



Reactions of $\text{Fe}_3(\text{CO})_{12}$ with 2-methyl-3-butyn-1-ol and 3-pentyn-1-ol under basic methanolic conditions: The crystal structures of $\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-}\eta^2\text{-}[\text{HC}=\text{C}\{\text{C}(\text{CH}_3)_2\}\text{C}(\text{=O})(\text{OCH}_3)])$ and of $(\mu\text{-H})\text{Fe}_3(\text{CO})_9(\mu_3\text{-}\eta^3\text{-}[\text{H}_3\text{CCC}(\text{CH}_2)(\text{CH}_2)\text{CO}]$

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This work is dedicated to the memory of Professor Lamberto Malatesta.

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ABSTRACT

The reactions of $\text{Fe}_3(\text{CO})_{12}$ with 2-methyl-3-butyn-2-ol and 3-pentyn-1-ol in $\text{CH}_3\text{OH}/\text{KOH}$ solution lead, respectively, to the binuclear complex $\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-}\eta^2\text{-}[\text{HC}=\text{C}(\text{CH}_3)_2]\text{C}(\text{=O})(\text{OCH}_3)]$ (as the main product) and to the closed trinuclear hydridic complex $(\mu\text{-H})\text{Fe}_3(\text{CO})_9(\mu_3\text{-}\eta^3\text{-}[\text{H}_3\text{CCC}(\text{CH}_2)(\text{CH}_2)\text{CO}]$ (as the unique product). The oxygenated ligands of these complexes are formed, respectively, by coupling of a formerly coordinated CO with a methoxy group and by coupling of a formerly coordinated CO with a deoxygenated alkyne residual.

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1. Introduction

Functionalized alkynes have been inserted or anchored into silica-based sol–gel materials to form inorganic–organic materials useful for catalysis and other purposes [1]. The reactions of alkynols and alkyne-diols with metal carbonyls have also been exploited to form new silica-based inorganic–organometallic systems; indeed, the OH functionalities can undergo hydrolysis with tetraethyl-orthosilicate [2].

In some instances, however, the alkynols react with the iron or ruthenium carbonyls undergoing modifications or loss of the functionalities [3]. For example, a well established behaviour of alkynols (when reacted with metal carbonyls) is dehydration. Two main dehydration pathways have been found, that is: (a) release of the terminal alkynic hydrogen and of the OH group to give the allenylidene clusters $\text{M}_3(\text{CO})_9(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{-C}=\text{C}=\text{CRR}')$ and (b) loss of the OH and of the hydrogen of an alkynic substituent to give vinyl-acetylide substituted clusters [4]. Also different products are formed when the same alkyne is reacted with $\text{Fe}_3(\text{CO})_{12}$ under thermal or under basic methanolic conditions ($\text{CH}_3\text{OH}/\text{KOH}$ solution, followed by acidification) [3d,3e]; this was expected consider-

ing that, in these conditions, the anion $[\text{HFe}_3(\text{CO})_{11}]^-$ is formed. Finally, the nature of the alkyne (e.g. with the $\text{C}\equiv\text{C}$ in terminal or internal position) also plays an important role [3e,5].

In the above-mentioned reactions new compounds were formed and previously not reported coordination modes of hydrocarbyl fragments to the iron or ruthenium clusters were found. On these grounds, a systematic study of the reactivity of different alkynols with the $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Fe}, \text{Ru}$) carbonyls was undertaken. As a part of this study the behaviour of two isomeric alkynes towards $\text{Fe}_3(\text{CO})_{12}$ is compared: the terminal 2-methyl-3-butyn-2-ol [$\text{HC}\equiv\text{C}(\text{Me})_2\text{OH}$, **mbo**] and the internal 3-pentyn-1-ol [$\text{EtC}\equiv\text{CCH}_2\text{OH}$, **pol**] have been reacted with the iron carbonyl in $\text{CH}_3\text{OH}/\text{KOH}$ solution (followed by acidification with HCl). With **mbo** the main reaction product is $\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-}\eta^2\text{-}[\text{HC}=\text{C}(\text{CH}_3)_2]\text{C}(\text{=O})\text{OCH}_3]$ (complex **1**) containing an acetate ligand formed by coupling of an allenylidene with a coordinated CO and a methoxy group. With **pol** the only product, obtained in good yields, is the hydride $(\mu\text{-H})\text{Fe}_3(\text{CO})_9(\mu_3\text{-}\eta^3\text{-}[\text{H}_3\text{CCC}(\text{CH}_2)(\text{CH}_2)\text{CO}]$ (complex **5**) containing the hydrocarbyl ligand coupled with a coordinated CO to form a heterocyclic organic moiety.

The formation pathways leading to these complexes are discussed in the light of previous findings for the reactions of $\text{Fe}_3(\text{CO})_{12}$ and $[\text{HFe}_3(\text{CO})_{11}]^-$ with alkynols under thermal and basic methanolic conditions.

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2. Experimental

2.1. General experimental details. Analysis of the products

$\text{Fe}_3(\text{CO})_{12}$ (Strem Chemicals) and the alkynes (Lancaster Syntheses) were used as received. Methanol, KOH (pellets) and HCl (37%) were laboratory grade chemicals as the organic solvents (hexane, heptane, diethyl ether). These were dried over sodium (when possible). The reactions were performed under dry nitrogen in conventional three necked flasks equipped with gas inlet, cooler, mercury check valve and magnetic stirring.

