

# Activation of alkynols on transition metal carbonyl clusters. Reactions of 1-ethynylcyclohexanol with $\text{Fe}_3(\text{CO})_{12}$ and $\text{Co}_2(\text{CO})_8$ . Crystal structures of $\text{Co}_3(\text{CO})_9[\mu_3\text{-CCH}_2(\text{C}_6\text{H}_{10}\text{OH})]$ , $\text{Fe}_3(\text{CO})_9\text{-(}\mu\text{-CO)}[\mu_3\text{-}\eta^2\text{-C=C(C}_6\text{H}_{10})]$ and $\text{Co}_2\text{Fe(CO)}_6(\mu\text{-CO)}[\mu_3\text{-}\eta^7\text{-(C}_6\text{H}_9\text{)-CC(H)C(H)C(H)(C}_6\text{H}_{10})]$

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Received 2nd February 2001, Accepted 7th March 2001

First published as an Advance Article on the web 4th April 2001

The reactions of  $\text{Co}_2(\text{CO})_8$  with 1-ethynylcyclohexanol ( $\text{HC}\equiv\text{CC}_6\text{H}_{10}\text{OH}$ , ECY) in benzene led mainly to  $\text{Co}_2(\text{CO})_6(\text{ECY})$  **1** and to smaller amounts of the methylidyne complex  $\text{Co}_3(\text{CO})_9[\mu_3\text{-CCH}_2(\text{C}_6\text{H}_{10}\text{OH})]$  **2**. The reactions of  $\text{Fe}_3(\text{CO})_{12}$  with ECY in the same solvent led to binuclear metallacyclic derivatives  $\text{Fe}_2(\text{CO})_6(\text{ECY})_2$  (isomers **3a**, **3b**) or  $\text{Fe}_2(\text{CO})_6[(\text{ECY})_2 - \text{H}_2\text{O}]$  **3c** as the main products; small yields of trinuclear complexes  $\text{Fe}_3(\text{CO})_9(\mu\text{-CO)}[\mu_3\text{-}\eta^2\text{-1,2-HC}\equiv\text{C(C}_6\text{H}_{10}\text{OH})]$  **4**,  $\text{Fe}_3(\text{CO})_9(\mu\text{-CO)}[\mu_3\text{-}\eta^2\text{-1,2-C=C(C}_6\text{H}_{10})]$  **5** and  $\text{Fe}_3(\text{CO})_7\text{-(}\mu_3\text{-}\eta^7\text{-(C}_6\text{H}_{10}\text{OH)CCHCHC(C}_6\text{H}_9\text{))}$  **6** {containing respectively a parallel alkynol, an allenylidene and a dimeric metallacyclic ligand} were also obtained, together with **7**, a thermal decomposition product of **6**. Finally, when  $\text{Co}_2(\text{CO})_8$  was treated with ECY in benzene, and  $\text{Fe}_3(\text{CO})_{12}$  was added, the heterometallic complex  $\text{Co}_2\text{Fe(CO)}_6\text{-(}\mu\text{-CO)}[\mu_3\text{-}\eta^7\text{-(C}_6\text{H}_9\text{)CC(H)C(H)C(H)(C}_6\text{H}_{10})]$  **8** was obtained in low yields. The complexes have been characterized by means of IR and  $^1\text{H}$  NMR spectroscopies and by mass spectrometry. The structures of **2**, **5**, **8** have been determined by X-ray diffraction. Complex **2** contains an “hydrogenated” ECY ligand, **5** an allenylidene ligand formed upon dehydration of ECY (loss of the OH and of the terminal hydrogen), whereas **8** contains a ligand formed by tail-to-tail coupling of two ECY molecules, with loss of water and oxygen and shift of hydrogen. The elemental analysis of complex **8** gave a Co : Fe ratio of 2 : 1; on the basis of this analysis, the refinement of the diffraction data allowed a hypothesis on the distribution of the metal atoms in the cluster. Reaction pathways for the formation of these clusters are proposed and dehydration mechanisms for the ligand discussed.

## Introduction

Propargyl (2-propynyl) alcohols have played a considerable role in the synthesis of important chemical intermediates; isoprene, for example, was obtained in good yields from acetone and acetylene through the intermediacy of 2-methyl-3-butyn-2-ol.<sup>1</sup> Other alkynols were used as synthons for commodity chemicals; among these, 1-ethynylcyclohexanol (ECY) is a precursor of corrosion inhibitors, a stabilizer for chlorinated organics and an intermediate in the synthesis of pharmaceutical and perfumery materials.<sup>2</sup> A recent example of the use of ECY in organic syntheses has also been reported.<sup>3</sup>

Here we report on the reactions of  $\text{Co}_2(\text{CO})_8$  and/or  $\text{Fe}_3(\text{CO})_{12}$  with ECY in hydrocarbon solvents. Binuclear products and trinuclear clusters were obtained and fully characterized using analytic, spectroscopic and mass spectrometry techniques. On the basis of spectroscopic results, structures have been proposed for complexes  $\text{Fe}_2(\text{CO})_6(\text{ECY})_2$ ,  $\text{Fe}_2(\text{CO})_6[(\text{ECY})_2 - \text{H}_2\text{O}]$ ,  $\text{Fe}_3(\text{CO})_9(\mu\text{-CO)}[\mu_3\text{-}\eta^2\text{-1,2-HC}\equiv\text{C(C}_6\text{H}_{10}\text{OH})]$ ,  $\text{Fe}_3(\text{CO})_7[\mu_3\text{-}\eta^7\text{-(C}_6\text{H}_{10}\text{OH)CCHCHC(C}_6\text{H}_9\text{)}]$  and its thermal decomposition product. The structures of three complexes have been determined with X-ray diffraction analyses. All of the clusters, but one, contain “modified” ECY ligands. This behaviour is discussed and reaction (and dehydration) mechanisms are proposed.

## Experimental

### General details, materials, analysis of the products

Dicobalt octacarbonyl, triiron dodecacarbonyl (Strem

Chemicals) and 1-ethynylcyclohexanol (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  $\text{N}_2$ , brought to small volume under reduced pressure and separated on TLC plates (Merck Kieselgel PF, eluent mixtures of hexane and diethyl ether in variable v/v ratios, depending on the reaction mixtures). The products were crystallized when possible<sup>4</sup> and analysed by means of a Bruker Equinox 55 IR spectrophotometer (KBr cells); the  $^1\text{H}$  NMR spectra were obtained on a JEOL JNM 270/89 instrument and 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). The  $^1\text{H}$  NMR spectrum of pure ECY in  $\text{CDCl}_3$  has been registered for comparison with those of the (dehydrated or non-dehydrated) ligands bound to the clusters;  $\delta$  3.07 s (1H,  $\text{HC}\equiv$ ), 2.39 s (1H, OH), 1.80 m, 1.59 m, 1.44 m, 1.14 m (10 H, cyclohexanol ring).

