

Metal fragment condensation and carbon–carbon bond cleavage in reactions of $[\text{Fe}_3(\text{CO})_{12}]$ with internal propargyl alcohols. Structures of the “bow tie” acetylide complexes $[\text{Fe}_5(\text{CO})_{14}(\text{C}_2\text{R})_2]$ ($\text{R} = \text{Me}$ or Et)

Sabrina Brait,^a Giuliana Gervasio,^a Domenica Marabello^a and Enrico Sappa^{*b}

^a Dipartimento di Chimica IFM, Università di Torino, Via Pietro Giuria 7, I-10125 Torino, Italy

^b Dipartimento di Scienze e Tecnologie Avanzate, Università del Piemonte Orientale Amedeo Avogadro, Corso Borsalino 54, I-15100, Alessandria, Italy

Received 18th October 1999, Accepted 21st January 2000

The propargyl alcohols $\text{RC}_2\text{C}(\text{H})(\text{OH})\text{R}'$ ($\text{R} = \text{H}$, $\text{R}' = \text{Et}$; $\text{R} = \text{Me}$, $\text{R}' = \text{Et}$; $\text{R} = \text{Et}$, $\text{R}' = \text{Me}$; $\text{R} = \text{Ph}$, $\text{R}' = \text{Pr}^i$) reacted with $[\text{Fe}_3(\text{CO})_{12}]$ in hydrocarbon solvents to give, as the final products, binuclear “ferrole” derivatives $[\text{Fe}_2(\text{CO})_6\text{L}_2]$ or $[\text{Fe}_2(\text{CO})_6(\text{L})(\text{L} - \text{H}_2\text{O})]$ [$\text{L} = \text{propargyl alcohol}$] in several isomers. Small amounts of tri- and penta-nuclear complexes were also obtained. In particular, when $\text{R} = \text{H}$ or Ph trinuclear complexes $[\text{Fe}_3(\text{CO})_9(\mu\text{-CO})\text{L}]$ **1** with a “parallel” alkyne ligand could be isolated and characterized by IR and NMR spectroscopies and mass spectrometry. When $\text{R} = \text{Me}$ or Et the “bow tie” acetylide complexes $[\text{Fe}_5(\text{CO})_{14}(\text{C}_2\text{R})_2]$ ($\text{R} = \text{Me}$ **2a** or Et **2b**) were isolated; their structures were determined by X-ray diffraction. The complexes **2a** and **2b** are formed by two Fe_3 triangles sharing a common vertex: each triangle is co-ordinated in a perpendicular fashion by an acetylide fragment and the carbon of one of the acetylide ligands is bound to four iron atoms. Complexes **2** are new examples of an uncommon type of cluster framework; they are presumably formed upon condensation of metal fragments generated by triiron dodecacarbonyl and upon cleavage of a carbon–carbon bond α to the alkyne triple bond. Possible formation mechanisms are discussed.

Introduction

Propargyl (prop-2-ynyl) alcohols are useful synthons for organic syntheses. Among his many achievements, Julius Walter Reppe, a legend in acetylene chemistry, prepared on the industrial scale butanediol, furan and tetrahydrofuran through the intermediacy of propargyl alcohol: he also designed an efficient synthetic process to isoprene through the intermediacy of 3,3-dimethylbut-1-yn-3-ol obtained from acetylene and acetone.¹ A related process, leading to the synthesis of arylacetylenes using, among others, palladium-based catalysts was developed later.² The mechanisms of these reactions are relevant to the present results and will be discussed.

In more recent times, propargyl alcohols have been used as intermediates for the synthesis of pharmaceuticals, surface agents, corrosion inhibitors and lubricants.³ In the presence of transition metal catalysts they also act as precursors of carbamates.⁴

During the above reactions dehydration of propargyl alcohols may occur; this is presumably a general process, which is also observed in the course of other reactions. For example, they may undergo dehydration on mononuclear transition metal complexes; some of these reactions are promoted by inorganic oxides⁵ and lead to cumulene derivatives of some interest for applications in non-linear optics (NLO). Dehydration may also occur on clusters or during condensation of metal fragments (favoured by the ligand) giving rise to allylic or allenyl derivatives.^{6–8}

We have recently reported on the reactions of terminal propargyl alcohols $\text{HC}_2\text{CRR}'(\text{OH})$ with $[\text{M}_3(\text{CO})_{12}]$ carbonyls ($\text{M} = \text{Ru}$ or Fe), including dehydration pathways.⁸ For triiron dodecacarbonyl, reactions leading to fully or partially dehydrated derivatives were observed;⁹ the allenylidene complexes $[\text{Fe}_3(\text{CO})_9(\mu\text{-CO})(\text{C}=\text{C}=\text{CRR})]$ **A**, the metallacyclic derivatives $[\text{Fe}_3(\text{CO})_6(\mu\text{-CO})_2(\text{L})(\text{L} - \text{H}_2\text{O})]$ **B** and the “ferrole”

complexes $[\text{Fe}_2(\text{CO})_6\text{L}_2]$ **C** or $[\text{Fe}_2(\text{CO})_6(\text{L})(\text{L} - \text{H}_2\text{O})]$ **C'** were obtained. We also found some unexpected reactions; for example $[\text{Fe}_3(\text{CO})_9(\mu\text{-CO})(\text{C}=\text{C}=\text{C}(\text{H})\text{Ph})]$ reacts with methanol to form a methoxy-substituted ferrole derivative **D**,¹⁰ whereas $\text{HC}_2\text{C}(\text{Me})(\text{OH})\text{Ph}$ reacts with $[\text{Fe}_3(\text{CO})_{12}]$ forming a binuclear complex (**E**) with a “deoxygenated” ligand.¹¹