For all the reactions in $\text{CH}_3\text{OH}/\text{KOH}$ solution, the “standard” conditions reported in previous works [3] were used. Dissolution of KOH (20 pellets) in 200 cm^3 of CH_3OH , then addition of 5.0 g (ca. 10 mmol) of the iron carbonyl and warming at $40\text{ }^\circ\text{C}$ for 10–15 min; addition of 4.0 cm^3 of the liquid alkynes and warming at $40\text{ }^\circ\text{C}$ for further 15–20 min. After cooling, acidification with HCl (37%) to pH 1. Extraction with three 75 cm^3 portions of *n*-heptane. Reduction to small volume under reduced pressure, then t.l.c. purification [Kieselgel PF Merck, eluents mixtures of light petroleum (40–70 $^\circ\text{C}$) and diethyl ether in variable (v/v) ratios depending on the reaction mixtures]. Extraction of the t.l.c. bands with diethyl ether.

The mixtures from the thermal reactions were filtered under N_2 , brought to small volume under vacuum and chromatographed on t.l.c. plates as described above. The yields of the products (either under basic methanolic and under thermal conditions) are given on the $\text{Fe}_3(\text{CO})_{12}$ consumed.

Elemental analyses were performed in the laboratories of the DiSTA (Università del Piemonte Orientale). The IR spectra (in heptane) were obtained on a Bruker Equinox 55 (KBr cells, path length 0.5 mm). The ^1H and ^{13}C NMR (in CDCl_3) spectra were registered on a JEOL Eclipse 400 (Università del Piemonte Orientale). All the ^{13}C NMR were hydrogen decoupled. The EI-MS spectra were obtained on a Finnigan-Mat TSQ-700 mass spectrometer (Servizio di Spettrometria di Massa, Dipartimento di Scienza e Tecnologia del Farmaco, Università di Torino).

2.2. Reaction of $\text{Fe}_3(\text{CO})_{12}$ with 2-methyl-3-butyn-2-ol

The reaction of $\text{Fe}_3(\text{CO})_{12}$ with **mbo** in hydrocarbons has already been described [6].

2.2.1. In $\text{CH}_3\text{OH}/\text{KOH}$ solution

Chromatography of the red heptane extract showed the presence of the following compounds: yellow (tr, not collected), $\text{Fe}_3(\text{CO})_{12}$ (15%), yellow (tr, not collected), red (25%, complex **1**), yellow (15%, complex **2**).

2.2.1.1. Complex 1. Anal. Calc. for complex **1**: C, 38.71; H, 2.30; Fe, 25.81. Found: C, 38.8; H, 2.4; Fe, 25.9%. M.w. 434. IR: 2103 w, 2073 m, 2060 m, 2045 m, 2029 vs, 1999 s, 1983 s (cm^{-1}). ^1H NMR: 8.50 s, (1H, H_1), 3.80–3.81 d (3H, CH_3 , MeO), 3.48 d (3H, CH_3), 3.32 s (3H, CH_3). EI/MS: M^+ = 434 m/z , loss of seven CO followed by complex fragmentation (including loss of acetate and methoxy fragments).

2.2.1.2. Complex 2. Anal. Calc. for complex **2**: C, 44.7; H, 3.3; Fe, 26.2. Found: C, 45.1; H, 3.4; Fe, 26.2%. $\text{C}_{16}\text{H}_{14}\text{Fe}_2\text{O}_7$, m.w. 430. IR: 2072 s, 2036 vs, 1996 vs(b), 1950 m(b) (cm^{-1}). ^1H NMR: 6.32 d (1H, HC=), 6.09 d (1H, HC=) [$J = 2.3\text{ Hz}$], 4.85 s, 4.74 s (2H, = CH_2), 1.99 s (3H, CH_3), 1.58 s (1H, OH), 1.56 s, 1.52 s (6H, CH_3). EI-MS: M^+ = 430 m/z (low intensity), loss of six CO followed by complex fragmentation. Identified as the “ferrole” $\text{Fe}_2(\text{CO})_6[\text{HC}_2\{\text{C}(\text{Me}_2)(\text{OH})\}\text{HC}_2\{\text{C}(\text{=CH}_2)\text{Me}\}]$ (see Ref. [6]).

2.3. Reactions of $\text{Fe}_3(\text{CO})_{12}$ with pent-3-yn-1-ol (**pol**)

2.3.1. Under thermal conditions

About 3.0 g (ca. 6 mmol) of $\text{Fe}_3(\text{CO})_{12}$ were suspended in heptane under N_2 and 1.5 cm^3 (ca. 18 mmol) of **pol** were added. After reflux (8 min to reflux plus 6 min reflux), chromatography of the brown solution showed the presence of the following products: brown (15%, complex **3**), $\text{Fe}_3(\text{CO})_{12}$ (10%), red (10%, complex **4**).