### Reaction of $\text{Co}_2(\text{CO})_8$ with 1-ethynylcyclohexanol

In a typical reaction 1.0 g (ca. 2.9 mmol) of the cobalt carbonyl was dissolved in benzene (50  $\text{cm}^3$ ) and 0.5 g (ca. 4.0 mmol) of ECY were added; the solution was refluxed for 4–5 min, then allowed to cool and filtered under  $\text{N}_2$ . It was then brought to small volume under reduced pressure; on the TLC plates a red-brown (complex **1**, ca. 80%) and a purple band (complex **2**, ca.

5%) were observed together with some decomposition. Complex **1**: C 43.0 (42.6), H 3.3 (3.1)% (Calc. values in parentheses); IR ( $\nu_{\text{CO}}$ ,  $\text{C}_7\text{H}_{16}$ ) 2095 s, 2055 vs, 2033 vs, 2023 s(sh)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , r.t.):  $\delta$  6.0 s (vb) (1H, HC $\equiv$ ), 2.26 s (1H, OH), 1.64 vb (10 H). Identified as  $\text{Co}_2(\text{CO})_6(\text{ECY})$ . Complex **2**: C 36.7 (36.8), H 2.5 (2.4)%; IR 2101 w, 2050 vs, 2035 vs, 2024 m(sh)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.96 s (2H,  $\text{CH}_2$ ), 3.68 s (1H, OH), 1.77–1.23 mm (10 H,  $\text{C}_6\text{H}_{10}$ ); EI mass spectrum  $\text{P}^+$  at  $m/z$  554, loss of 9 CO followed by complex fragmentation.

#### Reaction of $\text{Fe}_3(\text{CO})_{12}$ with 1-ethynylcyclohexanol and TMNO

In a typical experiment triiron dodecacarbonyl (2.0 g, ca. 4.0 mmol) was suspended in benzene (50  $\text{cm}^3$ ) and solid ECY (1.0 g, 1.08 mmol) added, together with  $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$  (TMNO). The suspension was refluxed for 4–7 min. TLC purification showed the presence of about 15% of unchanged parent carbonyl and of the following products: brown (complex **4**, ca. 1%), purple-brown (**5**, ca. 5%), orange (**3a**, ca. 10%), yellow-brown (**3c**, ca. 10%), yellow (**7**, ca. 10%) and of a band containing an orange and a purple oily complex (ca. 15%) which were not investigated. Decomposition products were also observed.

Complex **4**: C 37.6 (37.8), H 2.2 (2.1)%; IR 2081 w, 2052 s(sh), 2041 vs, 2034 s(sh), 1970 m, 1854 m  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  6.93 s (1H, HC $\equiv$ ), 2.21 s (1H, OH), 2.0–1.16 (10H); EI mass spectrum  $\text{P}^+$  at  $m/z$  572, loss of 10 CO followed by complex fragmentation, and a peak of medium intensity at  $m/z$  554 (loss of water?; see complex **5**). Complex **5**: C 39.2 (39.0), H 1.9 (1.8)%; IR 2090 m, 2052 s, 2031 vs, 1980 m, 1888 m-w  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  signals (multiplets) in the 2.0–1.0 region, corresponding to  $\text{C}_6\text{H}_{10}$ ; EI MS  $\text{P}^+$  at  $m/z$  554, loss of 10 CO. Complex **3a**: IR ( $\text{C}_7\text{H}_{16}$ ) 2073 vs, 2027 vs, 2008 vs, 1987 vs, 1972 m  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , r.t.)  $\delta$  9.18 s (1H, HC $\equiv$ ), 3.45 s (1H, HC $\equiv$ ), 2.60 m, 2.45 m (2H, OH), 2.16–0.89 mm (20H,  $\text{C}_6\text{H}_{10}$  rings); EI mass spectrum  $\text{P}^+$  at  $m/z$  528 (first intense peak 472, very intense 426). Complex **3c**: IR 2078 s, 2030 vs, 2013 s, 1995 s, 1980 m(sh), 1970 m  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  8.91 s (1H, HC $\equiv$ ), 7.98 s (1H, HC $\equiv$ ), 1.58 s (1H, OH), 1.27 m (20 H,  $\text{C}_6\text{H}_{10}$  rings); EI mass spectrum  $\text{P}^+$  at  $m/z$  510. Complex **7**: C 51.8, H 4.3%; IR 2067 m, 2031 vs, 1987 m-s  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  6.37 d (1H,  $J = 2.0$ ), 6.04 d (1H,  $J = 2.0$  Hz), 5.52 br (1H), 2.21–0.87 mm; EI mass spectrum decomposition. For the attribution see Discussion.

#### Reaction of $\text{Fe}_3(\text{CO})_{12}$ with ECY in the absence of TMNO

Under the same conditions as above, but in the absence of TMNO, the following products were obtained: brown (complex **5**, ca. 5%), orange (**3a**, ca. 15%), yellow (**7**, ca. 20%), green (**6**, ca. 25%) and yellow-brown (**3b**), two unidentified products in trace amounts and decomposition. Complex **6**: C 46.8 (46.5), H 3.8 (3.7)%; IR 2083 w, 2047 m-s, 2030 s(sh), 2016 vs, 1995 m, 1861 m,  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.26–7.25 d ( $J = 2.2$ ), 6.94–6.93 d ( $J = 2.2$ ) (1H, 1H, HC $\equiv$ ), 5.60 t (1H, CH,  $\text{C}_6\text{H}_9$  ring) [expansion shows that this signal is a triplet of triplets with  $J$  1.46 and 4.03 Hz], 1.88 s (1H, OH), 1.64–1.35 mm, 1.16 m (18 H,  $\text{C}_6\text{H}_9$ ,  $\text{C}_6\text{H}_{10}$  rings); EI mass spectrum  $\text{P}^+$  at  $m/z$  594, loss of 7 CO's; tentative attribution  $\text{Fe}_3(\text{CO})_7[(\text{ECY})_2 - \text{H}_2\text{O}]$ . Complex **3b**: IR 2068 m, 2028 vs, 2000 m-s, 1986 m, 1980 m  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  6.39 s (2H, HC $\equiv$ ), 1.73–1.57 mm (ca. 20H, OH,  $\text{C}_6\text{H}_{10}$  rings); EI mass spectrum  $\text{P}^+$  at  $m/z$  528, loss of 6 CO, see complex **3a**.