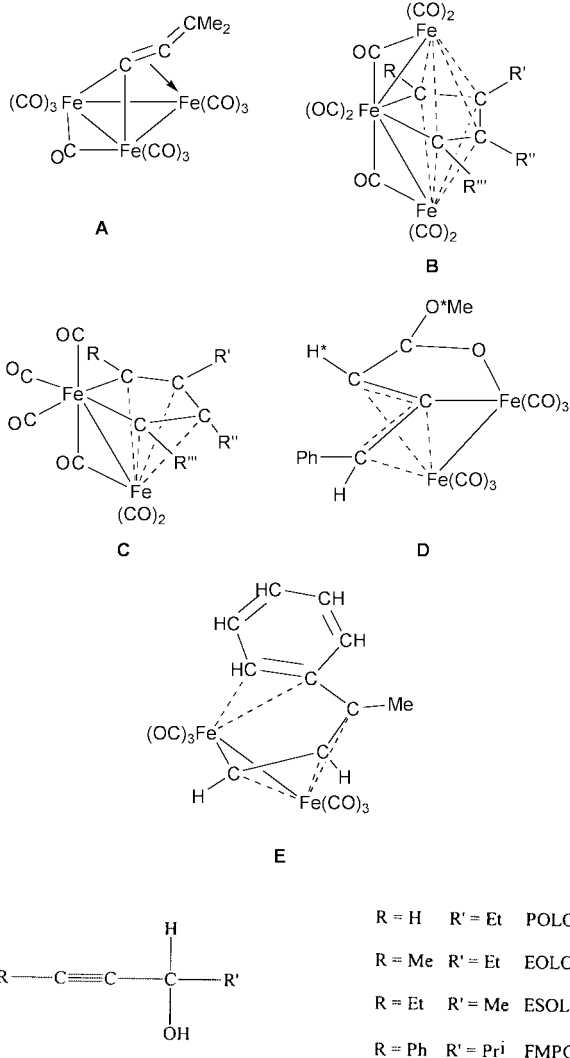
In this paper we report on the reactions of internal propargyl alcohols, which, at least in principle, would undergo different dehydration pathways. The ligands used were hex-4-yn-3-ol (EOLO), hex-3-yn-2-ol (ESOL) and 4-methyl-1-phenylpent-1-yn-3-ol (FMPO); the terminal alkyne pent-1-yn-3-ol (POLO) was also used for comparison.

The main products of the reactions in hydrocarbon solvents were binuclear ferrole derivatives of the type **C** (or **C'** when partial dehydration was observed, as discussed below) in several isomers. Somewhat unexpectedly we found, however, that FMPO and POLO also gave small amounts of the trinuclear derivatives $[\text{Fe}_3(\text{CO})_9(\mu\text{-CO})\text{L}]$ **1** which were characterized by IR and NMR spectroscopies and mass spectrometry; complexes **1** contain a (non-dehydrated) alkyne ligand co-ordinated in parallel fashion to one edge of a triangular cluster. In contrast, when EOLO and ESOL were used small yields of the pentanuclear “bow tie” complexes $[\text{Fe}_5(\text{CO})_{14}(\text{C}_2\text{R})_2]$ ($\text{R} = \text{Me}$ **2a** or Et **2b**) were formed: their structures were determined by X-ray diffraction. A discussion of the (uncommon) structures and of the possible formation pathways for complexes **2** is given.

Experimental

General details, materials, analysis of the products

Triiron dodecacarbonyl (Strem Chemicals) (contains about 10% of methanol as a stabilizer, see ref. 10) and the alkynes (Lancaster Syntheses) were commercial products used as



received. Solvents (benzene, toluene, heptane) were dehydrated over sodium. All the reactions were performed under a dry nitrogen atmosphere in conventional three necked flasks equipped with gas inlet, cooler, mercury check valve and magnetic stirring.

The reaction mixtures were filtered under N₂, brought to small volume under reduced pressure and separated on TLC plates (Merck Kieselgel PF; eluents, mixtures of hexane and diethyl ether in variable v/v ratios depending on the substrates). The products were crystallized when possible (sometimes oily products were obtained which could not be crystallized) and analysed by means of a Bruker Equinox 55 IR spectrophotometer (KBr cells); the ¹H NMR spectra were obtained on a JEOL JNM 270/89 instrument and the mass spectra with a Finnigan-Mat TSQ-700 mass spectrometer (Servizio di Spettrometria di Massa, Dipartimento di Scienza e Tecnologia del Farmaco, Università di Torino).

Reactions of Fe₃(CO)₁₂

With hex-4-yn-3-ol [EOLO]. Triiron dodecacarbonyl (1 g, *ca.* 2.0 mmol) was suspended in a benzene solution of the alkyne (1 cm³, *ca.* 12.0 mmol) and 100 mg of Me₃NO·2H₂O; the suspension was brought to reflux for 5 min, during which time foaming due to development of gases was observed. After reduction to small volume and TLC the following products could be detected: parent carbonyl (*ca.* 15%), two orange complexes **C(1)**, **C'(1)** (in about 10% yield each) and a dark blue band (1%) corresponding to complex **2a**, together with some (trace amount) unidentified compounds and considerable decomposition.

Complex C(1): IR, ν_{CO} (C₇H₁₆) 2071s, 2026vs, 2001s, 1987vs and 1969ms cm⁻¹; EI mass spectrum, P⁺ at *m/z* 476, loss of six CO. Tentative identification [Fe₂(CO)₆L₂].

Complex C'(1): IR, ν_{CO} (C₇H₁₆) 2075s, 2029vs, 2008s, 1990vs and 1976m cm⁻¹; EI mass spectrum, P⁺ at *m/z* 458, loss of 6 CO. Tentative identification [Fe₂(CO)₆(L)(L - H₂O)].

Complex 2a: IR, 2074m, 2028s, 2004m, 1999m cm⁻¹; ¹H NMR (CDCl₃, r.t., TMS as internal standard), δ 1.20 (m), 0.80 (m) (CH₃), slightly broad signals (presumably because of paramagnetic impurities); EI mass spectrum, P⁺ at *m/z* 750 loss of 7 CO (low intensity signals) followed by loss of other 7 CO (intense signals).

