Reaction of $Fe_3(CO)_{12}$ with but-2-yn-1,4-diol, 1,4-dichloro-but-2-yne, propargyl-alcohol and propargyl-chloride.
The X-ray structures of $[Fe_2(CO)_6\{H_2CCCCH_2\}]$, $[Fe_2(CO)_6\{H_2CCC(H)C(OCH_3)O\}]$ and $[Fe_3(CO)_{10}\{H_2CCC(H)-C(O)C\{CH_2(O)CH_3\}CCH_2\}]$

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Abstract

The reactions of $Fe_3(CO)_{12}$ with but-2-yn-1,4-diol (BUD), 1,4-dichloro-but-2-yne (DCB), propargyl alcohol (PA) and propargyl chloride (PC) in KOH/CH_3OH solutions (followed by acidification with HCl) and under thermal conditions have been examined. The complex $Fe_2(CO)_6\{H_2CCCCH_2\}$ is the main product of the reactions with BUD or DCB in all conditions. The complexes $Fe_2(CO)_6\{H_2CCC(H)C(OMe)O\}$ and $Fe_3(CO)_{10}\{H_2CCC(H)C(O)C\{CH_2(O)CH_3\}CCH_2\}$ are the main products obtained respectively in the reactions with propargyl chloride (PC) or propargyl alcohol (PA) in basic methanolic solution. The structures of the three complexes have been determined by means of X-ray analysis. Complex $Fe_2(CO)_6\{H_2CCCCH_2\}$ contains a butatrienyl ligand in an uncommon structural arrangement. The formation of complex $Fe_2(CO)_6\{H_2CCC(H)C(OMe)O\}$ requires CO and methanol activation; its ferrole like structure contains a coordinated acetate group. Complex $Fe_3(CO)_{10}\{H_2CCC(H)C(O)C\{CH_2(O)CH_3\}-CCH_2\}$ contains one $Fe(CO)_4$ and one $Fe_2(CO)_6$ fragments linked through a carbon atom chain derived from the insertion of CO and dimerization of propargyl alcohol (with substitution of OCH_3 from methanol in the place of OH). Comments on the syntheses and on the reaction pathways leading to the complexes are made.
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Keywords: Alkyne-diols; Iron carbonyl clusters; Hydrochloric acid; Dehydration and dehydroxylation reactions; Crystal structure

1. Introduction

We have started an investigation on the reactions of iron and ruthenium carbonyls $M_3(CO)_{12}$ [M = Fe, Ru] with functionalized alkynes. We have found that these ligands, when reacted with polymetallic centres, easily undergo dehydration reactions. In particular, we have found that the alkynols follow two main different dehydration pathways consisting in: (a) loss of a terminal alkynic hydrogen and of the OH to give *allenylidene* clusters $M_3(CO)_9(\mu-O)(\mu_3-\eta^2-C=C=CRR')$ (complexes of type **I**), a process more common when M = Fe, and (b) loss of OH and of one hydrogen of an alkylic substituent (e.g., Me) to give *vinyl-acetylide* clusters such as $(\mu-H)M_3(CO)_9[\mu_3-\eta^2-C\equiv CC(=CH_2)R]$ (complexes of type **II**). The latter process is more common when M = Ru especially under acidic conditions [1]. The structures of complexes of type **I** and **II** are shown in Scheme 1.

We have also found that hydration of ene-ynes coordinated on triiron clusters is promoted by the TLC silica

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Type I

Type II

Scheme 1.
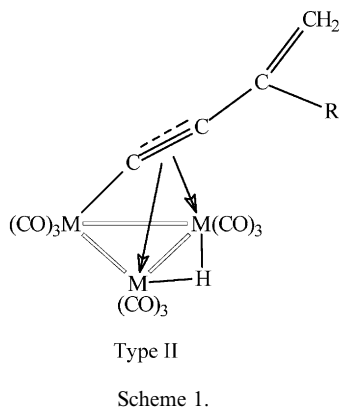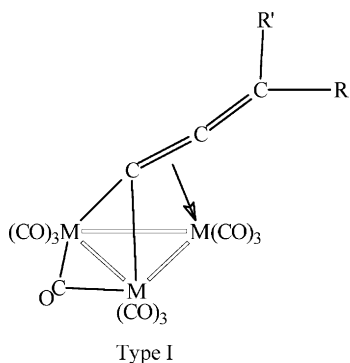
and that this process occurs via the splitting of a water molecule into its components [2]. In addition, methanol may react with the tri-iron allenyl complexes of type **I** undergoing splitting into H and CH_3O fragments to form compounds homologues of complex Fe_2-$(CO)_6\{H_2CCC(H)C(OMe)O\}$ reported in this paper [3]. Last, but not least, we have found that dehydration of cluster-bound alkynols (M = Ru) [4] is favoured by silica gel and that interconversions between allenylidene (type **I**) and vinyl-acetylide complexes (type **II**) on triruthenium clusters occur under acidic conditions [5] and that alumina and silica gel promote the interconversion and carbon–carbon coupling reactions of allenylidenes bound to triruthenium clusters [6,7].

The above results prompted us to investigate the reactivity of alkynols, alkyne-diols and related ligands towards $Fe_3(CO)_{12}$ both in hydrocarbons and in alkaline conditions, that is in KOH/CH_3OH solution (followed by acidification with HCl). It is commonly agreed that the same metal carbonyl anions are formed on the above mentioned alumina or silica surfaces as well as in methanolic alkaline solutions [1].

Here we report on the reactions of $Fe_3(CO)_{12}$ with 1,4-butyn-diol ($HOCH_2C\equiv CCH_2OH$, BUD), 1,4-dichloro-but-2-yne ($ClCH_2C\equiv CCH_2Cl$, DCB), propargyl alcohol ($HC\equiv CCH_2OH$, PA) and propargyl chloride ($HC\equiv CCH_2Cl$, PC) both in KOH/CH_3OH solutions and under thermal conditions. The title complexes are the main products obtained; their synthetic

pathways are discussed. We have found that activation of CO and of methanol under basic conditions occurs either with PA and PC and is, perhaps, a general method for obtaining complexes with coordinated acetate (or methoxy-carbonyl) groups.