2.3.1.1. Complex 3. Anal. Calc. for complex **3**: C, 31.58; H, 1.50; Fe, 31.58. Found: C, 33.6; H, 1.6; Fe, 31.6%. IR: 2091 w, 2048 s, 2032 vs, 2007 m(sh), 1992 m, 1883 w (cm^{-1}). ^1H NMR: 3.67 s (2H, CH_2), 2.39 s (2H, CH_2), 2.21 s (1H, OH), 1.79 s (3H, CH_3). EI-MS: M^+ = 532 m/z , loss of 10 CO. Identified as $\text{Fe}_3(\text{CO})_9(\mu\text{-CO})[\text{EtC}\equiv\text{C}-\text{CH}_2\text{OH}]$ with a parallel alkyne.

2.3.1.2. Complex 4. Anal. Calc. for complex **4**: C, 36.73; H, 2.04; Fe, 28.57. Found: C, 36.8; H, 2.1; Fe, 28.6%. IR: 2088 m-s, 2052 vs, 2034 s(sh), 2021 s, 1999 vs (sh), 1948 w, 1741 m, 1700 w (cm^{-1}). ^1H NMR: 4.50 mm (2H, CH_2), 3.48 q (3H, CH_3), 2.20 m (3H, CH_3). EI-MS: M^+ = 392, loss of six CO, followed by competitive fragmentation with loss of CO and iron fragments. Identified as $\text{Fe}_2(\text{CO})_6[\text{EtC}_2(\text{CH}_3)\text{C}(\text{=O})\text{O}]$ “ferrole” (see Section 3).

2.3.2. In $\text{CH}_3\text{OH}/\text{KOH}$ solution

Chromatography of the yellow-brown heptane solution yielded the following complexes: $\text{Fe}_3(\text{CO})_{12}$ (15%), purple (45%, complex **5**) and trace amounts of other complexes (not collected).

2.3.2.1. Complex 5. Anal. Calc. for complex **5**: C, 34.88; H, 1.5; Fe, 32.56. Found: C, 34.9; H, 1.6; Fe, 32.6%. IR: 2093 m, 2036 vs, 2014 s, 1982 m (cm^{-1}). ^1H NMR: 4.60 tt (2H, CH_2), 3.81 d (2H, CH_2), 1.30 s (3H, CH_3), –28.03 (1H, hydride). ^{13}C NMR (C_6D_6): 14.8 (CH_3), 29.0 (CH_2), 42.6 (CH_2), 76.9 (CMe), 186.6 (C–O), 212.2 m(broad) [fluxional CO's]. EI-MS: M^+ 516 m/z (low intensity), loss of 10 CO.

2.4. Reaction of $\text{Fe}_3(\text{CO})_9(\mu\text{-CO})(\text{C}\equiv\text{CMe}_2)$ (complex **a**) with methanol

About 0.2 g (0.4 mmol) of the complex (obtained from the thermal reaction of $\text{Fe}_3(\text{CO})_{12}$ with **mbo**) [6] were dissolved in 10 cm^3 of neat methanol and 0.2 cm^3 of HCl (37%) were added. After 10 min reflux about 50% of the parent complex, 35% of complex **1** and some decomposition were observed on the t.l.c. plates.

2.5. X-ray structural analysis of complex **1**

Crystal data and refinement parameters are reported in Table 1. The reflection data have been corrected semi-empirically for absorption, based on symmetry equivalent reflections. All non-hydrogen atoms were refined anisotropically. The methyl hydrogen atoms were found in the last difference maps; it was however preferred to calculate and refine their coordinates with U_{iso} set at 1.2 times U_{eq} of the corresponding C atom. The H atom bonded to C(3) was found on the difference maps and refined with free coordinates and free U_{iso} . The programs used were SHELXTL [8] for structure solution, refinement and molecular graphics, CrysAlis CCD (data collection), CrysAlis RED (data reduction and empirical absorption correction) [7].

2.6. X-ray structural analysis of complex **5**

Crystal data and refinement parameters are reported in Table 1. The reflection data have been corrected semi-empirically for absorption, based on symmetry equivalent reflections. The asym-

Table 1

Crystal data and details of data collection and structure refinement for $\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-}\eta^2\text{-}[\text{HCC}(\text{C}(\text{CH}_3)_2)\text{C}(\text{O})(\text{OCH}_3)])$ (complex **1**) and for $(\mu\text{-H})\text{Fe}_3(\text{CO})_9(\mu_3\text{-}\eta^3\text{-}[\text{H}_3\text{CCC}(\text{CH}_2)(\text{CH}_2)\text{CO}])$ (complex **5**)