#### Reaction of $\text{Co}_2(\text{CO})_8$ and of $\text{Fe}_3(\text{CO})_{12}$ with 1-ethynylcyclohexanol

In a typical reaction dicobalt octacarbonyl (1.0 g, 2.9 mmol) was dissolved in toluene (100  $\text{cm}^3$ ) under  $\text{N}_2$  and ECY (1.0 g, ca. 8.0 mmol) added; the solution was brought to reflux. After 2 min, 1.0 g (2.0 mmol) of triiron dodecacarbonyl was added and reflux was allowed for 6 min. During the reaction abundant foaming was observed. TLC purification showed the presence of trace amounts of complex **5** and of red-brown (**3a**, ca. 10%)

and dark brown bands (**8**, ca. 5%), unchanged iron carbonyl (ca. 10%), deep red (**1**, ca. 10%), purple (**2**, ca. 20%), brown-orange (**3b**, ca. 5%), and light green bands (not investigated, ca. 3%) and decomposition. Complex **8**: Fe 9.51 (9.56), Co 20.10 (20.17)%; IR 2097 m-w, 2050 vs, 2043 s, 2035 s, 1975 m(br), 1887 m-w(br)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.37 s (1H), 6.03 s(br) (1H) [H on  $\text{C}^3$  and  $\text{C}^2$  respectively]; 3.79 d-t [H on  $\text{C}^1$ ], 2.98 t [H on  $\text{C}^6$ ], 1.90 m, 1.36 m, 1.27 s, 0.89 t [18 H, cyclohexane rings]; EI mass spectrum  $\text{P}^+$  at  $m/z$  584 loss of 7 CO (intense peaks), isotopic pattern  $\text{Co}_2\text{Fe}$ . This reaction is particularly well reproducible regardless of the reflux time before adding the iron carbonyl.

#### Reaction of $\text{Co}_2(\text{CO})_6(\text{ECY})$ with $\text{Fe}_3(\text{CO})_{12}$

Complex **1** (0.20 g) was dissolved in benzene (50  $\text{cm}^3$ ) and 0.50 g of triiron dodecacarbonyl added; the suspension was allowed to reflux for 7 min. After filtering away the unchanged iron carbonyl and decomposition products, TLC purification showed the presence of brown (**8**, ca. 5%), orange (**1**, ca. 15%), orange-brown (unidentified, ca. 5%), purple (**2**, ca. 20%) and orange-red bands (unidentified, 5%), traces of complex **6** and decomposition.

#### Reaction of $\text{Co}_2(\text{CO})_8$ with ECY and $\text{Fe}(\text{CO})_5$

To a suspension of the cobalt (1.0 g) and iron carbonyl (2.0 ml) in benzene (50  $\text{cm}^3$ ), ECY (0.5 g) was added; the suspension was refluxed for 4 min. After TLC separation the following products were obtained;  $\text{Co}_2(\text{CO})_6(\text{ECY})$  (**1**, about 40%) and complex **2** (10%) together with some decomposition.

#### Reaction of complex **5** with ECY

Complex **5** (50 mg) was dissolved in benzene (50  $\text{cm}^3$ ) and ECY (0.4 g) added; the suspension was refluxed for 4 min. TLC purification showed the presence of some complex **6** (IR identification), traces of an unidentified yellow compound and decomposition.

#### Reaction of complex **6** with $\text{Co}_2(\text{CO})_8$

Complex **6** (200 mg) was dissolved in benzene (50  $\text{cm}^3$ ) and 0.5 g of cobalt carbonyl added. After 5 min reflux, TLC separation yielded trace amounts of two unidentified complexes (dark orange and yellow), about 30% of yellow complex **7**, 30% of unchanged **6** and decomposition. No cobalt-containing derivatives could be obtained.

#### X-Ray analysis

**Crystal data.** Complex **2**.  $\text{C}_{23}\text{H}_{22}\text{Co}_3\text{O}_7$ ,  $M = 554.06$ , monoclinic, space group  $P2_1/c$  (no. 14),  $a = 8.717(3)$ ,  $b = 13.524(5)$ ,  $c = 20.427(7)$  Å,  $\beta = 93.23(2)^\circ$ ,  $U = 2091(1)$  Å $^3$ ,  $Z = 4$ ,  $T = 293$  K,  $\mu = 2.403$  mm $^{-1}$ . 8058 Reflections on a Siemens P4 diffractometer, 6105 ( $R_{\text{int}} = 0.037$ ) being unique; non-hydrogen atoms anisotropically refined. The last Fourier-difference maps showed the peaks corresponding to the H atoms of the ligands: they were put in the positions derived from maps and refined. For 3446 data with  $F_o > 4\sigma(F_o)$  the final  $R1 = 0.0474$ .

Complex **5**.  $\text{C}_{18}\text{H}_{10}\text{Fe}_3\text{O}_{10}$ ,  $M = 553.81$ , monoclinic, space group  $P2_1/c$  (no. 14),  $a = 17.095(2)$ ,  $b = 10.366(2)$ ,  $c = 12.665(2)$  Å,  $\beta = 109.84(1)^\circ$ ,  $U = 2111.1(6)$  Å $^3$ ,  $Z = 4$ ,  $T = 293$  K,  $\mu = 2.086$  mm $^{-1}$ . 8022 Reflections collected on a Siemens P4 diffractometer, 6159 ( $R_{\text{int}} = 0.029$ ) being unique; non-hydrogen atoms anisotropically refined. The peaks of the last Fourier-difference maps corresponding to the H atoms of the ligands were refined with variable coordinates and fixed  $U_{\text{iso}}$ . For 3822 data with  $F_o > 4\sigma(F_o)$  the final  $R1 = 0.0444$ .

