Reactions of $Fe_3(CO)_{12}$ and $Fe(CO)_5$ with functionalized alkynes in CH_3OH–KOH solution — The crystal structure of $Fe_2(CO)_6(PPh_3)[\mu\text{-}\eta^3\text{-}(H_2CCCH_2)]$[1]

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Abstract: The complex $Fe_2(CO)_7(H_2CCCH_2)$ (**1**) is obtained starting from a variety of functionalized alkynes that can release C_3 fragments during the reactions with $Fe_3(CO)_{12}$ or $Fe(CO)_5$ in CH_3OH–KOH solutions. Owing to the oily nature of **1**, it was reacted with triphenylphosphine, and the structure of the resulting title compound (**1a**) has been determined by X-ray analysis. Complex **1a** shows a new coordination mode of a $H_2C{=}C{=}CH_2$ ligand to a diiron centre and is, to our knowledge, unprecedented. We have also found that **1** (and **1a**) are by-products, and not intermediates in the formation of complex **3**. A discussion of the possible reaction pathways is given.

Key words: iron carbonyls, alkynols, CO and methanol activation, acetyl and acetate complexes, allenyl iron complexes, crystal structure.

Résumé : Le complexe $Fe_2(CO)_7(H_2CCCH_2)$ (**1**) a été préparé à partir d'une variété d'alcynes fonctionnalisés qui peuvent perdre des fragments en C_3 au cours de réactions avec du $Fe_3(CO)_{12}$ ou du $Fe(CO)_5$ dans des solutions de CH_3OH–KOH. En raison de la nature huileuse du composé **1**, on l'a fait réagir avec de la triphénylphosphine et on a fait appel à la diffraction des rayons X pour déterminer la structure cristalline du produit qui en résulte et qui est mentionné dans le titre (**1a**). Le complexe **1a** présente un nouveau mode de coordination du ligand $H_2C{=}C{=}CH_2$ au centre difer qui, à notre connaissance était inconnu jusqu'à maintenant. On a aussi trouvé que les composés **1** (et **1a**) sont des sous-produits et non pas des intermédiaires dans la formation du complexe **3**. On présente une discussion des voies réactionnelles potentielles.

Mots clés : fer carbonyles, alkynols, activation du CO et du méthanol, complexes acétyles et acétates, complexes d'allényl fer, structure cristalline.

[Traduit par la Rédaction]

Introduction

Propargyl alcohols react with $M_3(CO)_{12}$ carbonyls (M = Fe, Ru, or Os) both under thermal (hydrocarbons, reflux) and basic conditions (CH_3OH–KOH solution, followed by acidification with HCl) undergoing different processes, among which the more important is dehydration. Two main dehydration pathways leading, respectively, to coordinated ene-yne (or vinylacetylene) or to allenylidene ligands have been evidenced (1). The latter is apparently preferred when M = Fe, as discussed in the following. Most of the dehydration–hydration reactions are promoted by acids (2), silica surfaces (3), or silica and alumina slurries (4). Other processes observed are deoxygenation (5) and loss of functionalities (6).

We have recently reported the reactions of $Fe_3(CO)_{12}$ with propargyl alcohol ($HC{\equiv}CCH_2OH$) and propargyl chloride ($HC{\equiv}CCH_2Cl$), both under thermal and basic methanolic conditions. The products obtained were: $Fe_2(CO)_7(C_3H_4)$ (**1**), the allenylidenic $Fe_3(CO)_9(\mu\text{-}CO)(C{=}C{=}CH_2)$ (**2**) in very small yields, $Fe_2(CO)_6[H_2CCC(H)C(=O)OCH_3]$ (**3**), and $Fe_3(CO)_{10}[H_2CCC(H)C(=O)C\{CH_2(O)CH_3\}CCH_2]$ (**4**) (7). The structures of complexes **2**–**4** are shown in Scheme 1.

On the basis of previous results (8), the formation of com-

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Dr. Carty is now at the top of a brilliant career. This paper is dedicated to the chemist who agreed to collaborate with us, the teacher who told me how to decently write a paper in English, and to the friend with whom we shared nice ski and walking runs in the Alps. In a word: Arthur Carty.

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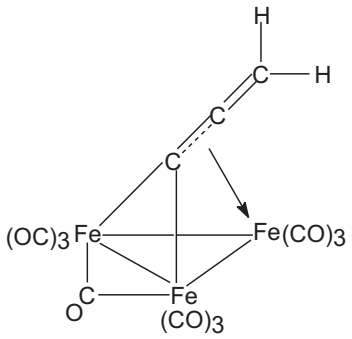
Scheme 1.