2. Experimental

2.1. General experimental details. Purification and analysis of the products

$Fe_3(CO)_{12}$ (Strem Chemicals), BUD, DCB, PA and PC (Lancaster Synthesis) were used as received, after purity checks. Methanol, KOH (pellets) and HCl (concentrated, 37%) were laboratory grade chemicals. Solvents (hexane, heptane, toluene) were dehydrated over sodium. 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 KOH/CH_3OH solutions the following "standard" reaction conditions 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 °C for 10 min; addition of 4.0 cm^3 of liquid alkyne (or 15 pellets of solid BUD, ca. 1.5 g) and warming at 40 °C for further 10 min. After cooling, acidification with HCl (37%) to pH 1. Extraction with three 75 cm^3 portions of *n*-heptane. Reduction to small volume in under reduced pressure, then TLC purification (Kieselgel P.F. Merck, eluants mixtures of light petroleum {40–70 °C} and diethyl ether in variable v/v ratios depending on the reaction mixtures); extraction of the TLC bands with diethyl ether.

The mixtures from the thermal reactions were filtered under N_2, brought to small volume under vacuum and chromatographed on TLC plates (conditions as above).

Elemental analyses were performed in the laboratories of the DiSTA (Università del Piemonte Orientale). The IR spectra were obtained on a Bruker Equinox 55 (KBr cells, path length 0.5 mm). The ^{1}H and ^{13}C NMR spectra were registered on a JEOL GX 270 spectrometer (Dipartimento Chimica IFM, Università di Torino); all the ^{13}C NMR spectra were hydrogen decoupled. The EI-MS 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. Reactions of $Fe_3(CO)_{12}$ with BUD

2.2.1. In hydrocarbons

Two grams of $Fe_3(CO)_{12}$ (ca. 4 mmol) were reacted with 10 pellets of BUD (ca. 1 g, 12 mmol) in 100 cm^3

of benzene, under nitrogen (10 min to reflux point, then 6 min reflux). A dark brown suspension was obtained. TLC purification showed the presence of about 30% of unreacted $Fe_3(CO)_{12}$ and of traces only of orange-red complex **1**, of a brown unidentified product and decompostion.

One gram of $Fe_3(CO)_{12}$ was suspended in 100 cm³ of heptane and added to a saturated methanolic solution of BUD (30 cm³) and $Me_3NO \cdot 2H_2O$ and heated to reflux point under N_2. After 5 min reflux the dark brown suspension was filtered from the unreacted iron carbonyl (about 30%) and a dark oily solid (presumably excess of BUD, in part polymerized). TLC showed the presence of an unidentified yellow product in trace amounts and of (**1**) in about 20% yields.

Complex **1**: Anal. Calc.: C, 36.1; H, 1.2; Fe, 33.7%. Found: C, 36.2; H, 1.3; Fe, 33.5%. IR (CH_2Cl_2): 2069 m-s (b), 2033 vs, 2000s, vs cm⁻¹. IR (heptane): 2078 m-s, 2036 vs, 2009 vs, 1999 s, 1985 m-w, cm⁻¹. ¹H NMR ($CDCl_3$, r.t.): 4.72 d (2H), 4.08 d (2H) [8] . ¹³C NMR ($CDCl_3$, r.t.): 54.7 s, 58.3 s ($=CH_2$), 65.1 s, 75.8 s (internal C=C), 188.1 s, 196.8 s (CO, int. 1:2). A broad peak of low intensity at 210 ppm is also observed. EI-MS: $P^+ = 332$ m/z, release of six CO.

2.2.2. In alkaline solution

After TLC purification of the green-yellow clear solution obtained after acidification and extraction, the following bands were observed: $Fe_3(CO)_{12}$ (ca. 10%), orange (**1**, 10%), and yellow (**2**, 10%).

Complex **2**: Anal. Calc.: C, 36.1; H, 1.2; Fe, 33.7. Found: C, 36.4; H, 1.3; Fe, 33.5%. IR (heptane): 2065 vs, 2015 vs, 2007 s(sh), 1971 m-w, cm⁻¹. ¹H NMR: 6.80 s (2H), 3.22 s (2H) (slightly broad signals). EI-MS: $P^+ = 332$ m/z, release of six CO. Identified as $Fe_2(CO)_6(C_4H_4)$ "ferrole".

2.3. Reaction of $Fe_3(CO)_{12}$ with DCB

2.3.1. In hydrocarbons

One gram of $Fe_3(CO)_{12}$ was suspended in 100 cm³ of heptane under N_2 and was added to 2 cm³ of DCB: after 5 min reflux the brown suspension was filtered, reduced to small volume and purified on TLC plates. Unreacted $Fe_3(CO)_{12}$ (ca. 20%) and the following bands were observed: orange (**1**, 30%), yellow (**2**, 1%) and decomposition.

2.3.2. Under basic conditions

After TLC purification of the deep brown solution obtained upon acidification and extraction, the following bands were observed: $Fe_3(CO)_{12}$ (30%), orange (**1** about 10%) and decomposition.

2.4. Reactions of $Fe_3(CO)_{12}$ with propargyl alcohol (PA)

2.4.1. In hydrocarbons

Two grams of $Fe_3(CO)_{12}$ were suspended in 100 cm³ of heptane and 2 cm³ of liquid PA were added [9]. The suspension was brought at reflux point (10 min) and allowed to reflux for 3 min. A considerable amount of a brown deposit was observed in the reaction vessel. After filtering and bringing to small volume, TLC purification showed the presence of the following bands: brown (**3**, 3–5%), yellow (**4**, 15%), orange (**5**, 5%) and unreacted $Fe_3(CO)_{12}$ (ca. 5%).