	Complex 1	Complex 5
Chemical formula	$\text{C}_{14}\text{H}_{10}\text{O}_9\text{Fe}_2$	$\text{C}_{15}\text{H}_8\text{O}_{10}\text{Fe}_3$
Formula weight	433.92	515.76
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	6.6301(3)	9.1149(10)
b (Å)	18.0154(9)	14.1802(15)
c (Å)	14.4699(9)	15.0970(16)
α (°)	90	72.996(3)
β (°)	97.862(5)	84.782(4)
γ (°)	90	84.567(4)
V (Å ³)	1712.1(2)	1853.5(3)
Z	4	4
Crystal colour	Dark red	Dark purple
Crystal size (mm)	$0.08 \times 0.13 \times 0.23$	$0.10 \times 0.20 \times 0.28$
D_c (g cm ⁻³)	1.689	1.848
Diffractometer	Gemini R Ultra [7]	Siemens P4, Bruker APEX I
μ (Mo K α) (mm ⁻¹)	1.74	2.36
Absorption correction	0.89	0.84
factors $T_{\text{min}}/T_{\text{max}}$		
θ range for data collection (°)	3.05–32.64	1.41–36.66
Index ranges	$-9 \leq h \leq 9$, $-26 \leq k \leq 25$, $-21 \leq l \leq 21$	$-11 \leq h \leq 15$, $-23 \leq k \leq 18$, $-24 \leq l \leq 18$
Reflections collected	21 096	15 632
Unique reflections	5835	9951
R_{int}	0.077	0.050
Observed reflections ($I > 2\sigma(I)$)	2070	4962
Final R^a indices	$R_1 = 0.0404$ (0.15), $wR_2 = 0.0656$ (0.077)	$R_1 = 0.0631$ (0.15), $wR_2 = 0.0844$ (0.094)
G.O.F. ^a	0.77	0.95
Largest difference peak and hole (e Å ⁻³)	0.06, -0.22	0.56, -0.40

Details in common: $\lambda = 0.71073$ Å; $T = 283$ K; refinement method: full matrix least squares on F^2 .

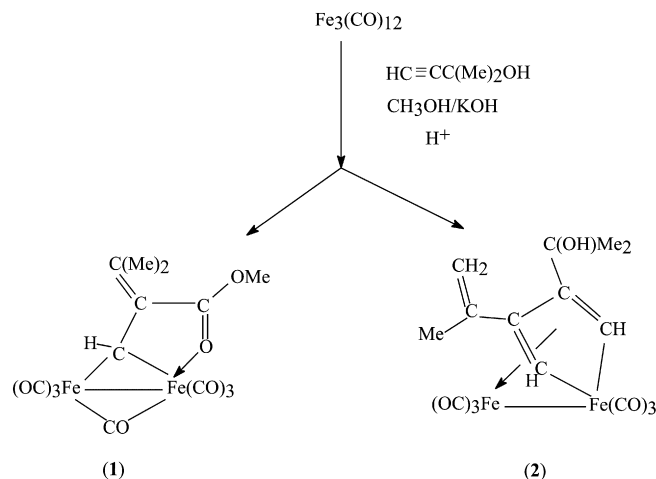
^a $R_1 = \sum(F_o - F_c)/\sum(F_o)$; $wR_2 = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ where $a = 0.0001$ for complex **1** and 0.0264 for complex **5**, and $P = [2F_o^2 + \text{Max}(F_o^2, 0)]/3$. G.O.F. = $[\sum\{w(F_o^2 - F_c^2)^2\}/(n-p)]^{1/2}$, where n number of reflections, p = number of refined parameters.

metric unit contains two molecules. All non-hydrogen atoms were refined anisotropically. The CH₃ and CH₂ hydrogen atoms were found in the last difference maps; it was however preferred to calculate and refine their coordinates with U_{iso} set at 1.2 times U_{eq} of the corresponding C atom. The bridging hydride atoms have been found on the difference maps and refined with free coordinates and free U_{iso} . The programs used were SHELXTL [8] for structure solution, refinement and molecular graphics, Bruker AXS SMART (diffractometer control), SAINT (integration), SADABS (absorption correction) [9].

3. Results and discussion

3.1. Products from the reactions of **mbo**

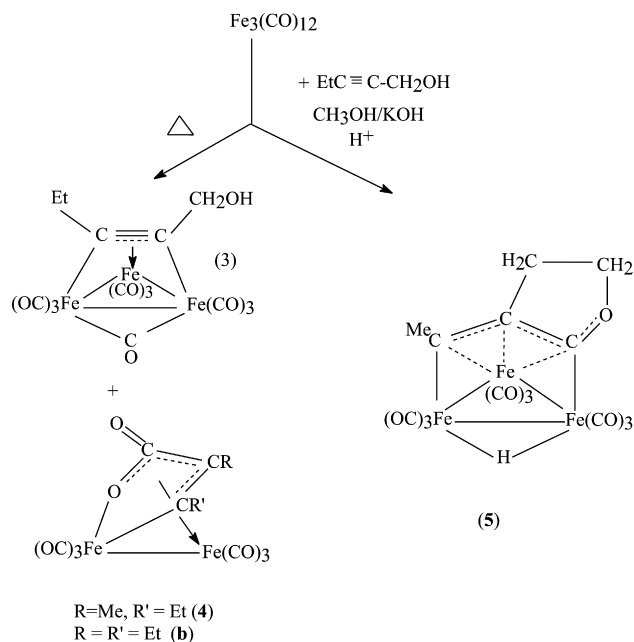
The reaction of **mbo** with $\text{Fe}_3(\text{CO})_{12}$ in hydrocarbons has been already reported [6]. Main products were the allenylidene derivative $\text{Fe}_3(\text{CO})_9(\mu\text{-CO})(\text{C}=\text{C}=\text{CMe}_2)$ (complex **a**), the open cluster $\text{Fe}_3(\text{CO})_6(\mu\text{-CO})_2[\text{HC}_2\{\text{CMe}_2(\text{OH})\}]\{\text{HC}_2\text{C}(\text{=CH}_2)\text{Me}\}$ and the ferrole $\text{Fe}_2(\text{CO})_6[\text{HC}_2\{\text{CMe}_2(\text{OH})\}]\{\text{HC}_2\text{C}(\text{=CH}_2)\text{Me}\}$ (complex **2** in this work) in one isomer each. Under basic methanolic conditions the main product obtained is complex **1** whose structure is discussed below; the “ferrole” complex **2** is also obtained in medium yields. The structures determined for complex **1** and proposed for complex **2** are in Scheme 1.

