepared by a literature procedure [10] and purged with nitrogen prior to use. Likewise, $[Et_3NH][HFe_3(CO)_{11}]$ was prepared by a literature method [11].

The progress of all reactions was monitored by thin layer chromatography (Baker Flex, Silica Gel 1B-F). Purification by filtration chromatography in which the reaction products were dissolved in a suitable solvent and chromatographed on a bed of EM Science or Sigma 100–300 mesh silicic acid (ca. 200 ml) in a 350 ml glass fritted filter funnel was used in most cases. Further purification by medium pressure column chromatography was accomplished with a 300 × 25 mm column using

Sigma 230-400 mesh silica gel. All chromatography was completed without exclusion of atmospheric moisture or oxygen. Solid products were recrystallized from deoxygenated solvents at −20 °C.

Solution infrared spectra (NaCl windows) were obtained using a Perkin–Elmer Model 1430 double beam grating infrared spectrophotometer. Proton NMR spectra were recorded on either a Bruker WM-250 or a Varian XL-300 NMR spectrometer operating at 250 or 300 MHz, respectively. Carbon-13 NMR spectra were recorded on a Bruker WH-270 or Varian XL-300 spectrometer operating at 67.9 or 75.4 MHz, respectively. Electron impact mass spectra were obtained using a Finnigan-3200 spectrometer operating at 70 eV. Masses were correlated using the following isotopes: ^{1}H, ^{12}C, ^{16}O, and ^{56}Fe. Melting points were determined in air on a Büchi melting point apparatus using analytically pure samples and are uncorrected. Microanalyses were perfomed by Scandinavian Microanalytical Laboratory, Herlev, Denmark.

X-ray crystallography

A saturated solution of **4a** (5/1 v/v pentane/CH_2Cl_2) was filtered through a fine porosity frit and then was concentrated under a stream of nitrogen to about 2/3 of the original volume. Slow cooling to −20 °C in a freezer produced plate-like crystals of **4a** after several days.

A suitable quality, irregularly shaped black crystal of **4a** was mounted on a glass fiber using epoxy resin. Unit cell parameters were obtained from a least-squares analysis of the setting angles of 25 reflections in the range $22.3° \leq 2\theta \leq 25.9°$, which were accurately centered at 22 °C on an Enraf–Nonius CAD4 diffractometer using Mo-K_α radiation. The $\bar{1}$ diffraction symmetry and the lack of systematic absences were consistent with the space groups $P1$ and $P\bar{1}$, the latter of which was ultimately established as the probable one. A cell reduction [16*] failed to show the presence of a higher symmetry cell.

Intensity data in the range $1.0° \leq 2\theta \leq 53.0°$ were collected at 22 °C on the CAD4 diffractometer in the bisecting mode employing the $\omega/2\theta$ scan technique and using graphite monochromated Mo-K_α radiation. Backgrounds were scanned for 25% of the peak width on either end of the peak scan. The intensities of three standard reflections were measured every 1 h of exposure to assess possible crystal decomposition or movement. No significant variations in the standards were detected so no correction was applied. A total of 3877 unique reflections were measured and processed in the usual manner using a value of 0.04 for p [17]. Of these, 3147 were considered to be observed and were used in subsequent calculations.

Table 4 summarizes pertinent crystal data.

The structure was solved in the space group $P\bar{1}$. The iron positions were obtained from the Patterson map and all other atoms were obtained by subsequent least-squares and difference-Fourier calculations. Atomic scattering factors for hydrogen [18] and the other atoms [19] were taken from the usual tabulations; anomalous dispersion terms [20] were included in the calculation of F_c. All hydrogen atoms were located and were input to the least-squares cycle as fixed contributions in their

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* A reference number with an asterisk indicates a note in the list of references.