With hex-3-yn-2-ol [ESOL]. Triiron dodecacarbonyl (1 g, *ca.* 2.0 mmol) was suspended in a benzene solution of the alkyne (1 cm³, *ca.* 10.0 mmol) and of Me₃NO·2H₂O; the suspension was brought to reflux for 4 min. After reduction to small volume and TLC the following products could be detected: parent carbonyl (*ca.* 15%), orange complex **C(2)** (about 10% yield), blue-brown complex **2b** (1%) and a yellow band (complex **C'(2)**).

Complex C(2): IR, ν_{CO} (C₇H₁₆) 2071vs, 2026vs, 2001vs, 1987vs and 1969ms cm⁻¹; ¹H NMR, δ 7.50 (s, 1 H)*, 7.0 (s, 1 H)*, 5.30 (s, 1 H, OH)*, 3.35 (s, 1 H, OH)*, 1.60 (s, 4 H, CH₂) and 0.80 (m, 6 H, CH₃) {* some of these attributions can be reversed}; EI mass spectrum: P⁺ at *m/z* 476, release of 6 CO. Tentative identification [Fe₂(CO)₆L₂].

Complex 2b: IR, 2075ms, 2029vs, 2007s and 1990s, cm⁻¹; ¹H NMR, δ 3.80 (m, CH₂) and 1.55 (m, CH₃); EI mass spectrum, P⁺ at *m/z* 778 (weak), loss of 7 CO (low intensity signals) followed by loss of other 7 CO (intense signals).

Complex C'(2): IR, 2069m, 2033vs, 2024s (sh), 1998m and 1942w cm⁻¹; EI mass spectrum, *m/z* 458, release of 6 CO. Tentative identification [Fe₂(CO)₆(L)(L - H₂O)].

With 4-methyl-1-phenylpent-1-yn-3-ol [FMPO]. Triiron dodecacarbonyl (1 g, *ca.* 2.0 mmol) was suspended in a benzene solution of the alkyne (1 cm³, *ca.* 5.7 mmol) and of Me₃NO·2H₂O; the suspension was brought to reflux for 15 min. After reduction to small volume, TLC was performed; because of the oily nature of the alkyne each band collected had to be chromatographed again. The following products were obtained: parent carbonyl (*ca.* 15%), brown complex **1b** (*ca.* 10%), two orange complexes (**C(3)**, **C(3a)**, in about 10% yield each), two yellow and one pink complexes (**F(3)**, **F(3a)**, **F(3b)** in about 5% yield each), two unidentified trace products together with some decomposition.

Complex 1b: IR, 2080w, 2048vs, 2035s, 2029s, 1986vsm. 1975vs and 1842m cm⁻¹; ¹H NMR, δ 7.55–7.25 (m, Ph), 6.02 (s, 1 H), 3.20 (m, 1 H, OH), 2.05 (m, CH₂), 1.40 (d, CH₂) and 1.20 (d, Me); EI mass spectrum, P⁺ at *m/z* 618, release of 10 CO.

Complex C(3): IR, 2075ms, 2034vs, 2005ms, 1996ms and 1978m cm⁻¹; EI mass spectrum, P⁺ at *m/z* 628, loss of 6 CO, then of water. Tentative identification [Fe₂(CO)₆L₂].

Complex C(3a): IR, 2075m, 2034vs, 2005m, 1996m and 1978m cm⁻¹; EI mass spectrum, P⁺ at *m/z* 618, release of 6–8 fragments with *m/z* 28. Tentative identification [Fe₂(CO)₆L₂].

Complex F(3): IR, 2065vs, 2058vs, 2021vs, 1996vs, 1986vs, 1918m and 1778m cm⁻¹; EI mass spectrum, P⁺ at *m/z*, 656, release of 7 CO. Tentative identification [Fe₂(CO)₆{L(CO)L}], “flyover”.¹²

Complex F(3a): IR, 2065vs, 2015vs, 1985vs, 1968 (sh) and 1734s cm⁻¹; ¹H NMR, δ 9.11 (s, 1 H), 7.99 (s, 1 H), 7.45–7.20 (m, Ph), 6.37 (s), 5.90 (s), 3.83 (s) (CH₂, OH) and 1.55 (s, Me); EI mass spectrum, P⁺ at *m/z* 656, release of 6 CO, then complex fragmentation. Tentative identification as for **F(3)**, “flyover” structure.

Complex F(3b): IR, 2065vs, 2039 (sh), 2029vs, 2006 (sh), 1985vs, 1968 (sh) and 1734m cm⁻¹; EI mass spectrum, P⁺ at *m/z* 638, release of 6 CO, then complex fragmentation.

Tentative identification $[\text{Fe}_2(\text{CO})_6\{\text{L}(\text{CO})(\text{LH}_2\text{O})\}]$, “flyover” structure.

With pent-1-yn-3-ol [POLO]. Triiron dodecacarbonyl (2 g, 4.0 mmol) was suspended in a benzene solution of the alkyne (1.5 cm³, *ca.* 2.0 mmol) and of $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$; the suspension was brought to reflux for 10 min, during which time foaming due to development of gases was observed. After reduction to small volume and TLC the following products could be detected: brown complex **1a** (*ca.* 10%), orange (**C(4)**), about 10%), two yellow complexes (**C'(4)**, **C'(4a)** 10% each), two red complexes (**F(4)**, **F(4a)**, 10% each), three trace, unidentified complexes, and considerable decomposition.

Complex 1a: IR, 2068w, 2027vs (sh), 1999mw, 1988mw and 1887m cm⁻¹; ¹H NMR (broad signals); δ 6.15 (s, 1 H), 3.50 (m, 1 H), 2.00 (m, 1 H, OH), 1.57 (m, CH₂) and 1.29 (s, Me); EI mass spectrum, P⁺ at *m/z* 532, release of a fragment with *m/z* 16 (oxygen or CH₄?) (low intensity), then release of 10 CO.

Complex C(4): IR, 2068m, 2055w, 2048w, 2033 (sh), 1999s and 1989s cm⁻¹; EI mass spectrum; *m/z* 448, release of 6 CO. Tentative identification $[\text{Fe}_2(\text{CO})_6\text{L}_2]$.