Complex **8**.  $\text{C}_{17}\text{H}_{13}\text{Co}_2\text{FeO}_{10}$ ,  $M = 584.12$ , monoclinic, space group  $P2_1/n$  (no. 14),  $a = 10.415(4)$ ,  $b = 11.316(3)$ ,  $c = 17.759(6)$  Å,  $\beta = 92.76(3)^\circ$ ,  $U = 2404(2)$  Å $^3$ ,  $Z = 4$ ,  $T = 293$  K,  $\mu = 1.999$  mm $^{-1}$ . 5833 Reflections collected on a Siemens P4 dif-

fractometer, 4228 ( $R_{\text{int}} = 0.048$ ) being unique. The H atoms of the ligands were put in computed positions (rings) or in the experimental positions (chain) with fixed coordinates and variable  $U_{\text{iso}}$ . The non-hydrogen atoms were anisotropically refined. According to the elemental analysis, where a Co : Fe ratio of 2 : 1 was found, three refinements were made with the iron atom alternatively in position 1, 2 and 3 (Fig. 3). The best refinement corresponded to iron in position 2 ( $R1 = 0.0594$  with respect to 0.0623 and 0.0630), even if some uncertainty exists owing to the difference of only one electron between Fe and Co. For 2789 data with  $F_o > 4\sigma(F_o)$  the final  $R1 = 0.0594$ .

In the three complexes acceptable values of the distances were obtained for the hydrogen atoms, even if their location must be considered with caution.

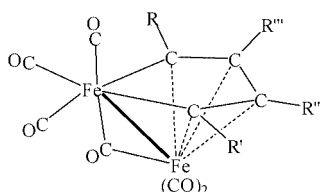
CCDC reference numbers 159811–159813.

See <http://www.rsc.org/suppdata/dt/b101119g/> for crystallographic data in CIF or other electronic format.

## Results and discussion

### Spectroscopic characterization of new complexes

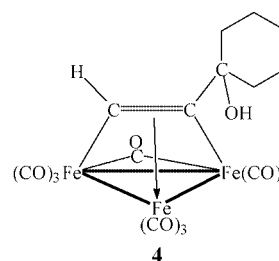
The reactions of  $\text{Co}_2(\text{CO})_8$  with ECY lead to high yields of  $\text{Co}_2(\text{CO})_6(\text{ECY})$  **1**, containing a non-dehydrated ligand; complex **1** belongs to a well established family of dicobalt–alkyne derivatives. Small yields of complex **2** are also obtained in these reactions. It is known that, under thermal conditions, dicobalt–alkyne complexes of type **1** may afford tricobalt methylidyne clusters showing structures comparable with that of complex **2**.<sup>5</sup> The reactions of  $\text{Fe}_3(\text{CO})_{12}$  with ECY in the presence of TMNO lead to the binuclear complexes **3a**, **3c**, **7** as the main products and to small amounts of the trinuclear clusters **4** and **5**; in the absence of TMNO the binuclear complexes **3a**, **3b**, **7** and the trinuclear complexes **5** and **6** were obtained. Analytical and spectroscopic results indicate that **3a** and **3b** are isomeric, non-dehydrated,  $\text{Fe}_2(\text{CO})_6(\text{ECY})_2$  ferrole complexes;<sup>6</sup> **3c** has been identified as a partly dehydrated ferrole derivative. Formation of similar structures containing dehydrated alkynols has been observed.<sup>7</sup> Finally, chemical evidence shows that **7** is the thermal decomposition product of **6**; we cannot propose an unequivocal structure for this complex, on the basis of the spectroscopic results only. We suspect that it also belongs to the ferrole family; however, attempts at crystallizing the complex gave only powders unsuitable for X-rays. The structures and isomerism proposed for complexes **3a,b,c** are in Scheme 1.



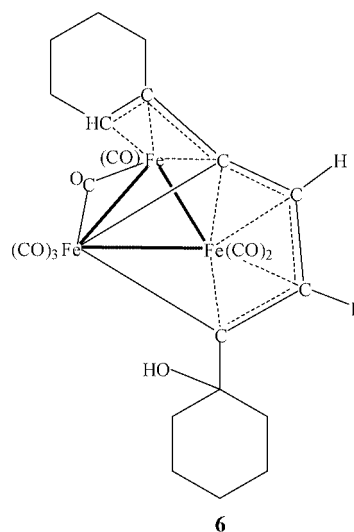
**Scheme 1**  $R = R'' = \text{C}_6\text{H}_{10}(\text{OH})$ ;  $R' = R''' = \text{H}$  **3a**;  $R = R' = \text{C}_6\text{H}_{10}(\text{OH})$ ;  $R'' = R''' = \text{H}$  **3b**;  $R = \text{C}_6\text{H}_{10}(\text{OH})$ ;  $R'' = \text{C}_6\text{H}_9$ ;  $R' = R''' = \text{H}$  **3c**.

The trinuclear complex **4** could not be obtained as X-ray grade crystals; it has been identified as  $\text{Fe}_3(\text{CO})_9(\mu\text{-CO})[\mu_3\text{-}\eta^2\text{-1,2-HC}\equiv\text{C}(\text{C}_6\text{H}_{10}\text{OH})]$  containing a non-dehydrated ECY ligand coordinated in parallel fashion. This type of structure is not very common for iron,<sup>8a</sup> however, some examples of similar complexes, obtained in the reactions of alkynols with triiron dodecacarbonyl, have been reported previously.<sup>8b</sup> It is likely that, under thermal conditions, complex **4** loses water to form the allenylidene complex **5**; mass spectrometric evidence for this process has been obtained (see Experimental section). The trinuclear complex **6** has been identified as  $\text{Fe}_3(\text{CO})_7\text{-(ECY)}_2\text{-H}_2\text{O}$  and contains two ECY ligands, one of which has been dehydrated; on the basis of the spectroscopic results, we propose for **6** a structure containing a ferrole ring with an

unsaturated substituent interacting with one iron atom. Some chemical evidence (e.g. the reaction of complex **5** with ECY) supports this hypothesis. In addition, a structure closely comparable with that proposed for **6** (see Scheme 2, below) has been



**4**



**6**

**Scheme 2**

reported for iron;<sup>9</sup> in this complex, a nitrogen-containing alkyne substituent interacts with one of the iron atoms, and two alkynes are linked together to form a ferrole-like ring. Finally, reactions of alkynols with  $\text{Ru}_3(\text{CO})_{12}$  lead, among others, to trinuclear clusters of type **4** and to a complex showing structural features similar to those proposed for cluster **6** (crystal structure).<sup>10</sup> Repeated attempts at crystallizing **6** were made but unfortunately only powders could be obtained; during these attempts partial decomposition to  $\text{Fe}_3(\text{CO})_{12}$  occurred. The structures proposed for complexes **4** and **6** are shown in Scheme 2.

When treating  $\text{Co}_2(\text{CO})_8$  and  $\text{Fe}_3(\text{CO})_{12}$  with ECY the diiron complexes **3a** and **3b** are still obtained; interestingly, however, the yields of **2** are increased and the heterometallic complex **8** is formed. The structures of complexes **2**, **5** and **8** were determined by X-ray crystallography and are discussed below.