Table 4

Summary of crystal data and details of intensity collection for compound **4a**

Compound	$Fe_3(CO)_{10}(CCHPh)$
Formula weight	549.78
Space group	$P\bar{1}$ (no.2)
a, Å	9.254(2)
b, Å	12.717(3)
c, Å	9.114(1)
α, deg	102.15(2)
β, deg	100.84(1)
γ, deg	75.45(2)
V, Å^3	1004.4
Z	2
ρ_{calcd}, g/cm^3	1.818
Radiation	Mo-K_α, $\bar{\alpha}$ 0.71069 Å
Detector aperture, mm	$4 \times (3.00 + 1.00 \tan \theta)$
2θ limit, deg	$1.0 \leqslant 2\theta \leqslant 53.0$
Scan type	$\omega/2\theta$
Scan width, deg	$(0.60 + 0.347 \tan \theta)$ in ω
Background	25% on low- and high-angle sides
Unique data collected	3877 (h, $\pm k$, $\pm l$)
Unique data used ($F_o^2 \geqslant 3\sigma(F_o^2)$)	3147
Absorbtion coefficient μ, cm^{-1}	21.904
Range in absorption correction factors	0.690–1.378
Crystal dimensions, mm	$0.28 \times 0.43 \times 0.10$
Final no. of parameters varied	280
Errors in observation of unit weight	1.747
R	0.031
R_w	0.043

idealized positions using C–H distances of 0.95 Å. Although these atoms were not refined, their positions were allowed to "ride" on those of their attached carbon atoms. The hydrogen atoms were assigned isotropic thermal parameters of 1 Å^2 greater than the equivalent isotropic B of their attached carbon atom. All other atoms were refined anisotropically. Absorption corrections were applied to the data using the method of Walker and Stuart [21].

Refinement by full-matrix techniques converged at $R = 0.031$ and $R_w = 0.043$. On the final difference-Fourier map, the largest peak was 0.34 eÅ^{-3}; this can be compared to carbon atom peaks on earlier Fourier maps that had intensities of 4.2–7.7 eÅ^{-3}. The alternate space group $P1$ was rejected owing to the satisfactory refinement in $P\bar{1}$.

Synthesis of $(\mu_3,\eta^2\text{-}C{=}CHPh)(\mu\text{-}CO)Fe_3(CO)_9$

A 200 ml Schlenk flask equipped with a magnetic stir-bar and a rubber septum was charged with 1.73 g (2.99 mmol) of $[Et_3NH][HFe_3(CO)_{11}]$ and subsequently degassed by three evacuation/nitrogen-backfill cycles. The flask then was charged with 30 ml of THF and 0.37 ml (3.00 mmol) of phenylbromoacetylene by syringe at room temperature. Over a period of several hours a gradual color change from purple-red to brown-green was observed along with slow gas evolution (CO) and formation of a white precipitate ($[Et_3NH][Br]$). After the reaction mixture had been