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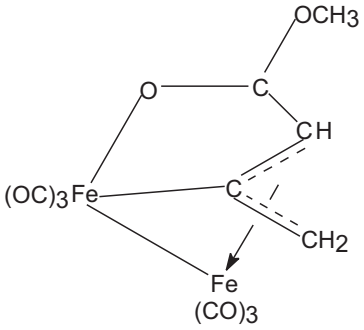

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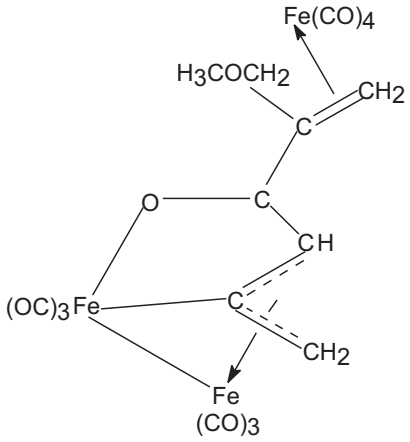

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plexes such as **3** had been explained by invoking the intermediacy of complexes of type **2**, with no evidence for the role of complex **1** in the reaction sequence. In this work the attention has been paid to the synthetic pathways leading to complexes **1** and **3** and on some aspects of their reactivity with the aim of obtaining more details on the reaction mechanisms leading to methoxycarbonyl derivatives (**3**, **4**). The reactions of $Fe(CO)_5$ and $Fe_3(CO)_{12}$ with the alkynes collected in Table 1, under basic methanolic conditions, have been therefore considered. These alkynes, except for the last two, are characterized by $C{\equiv}CCH_2OH$ or $HC{\equiv}CCH_2$ moieties, which could form cumulene systems.

Reacting the oily complex **1** with triphenylphosphine, the title complex (**1a**) was obtained as the major product, and its structure was determined by X-ray analysis. The structural features for this unprecedented derivative are discussed.

Table 1. These alkynes, except for the last two, are characterized by $C{\equiv}CCH_2OH$ or $HC{\equiv}CCH_2$ moieties, which could form cumulene systems.

Ligand	Name
$HC{\equiv}CCH_2OH$	Propargylic alcohol
$ClC{\equiv}CCH_2OH$	Propargyl chloride
$PhC{\equiv}CCH_2OH$	3-Phenyl-2-propyn-1-ol
$(CH_3)_3SiC{\equiv}CCH_2OH$	Trimethylsilyl propargyl alcohol
$(CH_3)_3SiOCH_2C{\equiv}CH$	Propargyloxytrimethylsilane
$H_2NCH_2C{\equiv}CH$	Monopropargylamine
$(CH_3COO)CH_2C{\equiv}CH$	Propargyl acetate
$(Ph)_2(OH)CC{\equiv}CH$	1,1-Diphenyl-2-propyn-1-ol
$(CH_3)_3SiC{\equiv}CH$	Trimethylsilyl acetylene

Experimental

$Fe(CO)_5$, $Fe_3(CO)_{12}$ (Strem Chemicals), and the alkynes (Lancaster Syntheses) were used as received. Methanol, KOH (pellets), and HCl (37%) were laboratory grade chemicals. Solvents (hexane, heptane, toluene, and dietyl ether) were dehydrated (over sodium when possible). The reactions were performed under dry nitrogen in conventional three-necked flasks, equipped with a gas inlet, cooler, mercury check valve, and magnetic stirring.

All reactions of $Fe_3(CO)_{12}$ were performed in CH_3OH–KOH solution and the following "standard" conditions were adopted: dissolution of KOH (20 pellets, ca. 1.5 g) in 200 cm^3 of CH_3OH, then addition and dissolution of 5.0 g (ca. 10 mmol) of $Fe_3(CO)_{12}$, and warming at 40 °C for 10 min; addition of 4.0 cm^3 of the liquid alkynes (or of 1.0 g for the solid ones) and warming at 40 °C for a further 10–15 min. After cooling, the substrate was acidified with HCl (37%) to pH 1. After 1 h, the solution was extracted with three 75 cm^3 portions of *n*-heptane. The solution was then reduced to a small volume under reduced pressure and then purified using TLC (Kieselgel PF Merck; eluants were mixtures of light petroleum (40–70 °C) and diethyl ether in a 9:1 *v*/*v* ratio). Finally, the TLC bands were extracted with diethyl ether.