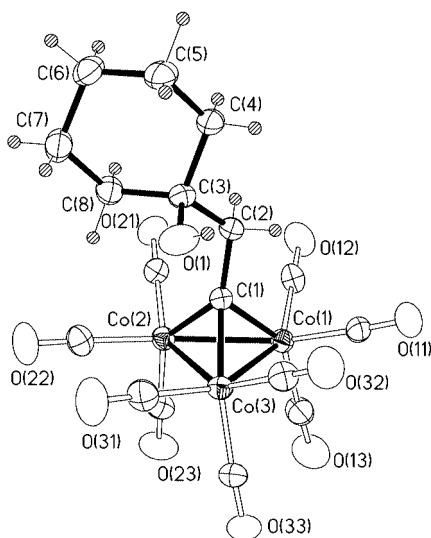
### X-Ray diffraction studies on complexes **2**, **5** and **8**

**$\text{Co}_3(\text{CO})_9[\mu_3\text{-CCH}_2(\text{C}_6\text{H}_{10}\text{OH})]$  **2**.** The structure of the complex is shown in Fig. 1 and relevant bond distances and angles are in Table 1. This complex is formed by an isosceles triangle of cobalt atoms [ $\text{Co}(1)\text{--Co}(2)$  2.462(1),  $\text{Co}(1)\text{--Co}(3)$  2.464(1),  $\text{Co}(2)\text{--Co}(3)$  2.476(1) Å] each bearing one axial and two equatorial CO's. A  $\mu_3\text{-CCH}_2\text{C}_6\text{H}_{10}(\text{OH})$  methylidyne ligand is bound to all three cobalt atoms via three M–C bonds of different lengths,  $\text{Co}(1)\text{--C}(1)$  1.936(3),  $\text{Co}(2)\text{--C}(1)$  1.911(3),  $\text{Co}(3)\text{--C}(1)$  1.890(3) Å. The  $\text{C}(1)\text{--C}(2)$  [1.504(4) Å] and  $\text{C}(2)\text{--C}(3)$  [1.535(5) Å] distances are typical of C–C single bonds.

This type of structure has long been known for cobalt,<sup>12</sup> and it is not common for iron.<sup>13</sup> It is perhaps interesting that, under the same reaction conditions, cobalt prefers the methylidyne structure, whereas iron gives the allenylidene complex **5**.

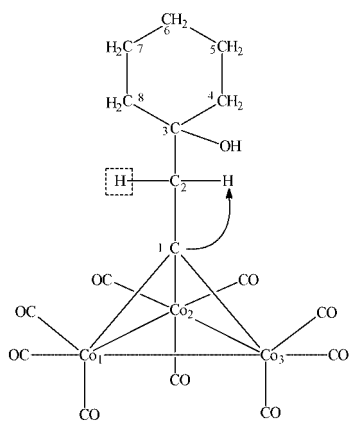
**Table 1** Selected bond lengths (Å) and angles (°) for  $\text{Co}_3(\text{CO})_9[\mu_3\text{-CCH}_2(\text{C}_6\text{H}_{10}\text{OH})]$  (complex **2**)

Co(1)–C(1)	1.936(3)	Co(2)–Co(1)–Co(3)	60.36(3)
Co(1)–Co(2)	2.4619(9)	Co(1)–Co(2)–Co(3)	59.85(2)
Co(1)–Co(3)	2.4634(9)	Co(1)–Co(3)–Co(2)	59.79(2)
Co(2)–C(1)	1.911(3)	C(2)–C(1)–Co(1)	123.4(2)
Co(2)–Co(3)	2.4759(9)	C(2)–C(1)–Co(2)	136.3(3)
Co(3)–C(1)	1.890(3)	C(2)–C(1)–Co(3)	134.7(3)
Co–C(CO) <sub>eq</sub> av.	1.790(4)	C(1)–C(2)–C(3)	121.2(3)
Co–C(CO) <sub>ax</sub> av.	1.829(4)	O(1)–C(3)–C(2)	109.4(3)
C–O(CO) av.	1.127(5)	O(1)–C(3)–C(4)	110.7(3)
C(1)–C(2)	1.504(4)	O(1)–C(3)–C(8)	107.3(3)
C(2)–C(3)	1.535(5)	C(8)–C(3)–C(4)	109.5(3)
C(3)–O(1)	1.429(4)		
C–C(ring) av.	1.518(6)		



**Fig. 1** An ORTEP<sup>11</sup> plot of  $\text{Co}_3(\text{CO})_9[\mu_3\text{-CCH}_2(\text{C}_6\text{H}_{10}\text{OH})]$  (**2**) with 30% thermal ellipsoids (as in all structures shown).

In spite of the abundance of reports on tricobalt methylidyne structures,<sup>12</sup> complex **2** is, to our knowledge, the first derivative containing a propargylic alcohol and showing the presence of two hydrogens on C(2) as shown in Scheme 3. One of them



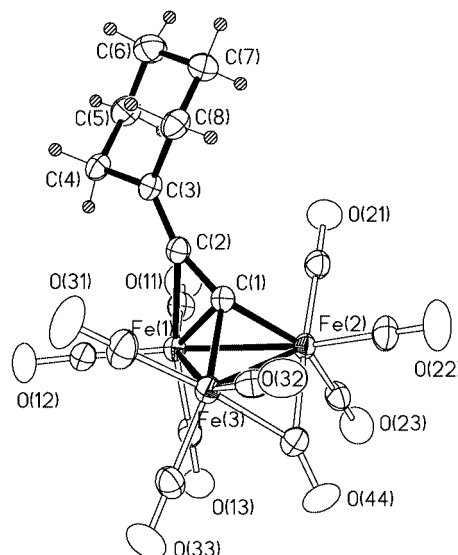
**2**  
**Scheme 3**

could be the terminal hydrogen of the alkyne, but the other one has to come either from the solvent (traces of moisture?)<sup>14</sup> or from another alkyne molecule. It is also worth noting that the yields of **2** are increased when iron is present; this behaviour is discussed below.