Complex C'(4): IR, 2068m, 2033vs (sh), 2001m, 1995m, 1970w and 1889w cm⁻¹; EI mass spectrum; P⁺ at *m/z* 430, release of 6 CO. Tentative identification $[\text{Fe}_2(\text{CO})_6(\text{L})(\text{L} - \text{H}_2\text{O})]$.

Complex C'(4a): IR, 2083w, 2070w, 2052m, 2034s, 2021w, 2002w and 1988w cm⁻¹; EI mass spectrum; *m/z* 430, release of 6 CO. Tentative identification as for **C'(4)**.

Complex F(4): IR, 2069m, 2034vs, 2022 (sh), 2010w, 2000m, 1987m and 1888w cm⁻¹; ¹H NMR; δ 8.70 (s, 1 H), 4.50 (dd, 1 H), 3.53 (m), (1 H, OH), 2.21 (m), (CH₂) and 1.07 (m), (CH₃); EI mass spectrum, P⁺ at *m/z* 474 (expected 476), release of 6 CO then complex fragmentation. Tentative identification “flyover” structure.

Complex F(4a): IR, 2068m (sh), 2053ms, 2034vs, 2021 (sh), 1999vs and 1887w cm⁻¹; EI mass spectrum, *m/z* 476, release of 6 CO. Tentative identification as above.

Crystallography

Crystal data. Complex **2a**, C₂₀H₆Fe₅O₁₄, *M* = 749.50, monoclinic, space group *P*2₁/*c* (no. 14), *a* = 8.784(2), *b* = 20.684(6), *c* = 14.325(3) Å, β = 100.24(2)°, *U* = 2561(1) Å³, *Z* = 4, *T* = 293 K, $\mu(\text{Mo-K}\alpha)$ = 2.833 mm⁻¹.

Complex 2b, C₂₂H₁₀Fe₅O₁₄, *M* = 777.55, triclinic, space group *P* $\bar{1}$, *a* = 9.009(4), *b* = 9.949(5), *c* = 15.673(8) Å, α = 88.53(4), β = 84.83(4), γ = 76.67(4)°, *U* = 1361(1) Å³, *Z* = 2, *T* = 293 K, $\mu(\text{Mo-K}\alpha)$ = 2.669 mm⁻¹.

4809 (**2a**) and 4932 (**2b**) reflections were measured on a Siemens P4 diffractometer, 4502 (*R*_{int} = 0.0245) and 4749 (*R*_{int} = 0.0331) being unique. Empirical absorption correction applied.¹³

The non-hydrogen atoms were anisotropically refined. The last Fourier-difference maps showed the peaks corresponding to the H atoms of the ligands; they were put in the experimental positions and refined with *U*_{iso} = 0.02 + *U*_{eq} of the corresponding C atom. The satisfactory results of the refinement, obviously with high e.s.d.s. justified this approach. For 2838 (**2a**) and 2723 (**2b**) data with *F*_o > 4σ(*F*_o) the final *R*1 = 0.0417 and 0.0532 respectively; *wR*2 = 0.0656 (**2a**) and 0.0946 (**2b**). Goodness of fit on *F*² 1.037 (**2a**) and 1.014 (**2b**).

CCDC reference number 186/1816.

See <http://www.rsc.org/suppdata/dt/a9/a908308a/> for crystallographic files in .cif format.

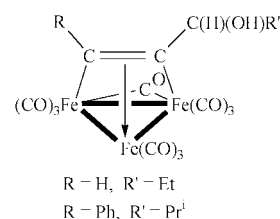
Results and discussion

Synthesis and characterization of the complexes

The thermal reactions of the propargyl alcohols are not selective and yield small amounts of several complexes each. The

majority of the products are binuclear ferrole complexes of type **C** (partially dehydrated ferrole derivatives, complexes **C'** have also been obtained) and flyover derivatives **F** which were characterized by spectroscopy and mass spectrometry. These derivatives presumably represent the stable end reaction products, and are obtained in several geometrical isomers containing (dimerized) original alkyne ligands or partially dehydrated ligands; the geometrical isomers were not identified, because this type of structure is quite common and has recently been reviewed.¹² Therefore they will not be discussed in detail in this paper.

In contrast, the trinuclear complexes **1** (*R* = H **1a** or Ph **1b**) are of some interest; under the conditions adopted in this work they were obtained only from POLO and FMPO. They contain intact (non-dehydrated) alkyne ligands as shown, in particular, by the mass spectra; therefore they cannot belong to the family of allenylidene complexes **A**. In the IR spectra a signal in the bridging CO region is also observed. On these bases we propose for complexes **1** a structure based on a triangular cluster with the alkyne parallel to the same edge bridged by the CO, as shown. This type of structure is not uncommon for ruthenium



and osmium⁸ but is quite rare for iron; the unique complex whose structure has been determined by X-ray analysis has been obtained from a lightly ligated derivative of $[\text{Fe}_3(\text{CO})_{12}]$.¹⁴ Unfortunately, we could not obtain crystals suitable for X-ray analysis in order to confirm our hypothesis.

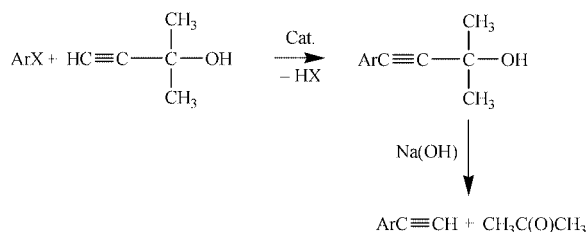
In the reactions of EOLO and ESOL small amounts of the new complexes **2** are formed; they belong to an uncommon type of cluster complexes whose identification was difficult if based only on the mass spectra and on the spectroscopic data. Therefore their structures were determined by X-ray diffraction.

Formation of complexes 2. A further example of clusters as models of intermediates in organic reactions

We could not follow the reaction pathways leading to complexes **2** because of their low yields and of the contemporary formation of several other derivatives; however, it is evident that their formation requires release and recondensation of metal fragments as well as the cleavage of the C–C bond α to the triple bond of the alkynic ligands. These two aspects are discussed.