**Scheme 1.**

3.2. Products from the reactions of **pol**

The reaction of **pol** with $\text{Fe}_3(\text{CO})_{12}$ in hydrocarbons gives complex **3** and complex **4** in medium yields. Complex **3** has been identified as $\text{Fe}_3(\text{CO})_9(\mu\text{-CO})[\text{EtC}\equiv\text{CCH}_2\text{OH}]$ with the alkyne coordinated in “parallel” fashion. A small number of this type of complexes is known for iron [10] but, to our knowledge, only one X-ray structure has been reported [10a]. Complex **4** has been identified as the binuclear $\text{Fe}_2(\text{CO})_6[\text{EtC}_2(\text{CH}_3)\text{C}(\text{=O})\text{O}]$ homologue with the already reported “ferrole”-like derivative $\text{Fe}_2(\text{CO})_6-[(\text{EtC})_2\text{C}(\text{=O})\text{O}]$ (complex **b**) [11]. The IR and ¹H NMR spectra of complex **4** are slightly different from those of the already reported complex **b**: these indicate the presence of an ethyl and a methyl substituents on the metallacyclic ring (see Scheme 2, below).

Under basic methanolic conditions only complex **5** is obtained in considerable yields. To our knowledge this is the first example of a iron-based structure of this type. This is further discussed below. The structure determined for complex **5** and those proposed for complexes **3** and **4** are summarized in Scheme 2.

**Scheme 2.**

3.3. The X-ray structure and formation of complex **1**

The structure of complex **1** is shown in Fig. 1 and relevant bonding distances and angles are in Table 2.

Complex **1** is formed by a di-iron atom core. The Fe(1)–Fe(2) bond (2.5717(5) Å) is bridged by an asymmetric CO group and by the C(3) atom of the organic moiety. Three terminal CO are bound to each iron atom.

The organic ligand is built up by the C(3)C(2)C(1)O(1) chain, with C(3) bearing an hydrogen atom, with C(2) linked via a formal double bond to the C(CH₃)₂ group, and with C(1) bonded to a methoxy group (C(1)–O(2) 1.317(3) Å) and to O(1) with a formal double bond (1.242(3) Å). The C(3) atom bridges the Fe–Fe bond and O(1) coordinates the Fe(1) atom, thus forming a penta-atomic ring. The counting of the total electrons allows to satisfy the E.A.N. (Effective Atomic Number) rule.

The organic moiety is formed by the five carbon atoms C(3)C(2)C(4)C(5)C(6) of a **mbo** ligand which has lost the OH group originally on C(4). The coordination of this unit to the metal atom is reminiscent of that of the intermediate allenylidene complex **a**. This fragment is linked to the acetate group [C(7)O(2)C(1)O(1)] obtained by the coupling of a coordinated CO [C(1)O(1)] with a methoxy group deriving from methanol.

The OH of **mbo** and the hydrogen of methanol have been probably eliminated as H₂O. This behaviour has already been reported in the literature [4]: the formation of a cluster with a CH₃O bridge was also observed [4b]. This behaviour is observed again when Fe₃(CO)₁₂ ("stabilized" with methanol) is reacted in hydrocarbons with 1-phenyl-2-propyn-1-ol [HC≡C(H)Ph(OH), **ppo**] to give the metallacyclic complex Fe₂(CO)₆[Ph(H)CCCH(OMe)O] (complex **c**) [12] and with but-2-yn-1,4-diol or with 1,4-dichloro-but-2-yne in basic methanolic solution to form (among other products) the complex Fe₂(CO)₆[H₂CCC(H)C(OCH₃)O] (complex **d**) [3d] whose structures are, however, different from that of **1**.

There is evidence that complexes **c** and **d** are formed through the intermediacy of the allenylidene derivatives Fe₃(CO)₉(μ-CO)[C=C=CRR'] (R = H, R' = Ph, complex **c**, R = R' = H, complex **d**)

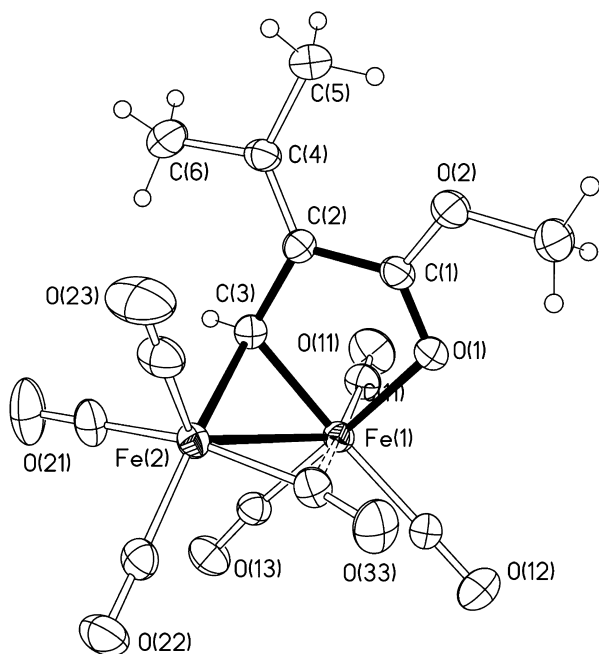


Fig. 1. ORTEP plot (30% of probability) of complex **1** Fe₂(CO)₆(μ-CO)(μ-η²-[HCC(=C(CH₃)₂)C(=O)(OCH₃)]).