$\text{Fe}_3(\text{CO})_9(\mu\text{-CO})[\mu_3\text{-}\eta^2\text{-1,2-C=C(C}_6\text{H}_{10})]$  **5**. The structure of the complex is shown in Fig. 2 and relevant bonding distances

**Table 2** Selected bond lengths (Å) and angles (°) for  $\text{Fe}_3(\text{CO})_9(\mu\text{-CO})[\mu_3\text{-}\eta^2\text{-1,2-C=C(C}_6\text{H}_{10})]$  (complex **5**)

Fe(1)–Fe(2)	2.6077(6)	Fe(3)–Fe(1)–Fe(2)	58.60(2)
Fe(1)–Fe(3)	2.6031(7)	Fe(3)–Fe(2)–Fe(1)	60.61(2)
Fe(2)–Fe(3)	2.5503(6)	Fe(2)–Fe(3)–Fe(1)	60.79(2)
Fe(1)–C(1)	2.002(3)	C(1)–Fe(2)–C(44)	99.3(1)
Fe(2)–C(1)	1.914(3)	C(1)–Fe(3)–C(44)	97.7(1)
Fe(3)–C(1)	1.911(3)	Fe(2)–C(1)–Fe(1)	83.5(1)
Fe(1)–C(2)	2.135(3)	Fe(3)–C(1)–Fe(1)	83.4(1)
Fe–C(CO) av.	1.805(4)	Fe(3)–C(1)–Fe(2)	83.6(1)
Fe(2)–C(44)	1.972(3)	C(3)–C(2)–C(1)	153.6(3)
Fe(3)–C(44)	2.021(3)	C(2)–C(3)–C(8)	120.7(3)
C–O(CO) av.	1.130(4)	C(2)–C(3)–C(4)	125.3(3)
C(44)–O(44)	1.149(4)	O(44)–C(44)–Fe(2)	141.9(3)
C(1)–C(2)	1.349(4)	O(44)–C(44)–Fe(3)	138.7(3)
C(2)–C(3)	1.324(4)	Fe(2)–C(44)–Fe(3)	79.4(1)
C–C(ring) av.	1.513(5)		



**Fig. 2** ORTEP plot of  $\text{Fe}_3(\text{CO})_9(\mu\text{-CO})[\mu_3\text{-}\eta^2\text{-1,2-C=C(C}_6\text{H}_{10})]$  (**5**).

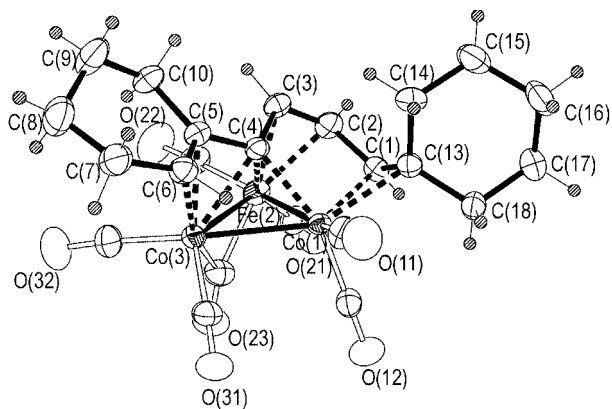
and angles are in Table 2. The complex is formed by an isosceles triangle of iron atoms [Fe(1)–Fe(2) 2.6077(6), Fe(1)–Fe(3) 2.6031(7) and Fe(2)–Fe(3) 2.5503(6) Å, the shorter edge being bridged by a CO group and by the organic ligand], each bearing two equatorial and one axial CO group; the bridging CO is slightly asymmetric. An allenyldiene ligand, formed upon dehydration of ECY (terminal hydrogen and alkynol OH), is coordinated *via* C(1) to all three metals and *via* C(2) to the third one; the coordination is asymmetric, Fe(1)–C(1) being shorter than Fe(2,3)–C(1).

In recent times some structures of triiron allenyldiene clusters derived (or not) from alkynols have been reported;<sup>15</sup> complex **5** represents the fourth example of such an X-ray structural study. A comparison with the other complexes<sup>16</sup> shows that these clusters are characterized by “rigid” bond distances and angles, at least as far as the cluster core and the C(3) and C(2) allenyldiene atoms are concerned; *i.e.* the doubly bridged Fe–Fe bond is the shortest metal–metal bond, the Fe(1)–C(1) bond is the longest Fe–C, the C(1)–C(2) and C(2)–C(3) distances are nearly equal and the C(1)–C(2)–C(3) angle is around 150°. The effect of the substituents on the organic moiety seems to be of less importance.

Complex **5** contains a dehydrated ECY ligand. Dehydration pathways occurring when alkynols react with the iron triad carbonyl clusters have recently been discussed.<sup>17</sup> Two main processes have been evidenced, that is: (i) loss of the terminal hydrogen and of the alkynic OH (route *A*) to form allenyldiene ligands and (ii) loss of the alkynic OH and of a hydrogen from a methyl group on the same carbon atom (route *B*) to form vinylacetylide derivatives. The process observed here

**Table 3** Selected bond lengths (Å) and angles (°) for  $\text{Co}_2\text{Fe}(\text{CO})_6(\mu\text{-CO})[\mu_3\text{-}\eta^7\text{-(C}_6\text{H}_9\text{)CC(H)C(H)C(H)(C}_6\text{H}_{10}\text{)}]$  (complex **8**)

Co(1)–Co(3)	2.518(1)	Co(3)–Co(1)–Fe(2)	60.12(4)
Co(1)–Fe(2)	2.547(1)	Co(3)–Fe(2)–Co(1)	59.37(4)
Fe(2)–Co(3)	2.537(1)	Co(1)–Co(3)–Fe(2)	60.51(4)
Co(1)–C(1)	2.150(6)	C(13)–C(1)–C(2)	126.7(6)
Co(1)–C(4)	1.960(5)	C(3)–C(2)–C(1)	119.9(5)
Co(1)–C(13)	2.164(6)	C(2)–C(3)–C(4)	115.8(5)
Co(3)–C(4)	2.175(6)	C(3)–C(4)–C(5)	122.1(5)
Co(3)–C(5)	2.184(6)	C(6)–C(5)–C(4)	121.3(5)
Co(3)–C(6)	2.339(6)	C(6)–C(5)–C(10)	119.5(5)
Co(3)–C(23)	1.939(7)	C(4)–C(5)–C(10)	119.1(5)
CO–C(CO) <sub>eq</sub> av.	1.784(8)	C(5)–C(6)–C(7)	124.5(6)
CO–C(CO) <sub>ax</sub> av.	1.791(8)	C(6)–C(7)–C(8)	113.0(6)
Fe(2)–C(2)	2.100(7)	C(9)–C(8)–C(7)	111.2(6)
Fe(2)–C(3)	2.076(6)	C(8)–C(9)–C(10)	114.4(7)
Fe(2)–C(4)	2.162(6)	C(9)–C(10)–C(5)	113.2(6)
Fe(2)–C(23)	1.901(7)	C(1)–C(13)–C(18)	117.6(5)
Fe–C(CO) <sub>eq</sub> av.	1.777(8)	C(1)–C(13)–C(14)	121.5(5)
C–O(CO) av.	1.139(9)	O(23)–C(23)–Fe(2)	143.5(6)
C(1)–C(2)	1.459(8)	O(23)–C(23)–Co(3)	133.8(6)
C(1)–C(13)	1.396(8)		
C(2)–C(3)	1.376(8)		
C(3)–C(4)	1.446(8)		
C(4)–C(5)	1.457(8)		
C(5)–C(6)	1.360(8)		
C(5)–C(10)	1.518(8)		
C(6)–C(7)	1.495(8)		
C(7)–C(8)	1.51(1)		
C(8)–C(9)	1.46(1)		
C(9)–C(10)	1.509(9)		
C(13)–C(18)(ring) av.	1.512(8)		