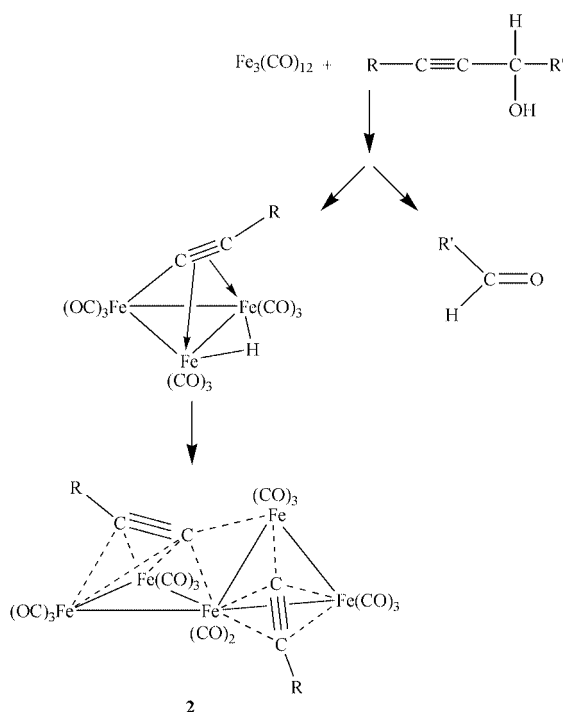
Carbon–carbon bond cleavage. The formation of the acetylidene ligands found in complexes **2** can easily be explained when considering that the propargyl alcohols are (i) the condensation products of alkynes with ketones¹ and (ii) intermediates in the synthesis of arylacetylenes² as previously pointed out. In the latter reaction a transition-metal catalysed arylation of propargyl alcohols occurs; this is followed by basic hydrolysis which results in the formation of an arylacetylene and of a ketone as shown in Scheme 1. Recent examples of this process are in ref. 15.

One could ask why only two of the four ligands examined give this behaviour; the answer could be that (a) the electronic effects of the *R* substituent on the alkyne C(α) could play a role [Taft's σ of H, Ph *versus* Me, Et] and/or (b) the stability of the ketones or aldehydes formed in the processes could be the driving force of the reactions. Unfortunately we could not isolate the organic products from the reaction mixtures (this is



Scheme 1

also due to the small yields obtained); there is, however, a literature example for a reaction of an acetylenic bialcohol with $[\text{Ru}_3(\text{CO})_{12}]$ which leads to an hydrido-acetylide trinuclear ruthenium cluster and to phenylmethyl ketone.¹⁶ A possible formation pathway for complexes **2** could be therefore represented by the reactions shown in Scheme 2. The “trapping” of



Scheme 2

an acetylide fragment during the formation of complexes **2** represents also a further example of the potential of transition metal clusters as “models of intermediates” in (transition metal catalysed) organic syntheses.¹⁷

Formation and condensation of metal fragments. It has long been known that the synthetic strategies leading to alkyne- or acetylide-substituted clusters may involve metal fragment condensation; this is particularly evident when heterometallic derivatives are obtained.¹⁸ We hypothesize that complexes **2** are formed upon condensation of acetylide-containing metal fragments (see Scheme 2). There are indeed some examples of condensation of (phosphido-bridged) bimetallic acetylide derivatives of iron and ruthenium leading to tetranuclear complexes with square-planar or lozenge structures.¹⁹ There is also one example of condensation of ruthenium bimetallic acetylides (with phosphido bridges) in the presence of cyclopentadienylnickel carbonyl dimer, affording a pentametallic complex;²⁰ the structure of this complex is, however, a flattened butterfly with a nickel atom spanning the wings.

Structures of complexes **2a** and **2b**

The structures of complexes **2a** and **2b** are shown in Figs. 1 and

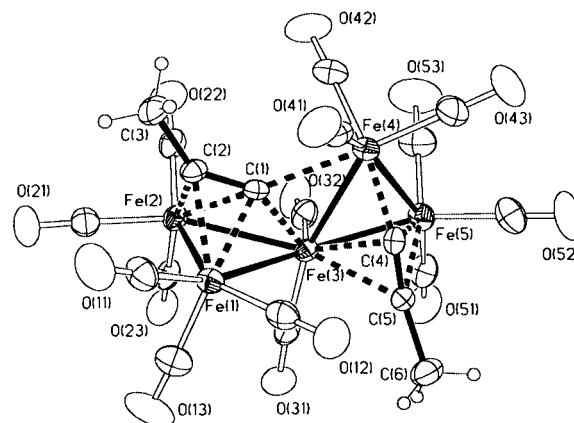


Fig. 1 An ORTEP²¹ plot of $[\text{Fe}_3(\text{CO})_{14}(\text{C}_2\text{Me})_2]$ **2a** with 30% thermal ellipsoids.

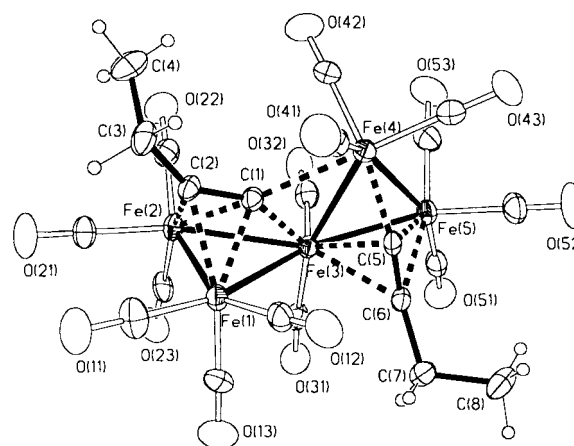


Fig. 2 An ORTEP plot of $[\text{Fe}_3(\text{CO})_{14}(\text{C}_2\text{Et})_2]$ **2b** with 30% thermal ellipsoids.