The reactions of $Fe(CO)_5$ with propargylic alcohol and propargyl chloride were performed under the following conditions: to a solution of 30 pellets of KOH in 200 cm^3 of methanol, 30 cm^3 (ca. 65 mmol) of $Fe(CO)_5$ was added. The resulting solution was stirred and warmed at 40 °C for 30 min after which time 6 cm^3 of the liquid alkynes were added. Stirring and warming were continued for a further 30 min. The resulting solution was allowed to cool and acidified (to pH 1) with HCl (32%). A violent evolution of gases and vapours was observed. After filtering, the solutions were extracted with three 75 cm^3 portions of heptane. After reduction to a small volume under vacuum, the solutions obtained were chromatographed as described previously.

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 ^1H and ^{13}C NMR were obtained on a JEOL GX 270 spectrometer. The EI (and CI) mass spectra were obtained on a Finnigan Mat TSQ-700 mass

spectrometer (Servizio di Spettrometria di Massa, Dipartimento di Scienza e Tecnologia del Farmaco, Università di Torino).

Reactions of propargyl alcohol with $Fe(CO)_5$

After extraction with heptane, the following products were obtained: complex **1** (20%), $Fe_3(CO)_{12}$ (15%), and orange complex **3** (20%).

Complex 1

IR (heptane, cm^{-1}) ν_{CO}: 2098 (m), 2040 (vs), 2020 (vs), 2012 (s sh), 1989 (m), 1980 (m sh). ^1H NMR ($CDCl_3$, r.t.) δ: 3.77 (s, 2H), 2.42 (s, 2H). ^{13}C NMR δ: 70.87 (s), 75.86 (s, CH_2), 186.0 (s, b), 206.1 (s, b, terminal CO), 212.0 (s, CO). EI-MS: M^+ = 348 *m/z*, release of a fragment with 16 *m/z*, then release of 7CO; intense signal at 152 *m/z* [$Fe_2(C_3H_4)$]. Anal. calcd. (%): C 34.5, H 1.15, Fe 32.2; found: C 34.6, H 1.2, Fe 32.1.

Complex 3

IR (cm^{-1}): 2078 (m-s), 2033 (vs), 2008 (s, sh), 1996 (vs), 1979 (m-s). ^1H NMR δ: 4.08 (s, 1H), 3.68 (s, 3H, Me), 3.56 (s, 1H), 2.97 (s, 1H). ^{13}C NMR δ: 54.4 (s, Me), 58.8 (d, CH_2), 66.3 (d, CH), 189.1 (d, C ring?), 197.1 (s, CO), 212.0 (vb, CO acetate). EI-MS: M^+ = 378 *m/z*, release of 6CO, then complex fragmentation. Anal. calcd. (%) C 34.9, H 1.6, Fe 29.6; found: C 35.0, H 1.7, Fe 29.7. The analytical results for complexes **1** and **3** have already been reported in ref. 7. These are given here for comparison with the other complexes described.

Reaction of propargyl chloride with $Fe(CO)_5$

After filtration of the acidified solution a considerable amount of solid residual was observed; this was partially soluble in methanol. The methanolic solution was added to the filtrate. After extraction with heptane, TLC gave the following bands: yellow (ca. 10%, complex **1**), $Fe_3(CO)_{12}$ (30%), orange (ca. 10%, complex **3**) and red (tr, not collected).

Reaction of $Fe_3(CO)_{12}$ with trimethylsilyl propargyl alcohol

After acidification and extraction, the red, clear heptane solution was chromatographed on TLC plates and the following bands were obtained: yellow (10%, complex **1**), triiron dodecacarbonyl (10%), orange (25%, complex **3**), orange-red (20%, complex **5**), and some decomposition.

Complex 5

IR (heptane, cm^{-1}): 2100 (m), 2074 (m-s), 2032 (vs), 2006 (s), 1992 (s, sh), 1974 (m). ^1H NMR δ: 4.18 (d), 3.95 (d), 3.86 (s, 1H), 3.75 (d), 3.67 (d), 3.53 (s, 1H), 3.28 (d), 3.04 (q, 2H), 2.94 (s, 1H), 2.77 (s, 1H), 2.55 (s, 1H). EI-MS: M^+ = 586 *m/z*, release of 12 fragments with *m/z* = 28. Anal. calcd. (%) C 38.1, H 1.7, Fe 29.1; found: C 38.3, H 1.7, Fe 28.8.