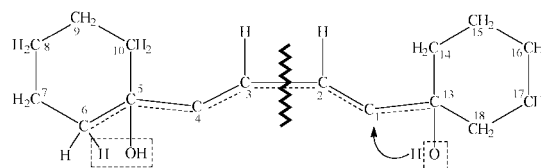
**Fig. 3** ORTEP plot of  $\text{Co}_2\text{Fe}(\text{CO})_6(\mu\text{-CO})[\mu_3\text{-}\eta^7\text{-(C}_6\text{H}_9\text{)CC(H)C(H)C(H)(C}_6\text{H}_{10}\text{)}]$  (**8**).

corresponds to route *A* which, in the light of actual knowledge, is more common for iron (under “spontaneous” thermal conditions). For ruthenium the above dehydration processes require acidic catalysis or the intermediacy of inorganic oxides.<sup>18</sup> Besides the knowledge of the solid-state structure, and dehydration process occurring, the interest in complex **5** lays in its behaviour as a reaction intermediate; experimental evidence shows, indeed, that it is a precursor of **6** (see Scheme 5, below).

**$\text{Co}_2\text{Fe}(\text{CO})_6(\mu\text{-CO})[\mu_3\text{-}\eta^7\text{-(C}_6\text{H}_9\text{)CC(H)C(H)C(H)(C}_6\text{H}_{10}\text{)}]$  **8**.** The structure of the complex is shown in Fig. 3 and relevant bonding distances and angles are in Table 3. The attribution of the nature of the metal atoms is described in the Experimental section.

The complex is formed by a scalene triangle of metal atoms; two terminal carbonyls are bound to each metal atom and a symmetrically bridging carbonyl spans the Fe(2)–Co(3) edge of the cluster [Fe(2)–C(23) 1.901(7), Co(3)–C(23) 1.939(7) Å]. A substituted organic ligand is coordinated to all the cluster metals; this is formed by tail-to-tail coupling of two ECY molecules, one of which [C(3) to C(10)] has lost water and the

other one [C(2) to C(18)] has undergone loss of oxygen and probably transfer of a hydrogen atom from C(13) to C(1) (Scheme 4).



**Scheme 4**

The C(1)–C(6) chain is roughly planar (0.07 Å mean deviation from planarity), whereas C(13) is clearly out of plane (1 Å); hydrogen atoms, affected by relevant uncertainty, were not considered in the computing of the mean plane. All angles around atoms C(1)–C(6) are quite similar and their mean value is 122°; the C–C distances in the C(13)–C(1)–C(6) chain cannot be rationalized in terms of double or single bonds. It is noticeable however that the significantly longest distances (1.46 Å av.) are those corresponding to the triple bonds of the ECY reagent [C(1)–C(2) and C(3)–C(4) and to C(4)–C(5)]. Interestingly the distribution of long and short C–C distances in the ligand is different from what could be expected by simply considering the coupling of two alkynes. Apparently, the loss of the oxygen atoms induces a rearrangement in the ligand. The coordination to the metals also is likely to induce modifications in the organic moiety. The C(13)–C(18) ring has a chair conformation, while the other  $\eta^2\text{-C(5)–C(10)}$  ring is flattened where coordinated to Co(3), as expected.

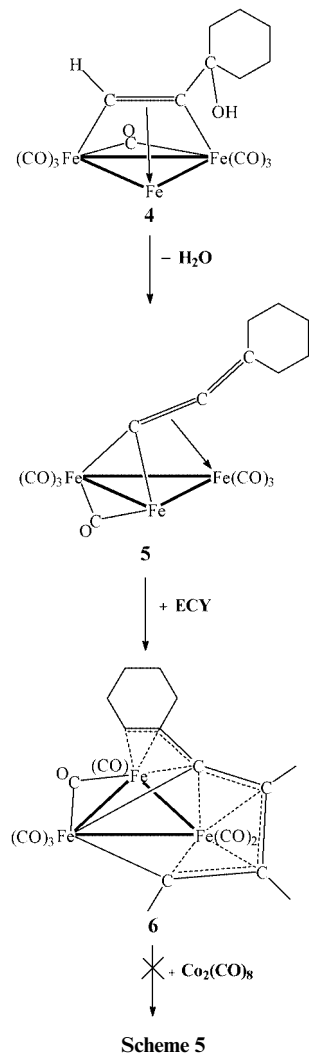
When considering the electron count around the metal atoms, 14 electrons are provided by the seven carbonyl groups and six by the metal–metal bonds; thus, according to the EAN rule, the ligand must be a donor of eight electrons. Clusters containing “linear” chains of four carbon atoms are not uncommon; some have been obtained starting from diynes<sup>19</sup> but a certain number has been obtained by coupling of alkynes and/or acetylides, during or after the coordination of the ligands on the metals.<sup>20</sup> However, the bonding of the organic ligand in cluster **8**, which involves also carbon atoms of the cyclohexanol rings, is to our knowledge unprecedented. Among the M–C bonds Co(1)–C(4) has the shortest distance (1.960(5) Å) and Co(3)–C(6) has the longest (2.339(6) Å). C(3), C(4), C(5) and Co(1) lie roughly on a plane (0.012 Å mean deviation), consistent with a Co(1)–C(4)  $\sigma$  interaction. The other M–C distances are intermediate between these two values, 2.08 to 2.18 Å.

## Reaction pathways

The reaction of ECY with  $\text{Co}_2(\text{CO})_8$  leads to cobalt-containing complexes of predictable structure;<sup>5,12</sup> it is interesting, however, that dehydrated cobalt-containing complexes could not be obtained. Instead, small amounts of the “hydrogenated” complex **2** were formed; better yields of **2** are obtained in the reactions where also iron is present. Literature evidence (further discussed below) indicates that iron favours dehydration and deoxygenation reactions and presumably promotes the formation of species which can transfer hydrogen on (free or coordinated) ethynylcyclohexanol, thus giving origin to the new ligand present on the tricobalt cluster.