Table 2

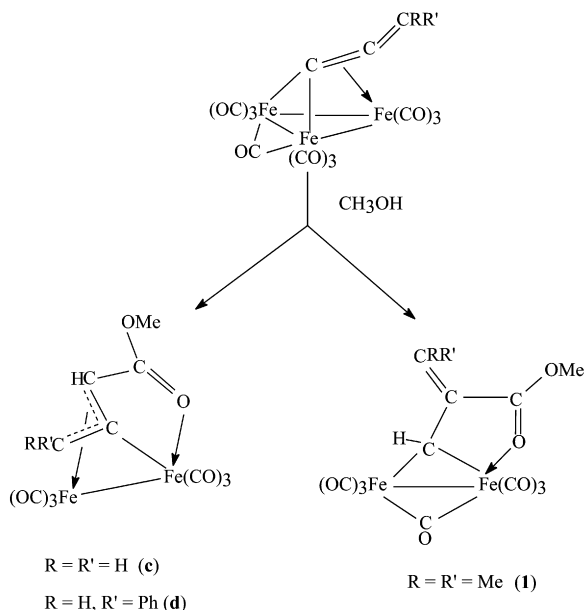
Selected bond lengths (Å) and angles (°) for complex **1** and for the two independent molecules of complex **5**

Complex 1	
Fe(1)–C(3)	1.978(4)
Fe(1)–O(1)	2.043(3)
Fe(1)–Fe(2)	2.5630(8)
Fe(2)–C(3)	2.067(4)
C(1)–O(1)	1.239(5)
C(1)–O(2)	1.321(5)
C(1)–C(2)	1.471(5)
C(2)–C(4)	1.353(5)
C(2)–C(3)	1.475(6)
O(2)–C(7)	1.451(5)
C(4)–C(5)	1.495(6)
C(4)–C(6)	1.503(6)
C(3)–Fe(1)–O(1)	81.1(1)
C(3)–Fe(1)–Fe(2)	52.2(1)
O(1)–Fe(1)–Fe(2)	97.95(8)
C(3)–Fe(2)–Fe(1)	49.2(1)
O(33)–C(33)–Fe(2)	160.5(4)
O(33)–C(33)–Fe(1)	123.4(4)
O(1)–C(1)–O(2)	120.7(4)
O(1)–C(1)–C(2)	119.7(4)
O(2)–C(1)–C(2)	119.6(4)
C(4)–C(2)–C(1)	125.4(4)
C(4)–C(2)–C(3)	124.9(4)
C(1)–C(2)–C(3)	109.6(3)
C(1)–O(2)–C(7)	116.5(4)
Complex 5	
Fe(1)–C(2)	2.116(5)
Fe(1)–C(3)	2.160(5)
Fe(1)–C(4)	2.185(5)
Fe(1)–Fe(3)	2.5552(9)
Fe(1)–Fe(2)	2.6218(10)
Fe(2)–C(4)	1.903(5)
Fe(2)–Fe(3)	2.8015(10)
Fe(2)–H(1)	1.62(4)
Fe(3)–C(2)	1.982(5)
Fe(3)–H(1)	1.57(5)
C(2)–C(3)	1.403(6)
C(3)–C(4)	1.401(7)
C(3)–C(7)	1.525(6)
C(4)–O(5)	1.362(5)
O(5)–C(6)	1.460(6)
C(6)–C(7)	1.515(7)
Fe(3)–Fe(1)–Fe(2)	65.51(3)
Fe(1)–Fe(2)–Fe(3)	56.10(3)
Fe(1)–Fe(3)–Fe(2)	58.39(3)
C(3)–C(2)–Fe(3)	120.4(4)
C(4)–C(3)–C(2)	121.6(5)
C(4)–C(3)–C(7)	109.0(4)
C(2)–C(3)–C(7)	129.2(5)
C(3)–C(4)–Fe(2)	127.8(3)
Fe(1)–C(2)	2.128(5)
Fe(1)–C(3)	2.154(5)
Fe(1)–C(4)	2.160(5)
Fe(1)–Fe(3)	2.5557(9)
Fe(1)–Fe(2)	2.6045(10)
Fe(2)–C(4)	1.895(5)
Fe(2)–Fe(3)	2.7927(10)
Fe(2)–H(1)	1.71(5)
Fe(3)–C(2)	1.967(5)
Fe(3)–H(1)	1.55(5)
C(2)–C(3)	1.396(7)
C(3)–C(4)	1.386(7)
C(3)–C(7)	1.520(7)
C(4)–O(5)	1.384(5)
O(5)–C(6)	1.442(7)
C(6)–C(7)	1.589(9)
Fe(3)–Fe(1)–Fe(2)	65.52(3)
Fe(1)–Fe(2)–Fe(3)	56.40(3)
Fe(1)–Fe(3)–Fe(2)	58.08(3)
C(3)–C(2)–Fe(3)	121.8(4)
C(4)–C(3)–C(2)	120.9(5)
C(4)–C(3)–C(7)	110.8(5)
C(2)–C(3)–C(7)	128.1(6)
C(3)–C(4)–Fe(2)	127.8(3)