Table 5

Positional parameters and their estimate standard deviation for compound **4a**

Atom	x	y	z	B (Å^2)
Fe(1)	0.30817(4)	0.32493(3)	0.08812(4)	3.392(8)
Fe(2)	0.16392(5)	0.32999(3)	0.30881(4)	3.755(8)
Fe(3)	0.42720(5)	0.20181(3)	0.28796(4)	3.532(8)
O(1)	0.6385(3)	0.3048(2)	0.1850(3)	6.97(7)
O(2)	0.4239(3)	0.2310(3)	−0.2008(3)	7.13(8)
O(3)	0.0068(3)	0.3764(2)	−0.0839(3)	5.18(6)
O(4)	0.3562(3)	0.5520(2)	0.1309(3)	7.19(7)
O(5)	−0.1336(3)	0.4724(2)	0.2328(3)	6.75(7)
O(6)	0.3124(3)	0.5036(2)	0.4862(3)	8.21(8)
O(7)	0.0681(3)	0.2846(2)	0.5729(3)	7.59(7)
O(8)	0.6290(4)	0.2833(2)	0.5581(3)	8.96(9)
O(9)	0.3419(3)	0.0814(2)	0.4882(3)	5.77(6)
O(10)	0.6118(3)	−0.0044(2)	0.1466(3)	6.22(7)
C(1)	0.5214(4)	0.2890(3)	0.1869(4)	4.77(7)
C(2)	0.3813(4)	0.2654(3)	−0.0880(4)	4.57(7)
C(3)	0.1222(3)	0.3592(2)	−0.0239(3)	3.94(6)
C(4)	0.3386(4)	0.4656(3)	0.1152(4)	4.65(7)
C(5)	−0.0178(4)	0.4169(3)	0.2592(4)	4.88(7)
C(6)	0.2561(4)	0.4361(3)	0.4140(4)	5.60(8)
C(7)	0.1064(4)	0.2986(3)	0.4690(4)	4.98(8)
C(8)	0.5511(4)	0.2532(3)	0.4535(4)	5.52(9)
C(9)	0.3670(4)	0.1301(3)	0.4077(3)	4.36(7)
C(10)	0.5439(3)	0.0767(2)	0.2018(3)	4.25(7)
C(11)	0.2462(3)	0.2084(2)	0.1461(3)	3.34(6)
C(12)	0.1105(3)	0.1800(2)	0.1383(3)	3.74(6)
C(13)	0.0931(3)	0.0801(2)	0.1873(3)	3.76(6)
C(14)	−0.0270(3)	0.0832(3)	0.2622(4)	4.84(7)
C(15)	−0.0399(4)	−0.0136(3)	0.3035(4)	5.92(8)
C(16)	0.0617(4)	−0.1110(3)	0.2691(4)	6.01(8)
C(17)	0.1781(4)	−0.1145(3)	0.1939(4)	5.71(9)
C(18)	0.1926(4)	−0.0193(2)	0.1521(4)	4.49(7)

stirred for 20 h at room temperature, the solvent was removed in vacuo and the resulting red-green tar was purified by filtration chromatography. Pentane/CH_2Cl_2 (9/1 v/v) eluted a green band which gave 0.83 g (1.52 mmol; 51%) of (μ_3,η^2-C=CHPh)(μ-CO)$Fe_3(CO)_9$ (**4a**) as an air-stable, green solid, m.p. 103.0–104.0 °C after recrystallization from pentane/CH_2Cl_2.

Anal. Found: C, 39.44; H, 1.18. $C_{18}H_6Fe_3O_{10}$ calcd.: C, 39.32; H, 1.10%.

IR (CCl_4): 3100vw, 3080vw, 2965vs, 2935vs, 2880s, 2870sh, 1878vs (μ-CO), 1604vw (Ph), 1582vw (Ph), 1548vw(Ph), 1498m, 1465m, 1434w, 1382w, 1318vw, 1264w, 1197vw, 1180vw, 1076w, 1030w, 1002vw, 923w, 910vw, 870w, 709s, 700s, 631s, 600vs, 580vs cm^{-1}. Terminal carbonyl region (pentane): 2095m, 2050vs, 2025vs, 1985m, and 1892s (μ-CO) cm^{-1}.

^{1}H NMR (CD_2Cl_2; 250 MHz): δ 7.27–7.56 (m, C_6H_5 and C=C*H*Ph).

^{13}C NMR ($CDCl_3$; 67.9 MHz): δ 102.73 (d, J 158.5 Hz, C=*C*HPh), 128.42 (d, J 165.0 Hz, C_6H_5), 129.51 (d, J 158.6 Hz, C_6H_5), 142.37 (s, *ipso*-C_6H_5), 210.40 (broad s, Fe–CO), 274.14 (s, *C*=CHPh).

Mass Spectrum (EI); m/z (relative intensity): 550 (M^+, 12), 522(M^+ − CO, 25), 494 ($M^+ - 2CO$, 7), 466 ($M^+ - 3CO$, 31), 438 ($M^+ - 4CO$, 42), 410 ($M^+ - 5CO$, 45), 382 ($M^+ - 6CO$, 85), 354 ($M^+ - 7CO$, 73), 326 ($M^+ - 8CO$, 57), 298 ($M^+ - 9CO$, 89), 270 ($M^+ - 10CO$, 100), 214 ($M^+ - 10CO - Fe$, 84), 168 (Fe_3, 9), 158 (FeC=CHPh, 24), 157 (FeC=CPh, 33), 112 (Fe_2, 58), 102 (C=CHPh, 21), 77 (Ph, 3), 56 (Fe, 29).