The reactions of ECY with  $\text{Fe}_3(\text{CO})_{12}$  give the somewhat expected binuclear ferrole complexes **3**; these are considered the final products of the reactions between triiron dodecacarbonyl and alkynes. However, we could not obtain their “parents”, i.e. the well known open clusters  $\text{Fe}_3(\text{CO})_6(\mu\text{-CO})_2(\text{ECY})_2$ ;<sup>6</sup> instead, we obtained complex **6** whose structure is closely related to that of the above open clusters. We obtained very small amounts of complex **4**; this is presumably the parent of the allenylidene complex **5**, as shown by mass spectrometric

(this work) and literature evidence.<sup>17</sup> Interestingly, we also obtained **6** containing two partially dehydrated and presumably linked ECY ligands; again, chemical evidence shows that it is formed through the intermediacy of the dehydrated allenylidene **5** upon addition of a second (non-dehydrated) molecule of ECY and shift of hydrogen from a cyclohexanol ring. This behaviour has been observed, at least in part, in literature reports.<sup>10</sup> We therefore propose a reaction pathway leading from complex **4** to **6**; this would occur through the dehydration and hydrogen shift processes shown in Scheme 5.



Complex **8**, however, is not formed starting from the above triiron clusters, upon metal fragment substitution (*e.g.* reaction of **6** with dicobalt octacarbonyl). It is obtained only when *both* parent carbonyls are treated with ECY. Chemical evidence also shows that **8** is not formed when ECY is treated with the cobalt carbonyl only or when the iron carbonyl only is used; it is however obtained when complex **1** is treated with  $\text{Fe}_3(\text{CO})_{12}$  (not with  $\text{Fe}(\text{CO})_5$ , thus indicating the need for a polynuclear source of iron fragments). Therefore, although the simultaneous formation of several products in these reactions makes difficult the elucidation of reaction mechanisms, a reasonable hypothesis for the formation of the metal core of complex **8** is the condensation of dicobalt fragments with cluster-derived mononuclear iron fragments. An alternative hypothesis could be substitution of iron fragments for cobalt in trinuclear structures, such as **2**. Isolobal substitution of cobalt- with iron-containing “fragments” has indeed been evidenced. For example, in a complex reaction sequence starting from clusters, hydration of cluster-bound diethylacetylene led to a propargyl alcohol coordinated to two cobalt atoms; in the presence of  $\text{Fe}(\text{CO})_5$  the complex underwent loss of OH and of H and

gradual substitution of iron for cobalt atoms until formation of a diiron derivative was observed.<sup>21</sup> Very recently, another example of “isolobal replacement” of  $\text{Co}(\text{CO})_3$  vertices by  $\text{Fe}(\text{CO})_3$  fragments has been reported for binuclear alkynol cobalt complexes.<sup>22</sup> The reverse process (*e.g.* replacement of iron fragments by cobalt) has not been observed, to our knowledge.

The formation of **8** also requires condensation and modification of two ECY molecules; to our knowledge, the condensation processes leading to complex **8** are unprecedented. Usually alkynes (and propargyl alcohols) undergo cyclotrimerization on dicobalt complexes<sup>23</sup> forming 1,2,4- or 1,3,5-substituted benzenes. Linear oligomerization of three molecules of ECY in the presence of nickel has also been reported;<sup>24</sup> of these, two are bound tail-to-tail and the third one head-to-tail. Interestingly, no dehydration, neither loss of OH nor of “O”, has been observed in this process. However, in some instances, partial dehydration occurs on nickel; for example 2,5-dimethylhex-3-yne-2,5-diol undergoes linear/cyclic oligomerization (5 alkyne molecules) with loss of water and formation of ether linkages.<sup>25</sup> Finally, the (carbonylative) formation of oxygenated metallacycles and of lactones from unsaturated diols in the presence of diiron nonacarbonyl has been reported; in this process loss of hydrogen and/or of water occurs.<sup>26</sup>

## Concluding remarks

Reactions of propargyl alcohols with  $\text{M}_3(\text{CO})_{12}$  clusters ( $\text{M} = \text{Fe}, \text{Ru}$  or  $\text{Os}$ ) have been investigated<sup>17</sup> and the alternative dehydration routes *A* and *B* established. For ruthenium, dehydration reactions occur only under severe conditions; in contrast, when  $\text{M} = \text{Fe}$ , route *A* is likely to occur easily, under relatively mild conditions, to give allenylidene-substituted trinuclear clusters. This process has been observed also in this work (*e.g.* formation of cluster **5**). “dehydroxylation” to form allenylidene derivatives<sup>17,18</sup> and “deoxygenation” reactions<sup>27</sup> have also been observed in the presence of ruthenium or iron. Some of these processes have been evidenced also during the formation of the complexes discussed above, in particular when **8** is formed. The evidence obtained in this work and the literature reports mentioned above suggest that these processes are likely to be promoted by the iron “fragments” involved in the reactions.

The results obtained in this work, therefore, represent further evidence for the role of iron fragments in inducing dehydration, dehydroxylation or deoxygenation reactions during the coordination and/or oligomerization of acetylenic alcohols on metal clusters. In particular, the formation of complexes **6** and **8** represent new examples of this behaviour, which is presumably a general trend in the reactions of iron carbonyls with acetylenic alcohols. Literature reports and experimental evidence (this work) indicate indeed that dehydration and other processes can occur, albeit to a lesser extent, on nickel, whereas on cobalt this behaviour is not observed.

As pointed out above, it is interesting that cobalt and iron, under comparable reaction conditions, apparently prefer different coordination modes for the ligand on clusters; thus, with cobalt, the methylidyne complex **2** is obtained, whereas for iron the (structurally related) allenylidene complex **5** is formed.

New coupling pathways for ECY have also been evidenced, especially in complex **8**. Isomerization of butadiyne ligands during the formation of hexa- and hepta-nuclear iron–cobalt complexes has been reported;<sup>28</sup> allenylidene ligands coordinated to three iron atoms are formed, as well as a four-carbon atom chain not dissimilar to that found in cluster **8**. These results show, once again, that alkyne- and alkynol-cluster chemistry is very versatile and far from being fully explored.

## Acknowledgements

Financial support to this work was obtained from MURST (Cofin98) and from the Universities of Torino and Piemonte Orientale.

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