Complex **3**: Anal. Calc.: C, 32.1; H, 0.4; Fe, 34.6. Found: C, 32.3; H, 0.5; Fe, 34.8%. IR: 2093 m, 2060 vs, 2035 vs, 2016 ms, 1989 ms, 1880 m, cm⁻¹. ¹H NMR: 5.90 d (1H), 5.75 d (1H). EI-MS: $P^+ = 486$ m/z, loss of 10 CO. Identified as $Fe_3(CO)_9(\mu\text{-}CO)(C=C=CH_2)$. One of the major peaks in the mass spectrum is at 348 m/z $[Fe_2(CO)_7(C_3H_4)]$.

Complex **4**: Anal. Calc.: C, 34.5; H, 1.15; Fe, 32.2. Found: C, 34.4; H, 1.16; Fe 32.4%. IR: 2098 m, 2040 vs, 2020 s, 2012 s(sh), 1989 m, 1981 m(sh), cm⁻¹. ¹H NMR: 3.77 s, 2.42 s (integration 1:1). EI-MS: $P^+ = 348$ m/z, release of a fragment of 16 m/z, the release of 7 CO, very intense peak at 152 m/z. $Fe_2(CO)_7(C_3H_4)$, see Section 3.

Complex **5**: Anal. Calc.: C, 34.9; H, 1.6; Fe, 29.6. Found: C, 34.7; H, 1.8; Fe, 29.8%. IR: 2078 m-s, 2033 vs, 2008 s(sh), 1996 vs, 1979 m-s, cm⁻¹. ¹H NMR: 4.08 s (1H,C_4), 3.68 s (3H, Me), 3.56 s (1H, C_4), 2.97 s(1H, C_2). ¹³C NMR:54.4 (CH_3), 58.8 d (CH_2), 66.3 d (CH), 189.1 d (C_{ring} or CO?), 197.1 s (CO), 212.0 vb ($C_1\text{-}O_2$). EI-MS: $P^+ = 378$ m/z, release of six CO.

2.4.2. In alkaline solution

After TLC of the dark orange extract after acidification the following bands were observed: yellow (**4**, 10%), brown (**6**, 10%), $Fe_3(CO)_{12}$ (5%), red (**7**, 15%) and red (**8**, 10%).

Complex **6**: Anal. Calc.: C, 40.0; H, 2.8; Fe, 30.5. Found: C, 39.9; H, 2.9; Fe, 30.7%. IR: 2069 m-s, 2052 w, 2035 m-s(sh), 2025 vs, 1993 s, 1976 m, cm⁻¹. ¹H NMR: 6.2–6.0 dd (2H, ≡CH), 3.8–3.6 m (4H, CH_2), 2.5 m (6H, CH_3). EI-MS: $P^+ = 420$ m/z, release of 6 CO, then of fragments with 32 and 16 m/z. Identified as $Fe_2(CO)_6\{HC_2(CH_2OCH_3)\}_2$ "ferrole".

Complex **7**: Anal. Calc.: C, 38.2; H, 1.8; Fe, 28.0. Found: C, 38.1; H, 1.7; Fe, 29.1%. IR: 2100 m, 2075 m-s, 2031 vs, 2026 vs, 1992 s, 1973 m, cm⁻¹. ¹H NMR ($CDCl_3$, r.t.): 4.16–4.12 d (2H, C_6), 3.89–3.78 d (2H, C_1), 3.68–3.66 d (1H, C_3), 3.29 s (3H, Me), 3.07–3.04 d (2H, CH_2), some attributions could be reversed. ¹³C NMR: 37.3 s, 58.4 s, 66.4 s, 68.2 s, 72.3 s [CH_3, CH_2C ring and vinyl], 203.3 s, 206.6 s

[CO, intensity 1:2], 220.0 [CO, inserted]. EI-MS: P^+ = 586, release of 12 fragments with 28 m/z. Intense signals at 278 m/z, 250 m/z, 220 m/z.

Complex **8**: Anal. Calc.: C, 36.7; H, 1.4; Fe, 30.2. Found: C, 36.6; H, 1.5; Fe, 30.3%. IR: 2099 m, 2074 m-s, 2031 vs, 2026 s(sh), 2007 s, 1991 s, 1974 m, cm^{-1}. ^{1}H NMR: 4.62–4.60 d (2H, C$_6$), 4.42 d (1H), 4.23 d (1H, hydrogens on C$_1$), 3.88–3.77 d (1H, C$_3$), 3.47 s (3H, Me), 3.29 s (3-6H). EI-MS: P^+ = 568, release of 11 fragments with 28 m/z, intense signals at 278 m/z, 250 m/z. Tentative attribution Fe$_3$(CO)$_{10}${H$_2$CCC(H)-C(=O)C(CH$_3$)CCH$_2$} see Section 3.

2.5. Reactions of Fe$_3$(CO)$_{12}$ with propargyl chloride (CP)

2.5.1. In hydrocarbons

About 3.0 g of iron carbonyl were suspended in 100 cm^3 of heptane under N$_2$; 3.0 cm^3 of CP were added and the suspension was brought to reflux point (8 min) and allowed to reflux for 5 min. Considerable amounts of unreacted iron carbonyl and of a brown insoluble residual were observed after cooling. On the TLC plates, unreacted iron carbonyl was observed, together with a brown (**3**, 2%), a yellow (**4**, 5%) and a orange band (**5**, 5%).

2.5.2. In alkaline solution

The green-yellow solution obtained after acidification and extraction showed the following TLC bands: brown (**3**, trace amount), yellow (**4**, ca. 5%), Fe$_3$(CO)$_{12}$ (15%), orange (**5**, ca. 25%) and decomposition.