2. Relevant bonding distances and angles are collected in Table 1. The complexes are formed by two triangles of iron atoms sharing one vertex; each triangle is co-ordinated by an acetylide ligand disposed in “perpendicular” fashion with respect to a Fe–Fe edge. Three terminal carbonyls are bound to each iron atom with the exception of the “central” Fe(3) which is coordinated by only two CO's. An analysis of the values of the Fe–C–O angles in complex **2a** shows that Fe(3)–C(32)–O(32) ($170.4(6)^\circ$) is significantly smaller than the average Fe–C–O angle ($177.2(6)^\circ$), thus suggesting a tendency to a semi-bridging arrangement. The same tendency, less evident however, is shown in complex **2b** (Fe(3)–C(32)–O(32) $172.7(7)^\circ$ versus $177.1(8)^\circ$ av.). In the clusters each iron atom is 18 electron precise; when considering the acetylides as five electron donors a total count of 78 electrons is obtained.

There are some features of interest in these structures, that is the uncommon “bow tie” arrangement and the co-ordination of one acetylide carbon to four iron atoms. The two Fe_3 triangles joined through a vertex form an angle of 76° in both complexes and have one short (2.471(2)–2.517(2) Å) and two long (2.614(1)–2.674(1) Å) edges. The short edges are bridged by the acetylide ligands. The C≡C bond distances in the range 1.28(1)–1.31(1) Å and the C–C angles $141.8(5)$ – $150.1(8)^\circ$ are a consequence of the usual great deformation of the acetylide ligand on co-ordination. The crystal packing of complex **2a** shows a short intermolecular contact $\text{O}(41) \cdots \text{O}(53)$ (2.858 Å) and complex **2b** is involved in an intermolecular C–H \cdots O hydrogen bond $\text{C}(3)\text{H}(3\text{A}) \cdots \text{O}(52)$ 2.566, $\text{C}(3) \cdots \text{O}(52)$ 3.356 Å).

The “bow tie” metal atom arrangement is not very common; to our knowledge only seven complexes containing four or five

Table 1 Selected bond lengths [Å] and angles [°] for complexes **2a** and **2b**

	Complex 2a	Complex 2b
Fe(1)–Fe(2)	2.485(1)	2.471(2)
Fe(1)–Fe(3)	2.639(1)	2.656(2)
Fe(2)–Fe(3)	2.661(1)	2.671(2)
Fe(3)–Fe(4)	2.614(1)	2.619(2)
Fe(3)–Fe(5)	2.509(1)	2.517(2)
Fe(4)–Fe(5)	2.674(1)	2.666(2)
Fe(1)–C(1)	2.038(4)	2.030(7)
Fe(1)–C(2)	2.096(5)	2.092(7)
Fe(2)–C(1)	2.145(5)	2.110(7)
Fe(2)–C(2)	2.026(5)	2.056(7)
Fe(3)–C(1)	1.886(5)	1.866(7)
Fe(3)–C(4)/Fe(3)–C(5)	2.055(5)	2.062(7)
Fe(3)–C(5)/Fe(3)–C(6)	2.169(5)	2.161(7)
Fe(4)–C(1)	2.223(5)	2.313(7)
Fe(4)–C(4)/Fe(4)–C(5)	1.833(5)	1.835(8)
Fe(5)–C(4)/Fe(5)–C(5)	2.022(5)	2.026(7)
Fe(5)–C(5)/Fe(5)–C(6)	2.090(5)	2.118(7)
Fe–C _{co} av.	1.800(6)	1.785(9)
C–O av.	1.136(6)	1.139(9)
C(1)–C(2)	1.285(6)	1.306(9)
C(2)–C(3)	1.495(7)	1.485(10)
C(4)–C(5)/C(5)–C(6)	1.279(6)	1.285(9)
C(5)–C(6)/C(6)–C(7)	1.480(7)	1.500(11)
Fe(2)–Fe(1)–Fe(3)	62.50(3)	62.66(5)
Fe(1)–Fe(2)–Fe(3)	61.60(3)	62.06(5)
Fe(1)–Fe(3)–Fe(2)	55.91(3)	55.28(5)
Fe(1)–Fe(3)–Fe(4)	94.26(3)	94.93(6)
Fe(1)–Fe(3)–Fe(5)	150.18(4)	145.12(6)
Fe(2)–Fe(3)–Fe(4)	105.63(3)	107.85(7)
Fe(2)–Fe(3)–Fe(5)	144.99(4)	153.30(6)
Fe(4)–Fe(3)–Fe(5)	62.88(3)	62.53(6)
Fe(3)–Fe(4)–Fe(5)	56.64(3)	56.87(5)
Fe(3)–Fe(5)–Fe(4)	60.48(3)	60.61(5)
Fe–C–O av.	177.2(6)	177.1(8)
Fe(1)–C(1)–C(2)	74.4(3)	74.1(5)
Fe(3)–C(1)–C(2)	146.7(4)	150.4(6)
Fe(4)–C(1)–C(2)	134.8(4)	132.8(5)
Fe(4)–C(4)–C(5)/Fe(4)–C(5)–C(6)	157.1(4)	156.9(6)
C(1)–C(2)–C(3)	141.8(5)	144.5(7)
C(4)–C(5)–C(6)/C(5)–C(6)–C(7)	148.9(5)	150.1(8)

iron atoms have been structurally characterized. They are mostly anionic derivatives, such as the heterometallic $[\text{MFe}_4(\text{CO})_{16}]^{2-}$ ($\text{M} = \text{Pd}$ or Pt),²² the chalcogenides $[\text{Fe}_5(\text{CO})_{14}\text{X}]^{2-}$ ($\text{X} = \text{S}$ or Se)^{23,24} and the heterometallic chalcogenide $[\text{MoFe}_4\text{S}_3(\text{CO})_{13}(\text{PEt}_3)]^{2-}$.²⁵ Other examples of neutral²⁶ or cationic²⁷ chalcogenide derivatives containing at least one iron atom have also been reported; finally, a pentanuclear osmium chalcogenide derivative is known.²⁸ The unique pentanuclear neutral iron derivative structurally characterized is “stabilized” by a large *syn*-bis-diazeno ligand.²⁹ These structures are not easily comparable with those reported in this work; therefore comparisons of bonding distances and angles will not be attempted.