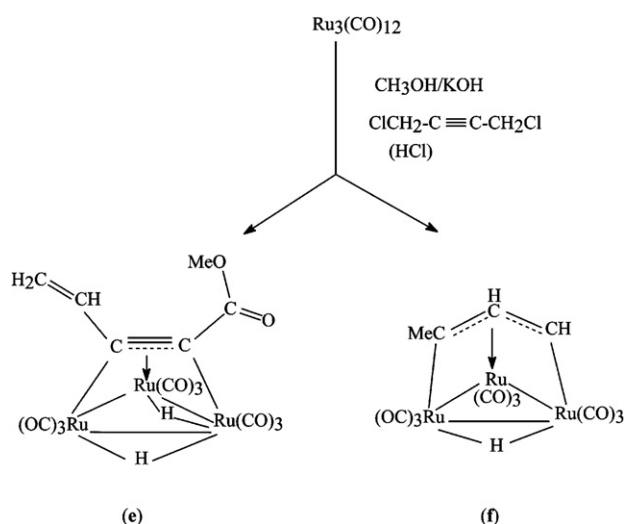
isolated in small amounts in the same reactions [3d,3e,12]. We could not isolate this type of intermediate in the reaction of Fe₃(CO)₁₂ with **mbo** under basic methanolic conditions. The complex Fe₃(CO)₉(μ-CO)(C=C=CMe₂) is formed, however, in the thermal reaction of **mbo**. We have shown that it reacts with methanol to form complex **1**. The reactions leading to complexes **c**, **d** and **1** starting from allenylidene intermediates are shown in Scheme 3.

Formation of a COOCH₃ group was also observed when Ru₃(CO)₁₂ was reacted in basic methanolic solution with 1,4-dichloro-but-2-yne forming the cluster H₂Ru₃(CO)₉[H₂C=C(H)C≡CC(=O)OCH₃] (**e**) and the allylic HRu₃(CO)₉[MeC(H)C(H)] (**f**). The above ruthenium complexes are shown in Scheme 4.

Formation of oxygenated ligands upon "insertion" of a cluster-bound CO into the organic moiety coordinated to a cluster has also been reported since long [13] and is discussed below together with the formation of complex **5**.



Scheme 3.



Scheme 4.

3.4. Formation of complexes 3 and 4 in hydrocarbon solution

The proposed structures of these complexes are shown in Scheme 2 (above). Complex 3 contains an intact alkyne ligand coordinated parallel [14] to the edge of a closed triangular cluster: a tempting hypothesis is that it could be the precursor of complex 5. However, we could not observe this complex under basic methanolic conditions.

Complex 4 is presumably formed by coupling of a CO with the oxygen of the alkyne ligand: this would account for the formation of the $\text{C}(\text{=O})\text{O}$ group in 4. Complex b is formed, instead, upon splitting of water contained in the t.l.c. plates used for the purification of the reaction mixture [11b].

3.5. X-ray structure and formation of complex 5

The structure of one molecule of complex 5 is shown in Fig. 2 and relevant bond distances and angles of both molecules of the asymmetric unit are listed in Table 2.

Complex 5 is formed by an isosceles triangle of iron atoms: the longest $\text{Fe}(2)\text{-Fe}(3)$ bond is bridged by a hydridic atom. Three terminal carbonyls are bound to each iron atom. All the iron atoms reach a precise electron count if one considers the allylic ligand as a five electron donor and the hydride as a one electron donor.

The organic moiety is formally σ coordinated to $\text{Fe}(2)$ and $\text{Fe}(3)$ and π bonded to $\text{Fe}(1)$ through the $\text{C}(2)\text{-C}(3)\text{-C}(4)$ allylic system. The $\text{C}(3)$ and $\text{C}(4)$ atoms belong to a penta-atomic C_4O ring, where also the short $\text{C}(4)\text{-O}(5)$ bond ($1.373(5)$ Å av.) can be considered delocalized. The whole organic moiety, with $\text{Fe}(2)$ and $\text{Fe}(3)$ enclosed, lies roughly on a plane, at 52° from the Fe_3 plane (0.06 Å mean deviation from plane). The hydridic atom lies above the Fe_3 plane folded towards the organic ligand (145° between the Fe_3 plane and the Fe_2H plane). The $\text{Fe}(1)\text{-C}(11)\text{-O}(11)$ angle is greatly deformed with respect to linearity (168°), with $\text{C}(11)\cdots\text{Fe}(2,3)$ of 2.70 Å av., thus suggesting an asymmetric $\mu_3\text{-CO}$, as already observed in similar compounds [3a].

Complex 5 is a neutral hydridic tri-iron allyl derivative also containing an oxygenated organic heterocycle. The ligand **pol** has formally lost only the oxygen atom: this behaviour has already been observed, although not very frequently [15]. It was not possible evidence if the hydridic ligand comes from the $[\text{HFe}_3(\text{CO})_{11}]^-$ anion which is formed in the basic methanolic solutions of $\text{Fe}(\text{CO})_5$ and $\text{Fe}_3(\text{CO})_{12}$ [16].