2.6. Crystallography

2.6.1. Complex 1

C$_{10}$H$_4$O$_6$Fe$_2$, M = 331.83, orthorhombic space group *Pna*2$_1$ (No. 33), a = 12.033(2), b = 8.137(1), c = 12.318(2) Å, V = 1206.1(3) Å^3, T = 283 K, Z = 4, μ (Mo Kα) = 2.42 mm^{-1}, 7183 reflections measured on a P4 diffractometer equipped with CCD APEX detector, 2683 unique (R_{int} = 0.033), which were used during refinement. Hydrogens were localized. The final R = 0.0424 for 2298 reflections with $F_o > 4\sigma(F_o)$.

2.6.2. Complex 5

C$_{11}$H$_6$O$_8$Fe$_2$, M = 377.86, monoclinic space group $P2_1/n$ (No. 14), a = 6.5869(10), b = 21.5234(36), c = 10.0471(16) Å, β = 95.409(3)°, V = 1418.1(4) Å^3, T = 283 K, Z = 4, μ (Mo Kα) = 2.08 mm^{-1}, 8428 reflections on the same diffractometer of complex **1**, 3197 unique (R_{int} = 0.029), which were used during refinement. Hydrogens were localized. The final R = 0.0407 for 2379 reflections with $F_o > 4\sigma(F_o)$.

2.6.3. Complex 7

C$_{19}$H$_{10}$O$_{12}$Fe$_3$, M = 585.81, monoclinic space group $P2_1/n$ (No. 14), a = 7.4212(16), b = 20.424(5), c = 15.073(9) Å, V = 2247.9(8) Å^3, β = 102.667(4) T = 283 K, Z = 4, μ (Mo Kα) = 1.99 mm^{-1}, 15362 reflections measured on the same diffractometer of complex **1**, 5167 unique (R_{int} = 0.065), which were used during refinement. Hydrogens were localized. The final R = 0.0600 for 2603 reflections with $F_o > 4\sigma(F_o)$.

3. Results and discussion

3.1. The synthesis of complexes 1 and 2

These complexes were obtained either from BUD and from DCB, both under thermal and under basic conditions, as shown in Scheme 2. Interestingly, the yields of **1** are higher under thermal conditions, especially in the presence of Me$_3$NO.

Thermal reactions of iron carbonyls with alkyne diols have been reported [10,11]. When "unsubstituted alkynols" were used, however, the yields were usually less than 1%. These could be slightly increased by using iodine in water/THF. In the conditions adopted in this work the yields are considerably increased. In some reactions we could also obtain small yields of complex **2** isomeric with **1**. According to the spectroscopic results, oily-solid complex **2** is a ferrole-like derivative [12,13] (structure proposed in Scheme 2). It is worthy of mention that the reactions of both BUD and DCB lead to the same products: both the alkynes lose their functionalities, leaving a C$_4$H$_4$ fragment which do not undergo oligomerization. In contrast, PA and PC loose their functionalities releasing C$_3$ fragments: these, however, undergo further reactions including oligomerization.

The loss of the OH groups is apparently a general trend; for example, when reacting BUD with Ru$_3$-(CO)$_{12}$ under basic conditions we obtained the cluster (μ-Cl)Ru$_3$(CO)$_9$[H$_2$CCC(H)CH$_2$] formed by deoxydrilation of the ligand and addition of the HCl used for acidifying the reaction mixture [14]. Recently it has been reported that BUD reacts with H$_2$Os$_3$(CO)$_{10}$ loosing the OH groups and forming coordinated ene-yne and di-yne ligands or giving coordinated furanic moieties [15]. Loss of hydroxyls and of substituents also happens with other functionalized alkynes, thus trimethylsilyl propargil alcohol [(Me$_3$Si)C≡CCH$_2$(OH)] under basic (and thermal) conditions looses Me$_3$Si and OH and forms the allylic derivative (μ-H)Ru$_3$(CO)$_9$(HCCHCH) [16] through addition or shift of hydrogen.

The loss of chlorine from DCB is also apparently a general trend: it has been found, indeed, that this alkyne reacts with titanocene derivatives undergoing reduction from 1,4-dichlorobut-2-yne to 1,2,3-butatriene: a

(i) Thermal conditions
(ii) KOH/CH₃OH then HCl
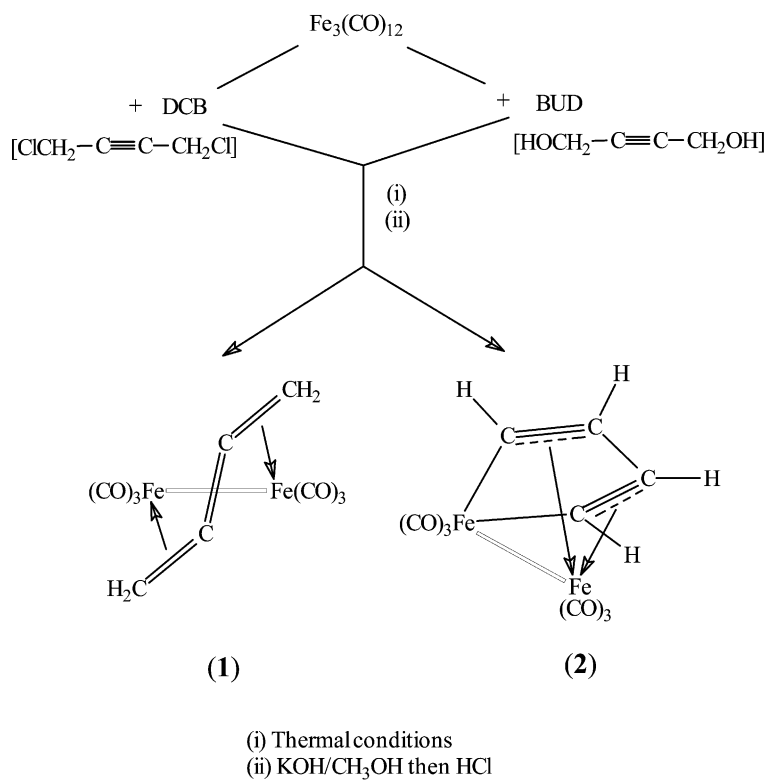
Scheme 2.