Synthesis of $(\mu_3,\eta^2\text{-}C{=}CHCH_2OCH_3)(\mu\text{-}CO)Fe_3(CO)_9$

In an experiment similar to the synthesis of **4a**, a THF solution containing 1.46 g (2.53 mmol) of $[Et_3NH][HFe_3(CO)_{11}]$ and 0.38 g (2.53 mmol) of methoxymethylbromoacetylene was stirred for 20 h at room temperature. The solvent then was removed in vacuo, and the resulting black oil was purified by filtration chromatography. Pentane eluted pale green and pale orange bands which were not collected and also a dark green band which gave 0.51 g (0.98 mmol; 39%) of $(\mu_3,\eta^2\text{-C=CHCH}_2\text{OCH}_3)(\mu\text{-CO})\text{Fe}_3(\text{CO})_9$ (**4b**) as a slightly air-sensitive, green oil. Anal. Found: C, 32.68; H, 1.23. $C_{14}H_6Fe_3O_{11}$ calcd.: C, 32.48; H, 1.17%. IR (CCl_4): 2990w, 2960w, 2925w, 2890w, 2820w, 1885vs(μ-CO), 1850sh(μ-CO), 1473w, 1450w, 1410w, 1363vw, 1285vw, 1260w, 1225vw, 1192w, 1115s, 1102s, 1063w, 1020w, 960w, 913w, 680m, 632s, 607vs, 580vs cm^{-1}. Terminal carbonyl region (pentane): 2090w, 2050s, 2020s, 1983w, and 1887w (μ-CO), 1860sh (μ-CO) cm^{-1}.
^1H NMR ($CDCl_3$; 300 MHz): δ 3.52 (s, 3H, OCH_3), 4.04 (m, 2H, CH_2OCH_3), 6.06 (t, J 6.30 Hz, 1H, $C{=}CHCH_2OCH_3$).
^{13}C NMR ($CDCl_3$; 75.4 MHz): δ 58.16 (q, J 141.5 Hz, OCH_3), 78.80 (t, J 137.7 Hz, CH_2OCH_3), 95.24 (d, J 159.0 Hz, $C{=}CHCH_2OCH_3$), 210.44 (s, Fe–CO), 288.16 (s, $C{=}CHCH_2OCH_3$).

Synthesis of $(\mu_3,\eta^2\text{-}C{=}CHSiMe_3)(\mu\text{-}CO)Fe_3(CO)_9$

In an experiment similar to the synthesis of **4a**, a THF solution containing 1.73 g (2.99 mmol) of $[Et_3NH][HFe_3(CO)_{11}]$ and 0.45 ml (2.99 mmol) of trimethylsilylbromoacetylene was stirred for 20 h at room temperature. Then the solvent was removed in vacuo, and the resulting dark red oil was purified by filtration chromatography. Pentane eluted orange and olive green bands which were collected together. The resulting red-brown oil was repurified by column chromatography. Pentane eluted a pale red band which appeared to decompose slowly on the column and was not collected. Pentane then eluted a brown green band which gave 0.28 g (0.52 mmol; 17%) of $(\mu_3,\eta^2\text{-C=CHSiMe}_3)(\mu\text{-CO})\text{Fe}_3(\text{CO})_9$ (**4c**) as a slightly air-sensitive, brown-green oil.
Anal. Found: C, 33.11; H, 2.04. $C_{15}H_{10}Fe_3O_{10}Si$ calcd.: C, 33.00; H, 1.85%.
IR (CCl_4): 2958m, 2925m, 2895m, 1880s(μ-CO), 1842w(μ-CO), 1632w, 1405m, 1370s, 1265m, 1250m, 1215vw, 842vs, 653s, 608vs, 568vs cm^{-1}. Terminal carbonyl region (pentane): 2090m, 2050vs, 2030vs, 2018vs, 1980w, 1973w, and 1880m (μ-CO), 1842vw (μ-CO) cm^{-1}.