There is, however, another interesting family of “bow tie” complexes which deserves discussion; these are the derivatives of $[\text{Os}_5(\text{CO})_{19}]$,³⁰ one of which, $[\text{Os}_5(\text{CO})_{17}(\text{HCCH})]$ is, to our knowledge, the unique “bow tie” structure containing an acetylene ligand (bound, however, parallel to one edge of a triangle).³¹ In this cluster, the dihedral angle between the two osmium triangles is 34–44° (two independent molecules) compared with 76° in the complexes **2**. The great difference of the two angle values is due obviously to the different arrangements of the acetylene and to the requirement of a bond between C(1) and Fe(4) in complexes **2**.

Other acetylene- or acetylide-containing “bow tie” clusters worthy of mention are $[\text{Fe}_2\text{Au}_2\text{Ir}(\text{CO})_7(\text{PPh}_3)_3]$ ³² and $[\text{Ru}_3\text{Co}_2(\text{CO})_{10}(\mu\text{-CO})(\text{dppm})(\text{C}_2\text{Ph})_2]$,³³ very recently the carbidic-acetylidic “bow tie” complex $[\text{Ru}_6(\mu\text{-H})(\mu_4\text{-C})(\mu_4\text{-CCMe})(\mu\text{-CO})(\text{CO})_{16}]$ has been reported.³⁴ Related acetylide- or acetylene-containing structures are represented by the “dimeric” cation $[\text{Fe}_6(\text{CO})_{18}\text{C}_4]^{2+}$ obtained from a triiron ketenylidene cluster³⁵ and by the open $[\text{Ni}_3(\text{RC}_2\text{R}')]$ clusters recently reported.³⁶

The co-ordination of an acetylide carbon atom to four metals has previously been reported for heterometallic tetra-nuclear (metallo-ligated triangular) derivatives; examples are in ref. 37. In these complexes, however, the acetylide is co-ordinated nearly parallel to one of the edges of the triangle of metal atoms, although there is a slight distortion towards the perpendicular bonding mode.³⁸ In complexes **2** the acetylide ligands are co-ordinated perpendicularly to one edge of the metal triangle; therefore these complexes represent, to our knowledge, the first example of such an interaction between acetylides and metal atoms. Complexes **2** are also characterized by the presence of two acetylides, bound to the metals in a slightly different way; this feature, also, is unprecedented.

Conclusion

The reactions reported in this paper have shown that propargyl alcohols bearing hydrogen atoms on the carbon in α position to the triple bond may react in different ways towards $[\text{Fe}_3(\text{CO})_{12}]$ forming tri- or penta-nuclear clusters. Their behaviour is presumably dependent on the type of substituents which can favour, or not, C–C bond cleavage near the triple bond. Complexes **1** represent uncommon examples of clusters with “parallel” alkynes whereas clusters **2** are new examples of the uncommon “bow tie” cluster family. The formation of clusters **2** involves a carbon–carbon bond cleavage reaction which has previously been reported in transition-metal-catalysed organic chemistry where no intermediates could be identified.^{1,3} Under this profile, the present report represents further evidence for the (not yet fully explored) potential of cluster chemistry.

Acknowledgements

Financial support to this work has been obtained from Ministero dell' Università e della Ricerca Scientifica e Tecnologica (Italy) and Consorzio I.N.C.M. (Italy).

References

- 1 J. W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Liebigs Ann. Chem.*, 1955, **596**, 1; 1956, **601**, 81.
- 2 T. Sabourin and A. Onopchenko, *J. Org. Chem.*, 1983, **48**, 5135; A. Carpita, A. Lessi and A. Rossi, *Synthesis*, 1984, 571.
- 3 R. J. Tedeschi, *Acetylene-based Chemicals from Coal and other Natural Resources*, M. Dekker, New York, 1982.
- 4 T.-J. Kim, K.-H. Kwon, J.-O. Beag, S.-C. Shin and D.-H. Lee, *J. Organomet. Chem.*, 1990, **389**, 205; C. Bruneau and P. H. Dixneuf, *Chem. Commun.*, 1997, 507 and references therein; W. Hartmann and H. Singer, *J. Mol. Catal.*, 1988, **48**, 81.
- 5 J. P. Selegue, *J. Am. Chem. Soc.*, 1983, **105**, 5921; B. M. Trost, *Chem. Ber.*, 1996, **129**, 1313; R. W. Lass, P. Steinert, G. Wolf and H. Werner, *Chem. Eur. J.*, 1996, **1**, 19; H. Werner, R. Wiedemann, N. Mahr, P. Steinert and J. Wolf, *ibid.*, 1996, **2**, 561; H. Werner, *Chem. Commun.*, 1997, 903; G. Jia, H. P. Xia, W. F. Wu and F. S. Ng, *Organometallics*, 1996, **15**, 3634; A. J. Hodge, S. L. Ingmann, A. K. Kakkar, M. S. Khan, J. Lewis, N. J. Long, D. G. Parker and P. R. Raithby, *J. Organomet. Chem.*, 1985, **488**, 205.
- 6 A. Wojcicki and C. E. Schuchart, *Coord. Chem. Rev.*, 1990, **105**, 35.
- 7 S. Doherty, J. F. Corrigan, A. J. Carty and E. Sappa, *Adv. Organomet. Chem.*, 1995, **37**, 39.
- 8 G. Gervasio, R. Gobetto, P. J. King, D. Marabello and E. Sappa, *Polyhedron*, 1998, **17**, 2937 and references therein.
- 9 E. Sappa, G. Predieri, A. Tiripicchio and F. Uguzzoli, *Gazz. Chim. Ital.*, 1995, **125**, 51.
- 10 G. Gervasio, D. Marabello and E. Sappa, *J. Chem. Soc., Dalton Trans.*, 1997, 1851.
- 11 G. Gervasio and E. Sappa, *Organometallics*, 1993, **12**, 1458.
- 12 E. Sappa, *J. Organomet. Chem.*, 1999, **573**, 139.