$[(Cp)_2Ti]_2(C_4H_4)$ complex, showing the same coordination pattern of the C_4H_4 to the metal centres as found for complex **1** was obtained [17]. This behaviour confirms our observations about the nature of the fragments released by DCB.

3.2. The synthesis of complexes 3, 4, 5 and 6, 7, 8

Complexes **3**, **5** and **4** are obtained both starting from PA or PC, under all conditions. Under basic conditions, complexes **6**, **7** (as the main product) and **8** were also obtained. These reactions are collected in the Scheme 3 where also the structures proposed for **3**, **4**, **6** and **8** are shown.
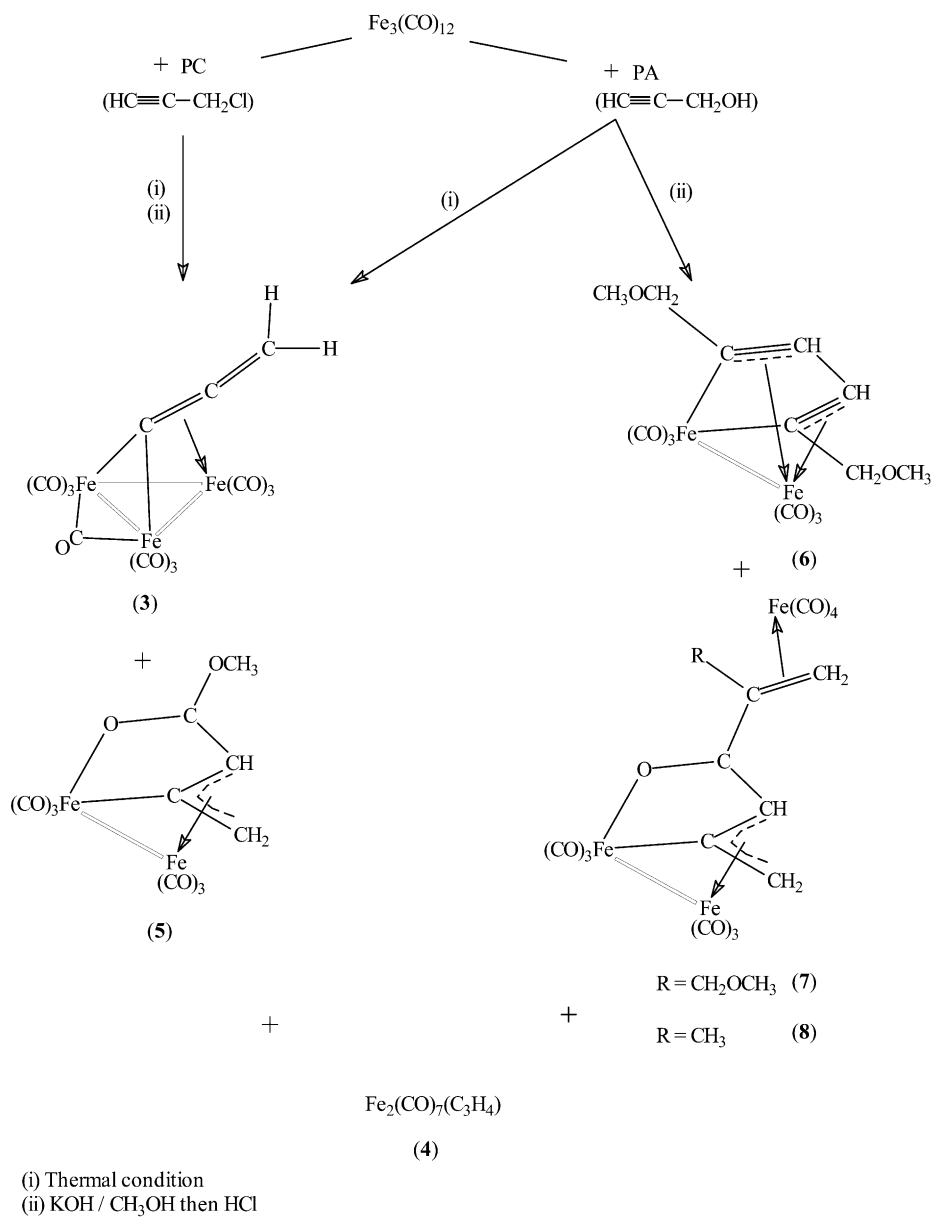
Complex **6** has been identified as a "ferrole" complex, as previously discussed for **2**. Three possible isomers are allowed for this structure; the ¹H NMR indicates that shown in Scheme 3. The presence of the –OMe substituents is presumably due to substitution of the OH with OMe (from methanol), catalyzed by HCl; this behaviour was observed in the reactions of $Co_2(CO)_8$ with the same alkynol ligands [18] and will be further discussed when considering the synthesis of complex **7**.

Crystals of complex **4** suitable for X-ray analyses were not obtained. A concentrated solution of **4** in heptane was cooled at −30 °C: after 1 day large and well formed orange crystals were deposited. However, after elimination of the solvent and warming at room temperature, 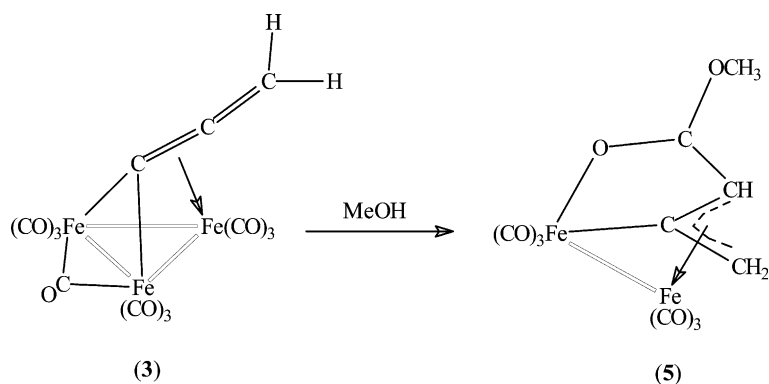immediate dissolution of the crystals into a thick oily liquid was observed. Thus, complex **4** was identified – mainly on the basis of the mass spectrum – as the binuclear $Fe_2(CO)_7(C_3H_4)$. Formation of this complex was also observed in the mass spectrum of **3**. The complex shows a very simple ¹H NMR spectrum indicating the presence of two couples of (non-equivalent) hydrogen atoms. Further attempts at determining a unequivocal structure for **4** and its role in the reactions reported in this paper are in progress.