^1H NMR ($CDCl_3$; 300 MHz): δ 0.34 (s, 9H, $Si(CH_3)_3$), 5.36 (s, 1H, $C{=}CHSiMe_3$).

^{13}C NMR ($CDCl_3$; 75.4 MHz): δ 0.91 (q, J 120.6 Hz, $Si(CH_3)_3$), 96.72 (d, J 133.8 Hz, $C{=}CHSiMe_3$), 211.34 (s, Fe–CO), 291.95 (s, $C{=}CHSiMe_3$).

Synthesis of $(\mu_3,\eta^2\text{-}C{=}CHEt)(\mu\text{-}CO)Fe_3(CO)_9$

In an experiment similar to the synthesis of **4a**, a THF solution containing 1.85 g (3.20 mmol) of $[Et_3NH][HFe_3(CO)_{11}]$ and 0.64 g (4.80 mmol) of ethylbromoacetylene was stirred for 40 h at room temperature. The solvent then was removed in vacuo, and the resulting dark solid was purified by filtration chromatography. Pentane eluted a pale yellow band which was not collected and also an olive green band which gave 0.75 g (1.49 mmol; 47%) of $(\mu_3,\eta^2\text{-C=CHEt})(\mu\text{-CO})Fe_3(CO)_9$ (**4d**) as a slightly air-sensitive, oily, green solid.

Anal. Found: C, 33.31; H, 1.29. $C_{14}H_6Fe_3O_{10}$ calcd.: C, 33.51; H, 1.20%.

IR (CCl_4): 2965w, 2925w, 2870w, 1880vs (μ-CO), 1850sh (μ-CO), 1453w, 1439w, 1408w, 1381vw, 1315vw, 1285vw, 1260w, 1098w, 1021w, 903w, 863w, 678m, 625vs, 607vs, 580vs cm^{-1}. Terminal carbonyl region (pentane): 2086w, 2042vs, 2028vs, 1979m, and 1885m (μ-CO), 1859sh (μ-CO) cm^{-1}.

^1H NMR (C_6D_6; 300 MHz): δ 0.96 (t, *J* 7.30 Hz, 3H, CH_2CH_3), 1.88 (very broad s, 1H, CH_2CH_3 diastereotopic CH_2), 2.10 (very broad s, 1H, CH_2CH_3 diastereotopic CH_2), 5.69 (t, *J* 6.95 Hz, 1H, $C{=}CHCH_2CH_3$).

^{13}C NMR (acetone-d_6); 75.4 MHz): δ 16.47(q, *J* 126.6 Hz, CH_2CH_3), 35.92 (t, *J* 129.4 Hz, CH_2CH_3), 105.05 (d, *J* 154.9 Hz, C=CHEt), 212.39 (s, Fe–CO). 287.78 (s, C=CHEt).

Synthesis of $(\mu_3,\eta^2\text{-C=CH}^n\text{Pr})(\mu\text{-CO})Fe_3(CO)_9$

In an experiment similar to the synthesis of **4a**, a THF solution containing 1.83 g (3.16 mmol) of $[Et_3NH][HFe_3(CO)_{11}]$ and 0.59 g (4.75 mmol) of n-propylbromoacetylene was stirred for 40 h at room temperature. Then the solvent was removed in vacuo, and the resulting dark green tar was purified by filtration chromatography. Pentane eluted a pale yellow band which was not collected and also an olive green band which gave 0.78 g (1.51 mmol; 48%) of $(\mu_3,\eta^2\text{-C=CH}^n\text{Pr})(\mu\text{-CO})Fe_3(CO)_9$ (**4e**) as a slightly air-sensitive, green oil.

Anal. Found: C, 35.02; H, 1.56. $C_{15}H_8Fe_3O_{10}$ calcd.: C, 34.93; H, 1.56%.