The structure of complex 5 is of some interest for the following reasons: (i) neutral tri-iron hydrides are rarely found [17]. In particular, complexes formed upon reaction with alkynes or related ligands have been obtained either starting from $[\text{HFe}_3(\text{CO})_{11}]^-$ upon insertion of the $\text{C}\equiv\text{C}$ bonds into the Fe-H bonds [18] or using very unusual reaction pathways [19]. In the first case anionic hydrides were obtained which, upon protonation, formed metal hydridic complexes with capping methylidyne ligands [18d,e]. In the second case reaction of $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$ with nickel atoms (under chemical vapour conditions) followed by reaction on a wet alumina surface, yielded $(\mu\text{-H})\text{Fe}_3(\text{CO})_9(\text{C}\equiv\text{CSiMe}_3)$ [19]. (ii) Complex 5 is, to our knowledge, a rare example of a trinuclear iron allylic complex structurally characterized; the other being $\text{Fe}_3(\text{CO})_7[\text{C}_5(\text{H})_2\text{Et}_3][\text{EtCCHCH}]$ obtained upon cleavage of a $\text{C}\equiv\text{C}$ triple bond [20]. The hydridic allyl structure found for 5 is instead very well known for ruthenium [21] and osmium [22]: in addition

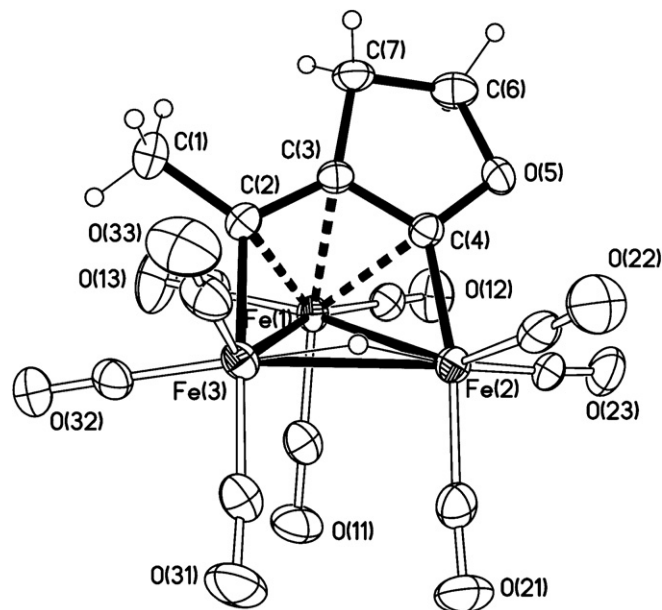


Fig. 2. ORTEP plot (30% probability) of complex 5 $(\mu\text{-H})\text{Fe}_3(\text{CO})_9(\mu_3\text{-}\eta^3\text{-[H}_3\text{CCC}(\text{CH}_2)(\text{CH}_2)\text{CO})$.

hydridic and non-hydridic triosmium allylic complexes also containing oxygenated heterocycles comparable with that of **5** are known. These have been obtained starting from alkyne-diols [22].

As previously mentioned, complex **5** is obtained upon reaction of $[\text{HFe}_3(\text{CO})_{11}]^-$ with **pol**; the heterocyclic ligand is formed by addition of the alkyne to a coordinated CO. This behaviour has already been reported for ruthenium complexes [13]. More recently, the formation of oxygenated metallacyclic rings involving a CO coordinated to iron has been observed when isopropenyl acetylene was reacted with $\text{Fe}_3(\text{CO})_{12}$ in hydrocarbons [23]. The open-cluster isomers $\text{Fe}_3(\text{CO})_{10}[\text{H}_2\text{CC}(\text{CH}_3)\text{CC}(\text{H})\text{C}(\text{H})\text{C}(\text{CO})\text{C}(\text{CH}_3)\text{CH}_2]$ and $\text{Fe}_3(\text{CO})_{10}[\text{HCC}(\text{CH}_3)\text{CC}(\text{H})\text{C}(\text{H})\text{C}(\text{H})\text{C}(\text{CO})\text{C}(\text{CH}_3)\text{CH}_2]$ were obtained.

During the formation of **5** the alkynic $\text{C}\equiv\text{C}$ bond is shifted and the OH group is lost (presumably as water, upon reaction with the H^+ of the hydrochloric acid). This behaviour has already been observed when other alkynols are reacted with tri-iron or ruthenium carbonyls [3].

4. Conclusions

The study of the reactivity of $\text{Fe}_3(\text{CO})_{12}$ and of $[\text{HFe}_3(\text{CO})_{11}]^-$ towards alkynes, alkynols and ene-yne represents an old and well established research field. In recent times, however, previously unknown structural arrangements and new reaction products have been reported [3–6]. Complexes **1** and **5** represent further examples of previously unknown structures obtained through already established reaction pathways. These reactions represent indeed a further example of the synthetic versatility of the basic methanolic reaction media especially when considering that isomeric alkynes give different products depending on their structure.

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Appendix A. Supplementary material

CCDC 681098 and 681099 contain the supplementary crystallographic data for **1** and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.04.045.

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