The complex **5** shows a "ferrole-like" structure homologue to $Fe_2(CO)_6\{Ph(H)CCCHC(OMe)O\}$ (**5a**) [3]. The formation of complex **5** and of **5a** containing a methoxy carbonyl group requires the activation of CO and of methanol; we could, indeed, evidence that complex **5a** was formed upon the reaction of the (Type I) allenylidene $[Fe_3(CO)_9(\mu\text{-}CO)\{C=C=C(H)Ph\}]$ (complex **3a**, homologue of **3**) with the methanol used to stabilize the iron carbonyl [3]. It is therefore presumable that **5** also, is obtained through this reaction pathway passing through the intermediacy of **3**, as shown in Scheme 4.

Allenylidene complexes, such as **3**, are preferentially formed upon dehydration of alkynols coordinated on $Fe_3(CO)_{12}$ [19]. Vinylic intermediates (instead of allenylidenes) had been proposed by Mathieu and coworkers for the synthesis of tri- and bi-nuclear iron derivatives [20]. In addition, formation of C-OMe groups was achieved upon addition of CH_3I to $[HFe_3(CO)_{11}]^-$ [21].

Fe$_3$(CO)$_{12}$

+ PC
(HC≡C−CH$_2$Cl)

+ PA
(HC≡C−CH$_2$OH)

(i)
(ii)

(i)

(ii)

(3)

(6)

+

(5)

(4)

Fe$_2$(CO)$_7$(C$_3$H$_4$)

R = CH$_2$OCH$_3$ **(7)**

R = CH$_3$ **(8)**

+

+

(i) Thermal condition
(ii) KOH / CH$_3$OH then HCl

Scheme 3.

(3)

MeOH

(5)

Scheme 4.

Dinuclear phosphido-bridged cobalt complexes containing a "ferrole-like" $C(R)=C(H)C(OMe)=O$ ring [R = COOMe] have been obtained by Mays and coworkers starting from trinuclear (phosphido-bridged) cobalt complexes bearing coordinated $RC\equiv CR$ alkynes [R = COOMe] [22]. In contrast, complexes **5** and **5a** have been obtained starting from alkyne fragments and activation of CO and CH_3OH. Evidence for coupling of CH_3 [from a bridging CH_2 under protonating conditions] and of a metal-bound CO has been recently obtained for Rh–Ru binuclear derivatives [23].

The reaction of PA with $Fe_3(CO)_{12}$ in CH_3OH/KOH solution leads also to complex **7** as the main product and to smaller yields of complex **8**. The structure proposed for complex **8** (see Scheme 3) is based on mass spectrometric and spectroscopic results; in particular, the fragmentations of the two complexes are closely comparable, as are the IR and, in part, the ^1H NMR spectra. Thus **8** could be a by-product in the formation of **7** formed by loss of OH from PA and uptake of hydrogen. It is presumable that the formation of these complexes in KOH/CH_3OH is due to the formation and fragmentation of the $[HFe_3(CO)_{11}]^-$ anion, which can be obtained under these reaction conditions [24]. Indirect evidence for this hypothesis is the synthesis of $[Fe_3(CO)_{10}\{Ph_2PCCHC(O)(OMe)\}]^-$ (complex **9**) [20b] which also contains a $Fe(CO)_4$ fragment bound to the di-iron moiety through the phosphorus atom of the phosphino-alkyne used in the synthesis; complex **9** (Scheme 5) was synthesized starting from the anion $[HFe_3(CO)_{11}]^-$. One should consider, however, that complex **9** has been obtained, once again, starting from an methoxycarbonyl-substituted phosphino alkyne, whereas **5** and **7** are formed upon CO and methanol activation.

In complexes **7**, **8** and **9** the binuclear fragment links a $[Fe(CO)_4]$ moiety through a 2-electron donation (from $C=C$ or P atom).

The formation of the oxygenated, allylic, ferrolic parts in the molecules of **7** and **8** could be explained by invoking the same reaction pathway leading to **5** and **5a** discussed above. The formation of the other part
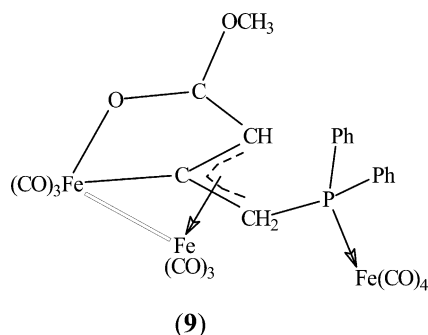
of the ligand in complex **7**, namely that containing $C(6)–C(5)–C(7)$ and the methoxy group can be explained considering that this moiety is originated upon co-oligomerization of PA and a CO coming from the triiron anion. A molecule of PA, bonded to the CO, has undergone dehydroxylation and uptake of methanol; the latter splits into the CH_3O group, which formally substitutes the lost OH, and one hydrogen atom which is bound to the three-carbon atom chain. This behaviour is not uncommon for methanol [1].

3.3. Crystal structures of complexes 1, 5, 7

3.3.1. The structure of complex 1

The complex is formed by a $Fe_2(CO)_6$ frame with a Fe–Fe distance of 2.6102(8) Å. Three terminal CO groups are bound to each iron atom and two of them are disposed in eclipsed way. The structure is shown in Fig. 1 and relevant distances and angles are in Table 1.