IR (CCl_4): 2980m, 2925vw, 2865w, 1882vs (μ-CO), 1850sh (μ-CO), 1465w, 1453w, 1440w, 1408w, 1380vw, 1340vw, 1295vw, 1260w, 1103w, 1090w, 993w, 963vw, 672s, 625vs, 608vs, 580vs cm^{-1}. Terminal carbonyl region (pentane): 2085w, 2042vs, 2025vs, 1979m, and 1885m (μ-CO), 1858sh (μ-CO) cm^{-1}.

^1H NMR (C_6D_6; 300 MHz): δ 0.81 (t, *J* 7.32 Hz, 3H, $CH_2CH_2CH_3$), 1.40 (m, 2H, $CH_2CH_2CH_3$), 1.99 (overlapping dt, *J* 7.43 Hz, *J* 6.62 Hz, 2H, $CH_2CH_2CH_3$), 5.74 (t, *J* 6.59 Hz, 1 H, $C{=}CHCH_2CH_2CH_3$).

^{13}C NMR ($CDCl_3$; 67.9 MHz): δ 13.54 (q, *J* 125.7 Hz, CH_3), 25.20 (t, *J* 126.6 Hz, $CH_2CH_2CH_3$), 43.92 (t, *J* 128.1 Hz, $CH_2CH_2CH_3$), 101.93 (d, *J* 153.7 Hz, $C{=}CH^nPr$), 211.09 (s, Fe–CO), 285.78 (s, $C{=}CH^nPr$).

Synthesis of $(\mu_3,\eta^2\text{-C=CH}^n\text{Bu})(\mu\text{-CO})Fe_3(CO)_9$

In an experiment similar to the synthesis of **4a**, a THF solution containing 1.74 g (3.01 mmol) of $[Et_3NH][HFe_3(CO)_{11}]$ and 0.39 ml (3.01 mmol) of n-butylbromoacetylene was stirred for 40 h at room temperature. The solvent then was removed in vacuo, and the resulting red-brown oil was purified by filtration chromatography. Pentane eluted a green band which gave 0.70 g (1.32 mmol; 44%) of $(\mu_3,\eta^2\text{-C=CH}^n\text{Bu})(\mu\text{-CO})Fe_3(CO)_9$ (**4f**) as a slightly air-sensitive, green oil.

Anal. Found: C, 36.54; H, 2.05. $C_{16}H_{10}Fe_3O_{10}$ calcd.: C, 36.27; H, 1.90%.

IR (CCl_4): 2955s, 2920s, 2870m, 2855m, 1885vs (μ-CO), 1860sh (μ-CO), 1455w, 1440w, 1408vw, 1380vw, 1290vw, 1260s, 1215vw, 1108w, 1008vw, 925vw, 890vw, 860vw, 695m, 670s, 625vs, 600vs cm^{-1}. Terminal carbonyl region (pentane): 2089m,

2055vs, 2032vs, 2010vs, 2002m, 1975m, and 1885m (μ-CO), 1858sh (μ-CO) cm^{-1}.
^1H NMR ($CDCl_3$; 300 MHz): δ 0.99 (t, J 7.32 Hz, 3H, CH_2CH_3), 1.54 (m, 2H, CH_2), 1.82 (m, 2H, CH_2), 2.39 (m, 2H, CH_2), 6.04 (t, J 6.38 Hz, 1H, $C{=}CHCH_2CH_2CH_2CH_3$).
^{13}C NMR ($CDCl_3$; 75.4 MHz): δ 13.77 (q, J 128.6 Hz, CH_3), 20.68 (t, J 123.3 Hz, $CH_2CH_2CH_2CH_3$), 34.12 (t, J 127.0 Hz, $CH_2CH_2CH_2CH_3$), 41.69 (t, J 129.4 Hz, $CH_2CH_2CH_2CH_3$), 102.28 (d, J 156.2 Hz, $C{=}CH^nBu$), 211.07 (s, Fe–CO), 285.55 (s, $C{=}CH^nBu$).

Supplementary material available. Listings of observed and calculated structure factor amplitudes and tables of anisotropic thermal parameters, and idealized hydrogen parameters (19 pages). Ordering information will be supplied by the authors upon request.

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