- 13 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
- 14 D. Lentz and M. Reuter, *Chem. Ber.*, 1991, **124**, 773.
- 15 K. Sonogashira, Y. Tohda and N. Hagihara, *Tetrahedron Lett.*, 1975, 4467; T. Hiyama, N. Wakasa, T. Ueda and T. Kusumoto, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 640; D. E. Ames, D. Bull and C. Takundwa, *Synthesis*, 1981, 364; S. Takahashi, Y. Kuroyama, N. Sonogashira and N. Hagihara, *Synthesis*, 1980, 627; G. T. Crisp, P. D. Turner and K. A. Stephens, *J. Organomet. Chem.*, 1998, **570**, 219.
- 16 S. Aime, L. Milone and A. J. Deeming, *J. Chem. Soc., Chem. Commun.*, 1980, 1168.
- 17 G. Predieri, A. Tiripicchio, M. Tiripicchio Camellini, M. Costa and E. Sappa, *Organometallics*, 1990, **9**, 1729; *J. Organomet. Chem.*, 1992, **423**, 129; E. Boroni, M. Costa, G. Predieri, E. Sappa and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.*, 1992, 2585.
- 18 (a) H. Vahrenkamp, *Adv. Organomet. Chem.*, 1983, **22**, 169; (b) E. Sappa and A. Tiripicchio, *New J. Chem.*, 1988, **12**, 599.
- 19 See for example: (a) A. J. Carty, G. Hogarth, G. Enright and G. Frapper, *Chem. Commun.*, 1997, 2668; (b) J. E. Davies, M. J. Mays, P. R. Raithby and K. Sarveswaran, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2668; (c) Y. Chi, A. J. Carty, P. Blenkiron, E. Delgado, G. D. Enright, W. Wang, S.-M. Peng and G.-H. Lee, *Organometallics*, 1996, **15**, 5296.
- 20 M. Lanfranchi, A. Tiripicchio, E. Sappa, S. A. MacLaughlin and A. J. Carty, *J. Chem. Soc., Chem. Commun.*, 1982, 538.
- 21 C. K. Johnson, ORTEP II. Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
- 22 G. Longoni, M. Manassero and M. Sansoni, *J. Am. Chem. Soc.*, 1980, **102**, 3242.
- 23 F. Calderoni, F. Demartin, M. C. Iapalucci, F. Laschi, G. Longoni and P. Zanello, *Inorg. Chem.*, 1996, **35**, 898.
- 24 R. L. Holliday, L. C. Roof, B. Hargus, D. M. Smith, P. T. Wood, W. T. Pennington and J. W. Kolis, *Inorg. Chem.*, 1995, **34**, 4392.
- 25 P. A. Eldredge, K. S. Bose, D. E. Barber, R. F. Bryan, E. Sinn, A. Rheingold and B. A. Averill, *Inorg. Chem.*, 1991, **30**, 2365.
- 26 I. L. Eremenko, A. A. Pasynskii, A. S. Katugin, V. R. Zalmanovitch, B. Orazsakatov, S. A. Sleptsova, A. I. Nekhaev, V. V. Kaverin, O. G. Ellert, V. M. Novotortsev, A. I. Yanovsky, V. E. Shklover and Yu. T. Struchov, *J. Organomet. Chem.*, 1989, **365**, 325.
- 27 Z. Tang, Y. Nomura, S. Kuwata, Y. Ishii, Y. Mizobe and M. Hidai, *Inorg. Chem.*, 1998, **37**, 4909.
- 28 R. D. Adams, I. T. Horvath and L.-W. Yang, *Organometallics*, 1983, **2**, 1257.
- 29 G. Fischer, G. Sedelmeier, H. Prinzbach, K. Knoll, P. Wilharm, G. Huttner and I. Jibril, *J. Organomet. Chem.*, 1985, **297**, 307.
- 30 D. H. Farrar, B. F. G. Johnson, J. Lewis, J. N. Nicholls, P. R. Raithby and M. J. Rosales, *J. Chem. Soc., Chem. Commun.*, 1981, 273; D. H. Farrar, B. F. G. Johnson, J. Lewis, P. R. Raithby and M. J. Rosales, *J. Chem. Soc., Dalton Trans.*, 1982, 2051.
- 31 B. F. G. Johnson, J. Lewis, P. R. Raithby and M. J. Rosales, *J. Chem. Soc., Dalton Trans.*, 1983, 2645.
- 32 M. I. Bruce, P. E. Corbin, P. A. Humphrey, G. A. Koutsantonis, M. J. Liddell and E. R. T. Tiekink, *J. Chem. Soc., Chem. Commun.*, 1990, 674; M. I. Bruce, G. A. Koutsantonis and E. R. T. Tiekink, *J. Organomet. Chem.*, 1991, **408**, 77.
- 33 M. I. Bruce, N. N. Zaitseva, B. W. Skelton and A. H. White, *J. Cluster Sci.*, 1996, **7**, 109.
- 34 M. I. Bruce, B. W. Skelton, A. H. White and N. N. Zaitseva, *J. Chem. Soc., Dalton Trans.*, 1999, 13.
- 35 D. M. Norton, C. L. Stern and D. F. Shriver, *Inorg. Chem.*, 1984, **33**, 2701; see also R. W. Eveland, C. C. Raymond and D. F. Shriver, *Organometallics*, 1999, **18**, 534.
- 36 I. Hyla-Krispin, J. Koch, R. Gleiter, T. Klettke and D. Walther, *Organometallics*, 1988, **17**, 4724.
- 37 M. Akita, H. Hirakawa, K. Sakaki and Y. Moro-oka, *Organometallics*, 1995, **14**, 2775; M. Akita, M. Terada, M. Tanaka and Y. Moro-oka, *Organometallics*, 1992, **11**, 3468; R. Rumin, F. Robin, F. Y. Petillon, K. W. Muir and I. Stevenson, *Organometallics*, 1991, **10**, 2274; C. Weatherell, N. J. Taylor, A. J. Carty, E. Sappa and A. Tiripicchio, *J. Organomet. Chem.*, 1985, **291**, C9.
- 38 P. Ewing and L. Farrugia, *Organometallics*, 1989, **8**, 1246 and references therein; see also S. Deabate, R. Giordano and E. Sappa, *J. Cluster Sci.*, 1997, **8**, 407.

Paper a908308a