The $H_2C=C=C=CH_2$ butatrienyl ligand is coordinated in equivalent way to both metal centres: it is bent and uses three of the four carbon atoms for bonding each of the iron atoms acting formally as a six (3 + 3) electron donor in order to achieve a 18 e^- situation around each metal atom. The ligand is not planar, the iron–carbon bonds are equal two by two [Fe(1)–C(4) 2.203(5) Å, Fe(2)–C(1) 2.211(6) Å, Fe(1)–C(3) 2.021(4) Å, Fe(2)–C(2) 2.035(4) Å, Fe(1)–C(2) 1.949(4) Å, Fe(2)–C(3) 1.931(4) Å] and Fe(1)–C(2) and Fe(2)–C(3) may be formally described as σ bonds and the remaining Fe–ligand bonds as π-asymmetric interaction.

The carbon–carbon distances in the C_4 ligand indicate a delocalized double bond situation. The angles around the carbon atoms: $C(1)–C(2)–C(3)$ 129.5(4)°, $C(2)–C(3)–C(4)$ 129.5(5)° are close to a sp^2 description. The short intermolecular contacts $O(23)\cdots H(1B)$ (2.54 Å) and $O(11)\cdots H(4A)$ (2.58 Å) and the related angles show that hydrogen bonds contribute to the crystal packing.
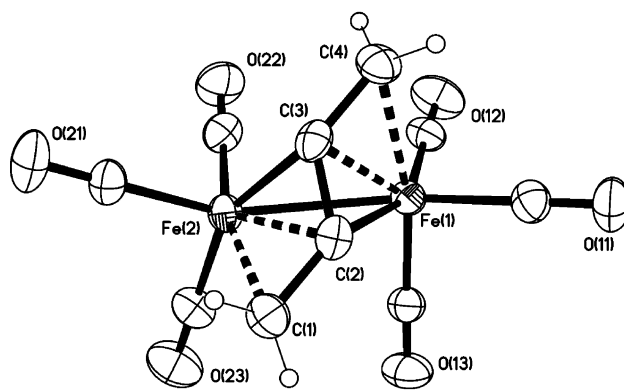

(9)

Scheme 5.

Fig. 1. ORTEP plot (30% of probability) of $[Fe_2(CO)_6\{H_2C=C=C=CH_2\}]$ (**1**).

Table 1
Selected bond distances (Å) and angles(°) for [Fe$_2$(CO)$_6$\{H$_2$C=C=C=CH$_2$\}] (1)

Fe(1)–C(2)	1.949(4)
Fe(1)–C(3)	2.021(4)
Fe(1)–C(4)	2.203(5)
Fe(1)–Fe(2)	2.6102(8)
Fe(2)–C(3)	1.931(4)
Fe(2)–C(2)	2.035(4)
Fe(2)–C(1)	2.211(5)
C(1)–C(2)	1.381(6)
C(2)–C(3)	1.350(6)
C(3)–C(4)	1.382(6)
C(3)–C(2)–C(1)	129.5(4)
C(2)–C(3)–C(4)	129.5(5)

Fig. 2. ORTEP plot (30% of probability) of [Fe$_2$(CO)$_6$\{H$_2$CCC(H)-C(OMe)O\}] (5).

Table 2
Some relevant bond distances (Å) and angles (°) for complex [Fe$_2$(CO)$_6$\{H$_2$CCC(H)C(OMe)O\}] (5)

Fe(1)–C(3)	1.938(3)
Fe(1)–O(1)	2.018(2)
Fe(1)–Fe(2)	2.6299(6)
Fe(2)–C(3)	1.951(3)
Fe(2)–C(2)	2.133(3)
Fe(2)–C(4)	2.157(3)
O(1)–C(1)	1.238(3)
O(2)–C(1)	1.313(3)
O(2)–C(5)	1.449(4)
C(1)–C(2)	1.437(4)
C(2)–C(3)	1.435(4)
C(3)–C(4)	1.396(4)
C(3)–Fe(1)–O(1)	84.21(10)
C(3)–Fe(2)–C(2)	40.85(11)
C(3)–Fe(2)–C(4)	39.33(11)
C(1)–O(1)–Fe(1)	110.15(18)
C(1)–O(2)–C(5)	116.9(2)
O(1)–C(1)–O(2)	122.4(3)
O(1)–C(1)–C(2)	120.5(3)
O(2)–C(1)–C(2)	117.0(3)
C(3)–C(2)–C(1)	112.9(2)
C(4)–C(3)–C(2)	114.8(3)

The structure of complex 1 is more close to that of the Co$_2$(CO)$_6$(RC$_2$R′) tetrahedral complexes [25] than to that of the ferrole derivatives Fe$_2$(CO)$_6$(RC$_2$R′)$_2$ which are among the commonest products of the reactions of iron carbonyls with alkynes [12]. Apparently, the coordination of C(1) and C(4) to the metals is necessary to meet the electron count rules which will not be respected by a Fe$_2$(CO)$_6$(RC$_2$R′) tetrahedral complex homologue of the cobalt derivatives. We have also found, however, small amounts of the ferrole-like complex 2, isomer of 1.

Structures of type 1 are rarely encountered in iron carbonyl chemistry. To our knowledge there is only one other structural study for Fe$_2$(CO)$_6$(C$_{28}$H$_{16}$) (1a) [26], while for Fe$_2$(CO)$_6$[Ph$_2$C=C=C=CPh$_2$] (1b) only preliminary and doubtful data are reported in [27]. Both complexes contain heavily substituted ligands and have been obtained through thermal reactions whereas 1 (obtained in better yields under thermal conditions) represents the unsubstituted parent structure. The comparison of complexes 1 and 1a shows the same trend in bond distances and angles.

3.3.2. The structure of complex 5

The structure of this complex is closely related to the "ferrole" complexes [12] which are the more common derivatives obtained in the reactions of iron carbonyls with alkynes. It is represented in Fig. 2 and the relevant distances and angles are in Table 2.

As previously discussed, this complex is homologue of Fe$_2$(CO)$_6$\{Ph(H)CCCHC(OMe)O\} (5a) [3], and shows two remarkable features: (i) a C(O)(OMe) group (with C(1)–O(1) significantly shorter than C(1)–O(2)) bound to one iron atom through the oxygen and (ii) an "allylic" HC=C=CH$_2$ group on the other side of the "ferrole" ring. Oxygen-containing di-iron heteroatomic metallacyclic rings have been discussed in [12]. A "ferrole" ring containing a similar methoxycarbonyl group is observed in the anionic complex [Fe$_3$(CO)$_{10}$-\{Ph$_2$PCCHC(O)(OMe)\}]$^-$ (complex 9) [20]. Intermolecular H(4B)···O(11) (2.56 Å) and H(2)···O(2) (2.57 Å)

distances with related angles show the importance of hydrogen bonds in crystal packing.

3.3.3. Structure of complex 7

This complex is formed by a binuclear and a mononuclear metal fragments linked by a carbon atom chain. The structure of 7 is shown in Fig. 3 and relevant bond distances and angles are in Table 3.

The diiron fragment [Fe(1)–Fe(2)] forms an oxygen-containing "allylic" ferrole system comparable with that found in 5. The C(1)–C(2)–C(3) atoms represent the "allylic" part of the ring. The C(4) atom is bound
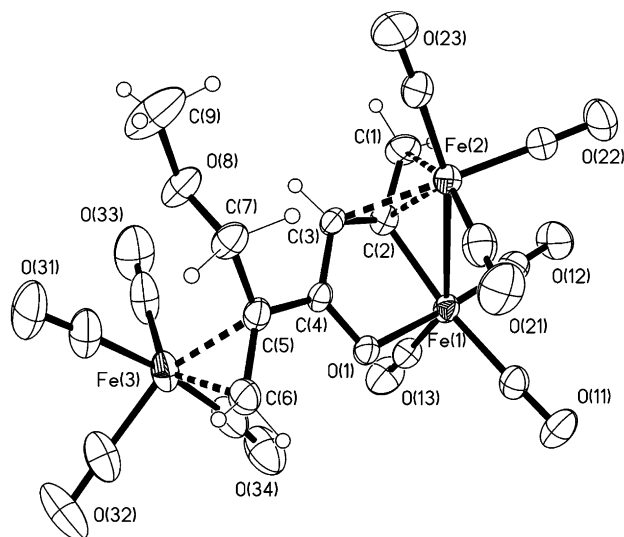
Fig. 3. ORTEP plot (30% probability) of [Fe₃(CO)₁₀{H₂CCC(H)-C(=O)C{CH₂(O)CH₃}CCH₂}] (**7**).

through C(5) to a moiety formed by one molecule of PA which has lost the OH and has added the fragments of methanol; thus CH_3O is found at the place of the OH and the hydrogen is one of the four of the C(7)–C(5)–C(6) chain. The vinylic moiety at one end of this ligand

Table 3
Some relevant bond distances (Å) and angles (°) for complex [Fe₃(CO)₁₀{H₂CCC(H)C(=O)C{CH₂(O)CH₃}CCH₂}] (**7**)

Fe(1)–C(2)	1.937(6)
Fe(1)–O(1)	1.998(4)
Fe(1)–Fe(2)	2.6468(12)
Fe(2)–C(2)	1.946(5)
Fe(2)–C(3)	2.123(5)
Fe(2)–C(1)	2.172(6)
Fe(3)–C(6)	2.074(5)
Fe(3)–C(5)	2.114(6)
C(1)–C(2)	1.387(8)
C(2)–C(3)	1.426(7)
C(3)–C(4)	1.422(7)
C(4)–O(1)	1.271(6)
C(4)–C(5)	1.457(7)
C(5)–C(6)	1.417(8)
C(5)–C(7)	1.524(8)
C(7)–O(8)	1.402(7)
O(8)–C(9)	1.418(8)
C(2)–Fe(1)–O(1)	83.90(19)
C(6)–Fe(3)–C(5)	39.5(2)
C(1)–C(2)–C(3)	116.7(5)
C(4)–C(3)–C(2)	116.3(5)
O(1)–C(4)–C(3)	116.5(5)
O(1)–C(4)–C(5)	120.5(5)
C(3)–C(4)–C(5)	123.0(5)
C(6)–C(5)–C(4)	120.3(5)
C(6)–C(5)–C(7)	119.1(5)
C(4)–C(5)–C(7)	115.4(5)
O(8)–C(7)–C(5)	111.3(5)
C(7)–O(8)–C(9)	111.5(5)
C(4)–O(1)–Fe(1)	112.2(3)

is π-bound to the Fe(CO)₄ fragment. In the complex, each iron atom is 18 electron precise. A short intermolecular hydrogen bond H(7B)···O(33) contribute to the crystal packing.

4. Conclusions

The reaction pathways leading to the complexes described in this work show, once again, that alkynols, alkyne-diols, and chloro-alkynes easily loose all the functional groups both under thermal and under basic conditions [1–6,14,16]. We propose, on the basis of strong indirect evidence, that, in KOH/CH_3OH solution, Fe₃(CO)₁₂ forms the [HFe₃(CO)₁₁]⁻ anion, which undergoes stepwise fragmentation to bi- and mono-nuclear iron fragments.

The formation of the methoxycarbonyl-ferrole ring of complex **5** requires the activation of CO and methanol. Complex **7** contains a complex organic ligand formed by co-oligomerization of CO and of two molecules of PA; one of the PA molecules has undergone exchange between the OH group and a CH_3O, a process recently evidenced in the chemistry of dicobalt alkynol derivatives [18]. Also in this case, activation, or splitting of methanol is observed and a methoxy-substituted ligand is formed.

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