Complex 4

IR (cm^{-1}): 2100 (m), 2075 (m-s), 2031 (vs), 2026 (vs), 1992 (s), 1973 (m). ^1H NMR δ: 4.16–4.12 (d, 2H), 3.89–3.78 (d, 2H), 3.68–3.66 (d, 1H), 3.29 (s, 3H, Me), 3.07–3.04 (d, 2H, CH_2). ^{13}C NMR δ: 37.3 (s), 58.4 (s), 66.4 (s), 68.2 (s), 72.3 (s), 203.3 (s), 206.6 (s), 220.0 (s). EI-MS: M^+ = 586 *m/z*, release of 12 fragments with *m/z* = 28. Anal. calcd. (%): C 38.1, H 1.7, Fe 29.1; found: C 38.2, H 1.8, Fe 28.0.

Reaction of $Fe_3(CO)_{12}$ with propargyloxytrimethylsilane

After extraction, the red-yellow heptane solution was chromatographed on TLC plates and the following bands were obtained: dark yellow (15%, complex **1**), $Fe_3(CO)_{12}$ (15%), orange (20%, complex **3**), red (**5**, 10%), trace amounts of a red and a yellow compound (not collected), and decomposition.

Reaction of $Fe_3(CO)_{12}$ with propargyl acetate

After extraction with heptane, TLC showed the following bands: yellow (20%, complex **1**), $Fe_3(CO)_{12}$ (20%), orange (20%, complex **3**), traces of a red compound, and decomposition.

Reaction of $Fe_3(CO)_{12}$ with monopropargylamine

After acidification, the dark yellow heptane extract was chromatographed and the following bands were observed: yellow (complex **1**, 13%), orange yellow (complex **3**, 30%) and some decomposition.

Reaction of $Fe_3(CO)_{12}$ with 3-phenyl-2-propyn-1-ol in methanol

After acidification and extraction, the greenish solution gave the following TLC bands: light yellow (10%, complex **6**), $Fe_3(CO)_{12}$ (15%), orange (15%, complex **7**), and orange, purple, purple (tr, not collected).

Complex 6

IR (cm^{-1}): 2074 (m), 2033 (vs), 2005 (s), 1996 (s, sh), 1978 (m, sh). ^1H NMR δ: 7.26–7.19 (m, 5H, Ph), 4.28 (s, 1H), 3.88 (s, 1H), 3.69 (s, 1H). EI-MS: M^+ = 424 *m/z*, loss of seven fragments with *m/z* = 28. Proposed formula: $Fe_2(CO)_7C_3H_3(Ph)$. Anal. calcd. (%): C 45.3, H 1.9, Fe 26.4; found: C 45.2, H 1.8, Fe 26.5.

Complex 7

IR (cm^{-1}): 2074 (m-s), 2033 (vs), 2005 (s), 1996 (s, sh), 1978 (m-s). ^1H NMR δ: 7.45–7.26 (m, 5H, Ph), 6.30 (s, 1H), 3.88 (s, 1H). EI-MS: M^+ = *m/z* 454, loss of 6CO (see ref. 7). Proposed formula: $Fe_2(CO)_6[RHC_3R'C(=O)OCH_3]$ (R, R′ = Ph, H). Anal. calcd. (%): C 45.0, H 2.2, Fe 24.6; found: C 45.1, H 2.3, Fe 24.5.

Reactions of complexes 1 and 3

Reaction of complex 1 with PPh_3 under thermal conditions

About 0.5 g of complex **1** (ca. 1.5 mmol) were dissolved in heptane; PPh_3 (0.5 g, ca. 1.9–2.0 mmol) and Me_3NO were added and the solution was warmed to reflux (10 min) under nitrogen. After 4 min reflux (after which time the colour turned from yellow to dark red), the suspension was allowed to cool, was reduced to a small volume under vacuum, and chromatographed on TLC plates. The following bands were obtained: orange (50%, complex **1a**) and red (50%, complex

1b). Complex **1b** is nearly insoluble in solvents commonly used for obtaining X-ray grade crystals.

*Complex **1a***

IR (cm^{-1}): 2061 (m-s), 2017 (s), 1988 (vs), 1978 (s, sh), 1946 (w). ^1H NMR δ: 7.56 (m), 7.45 (m), 7.32 (m, 15H, Ph), 3.55 (s, 2H), 2.86 (s, 2H). ^{31}P NMR δ: –4.50 (s). Anal. calcd. (%): C 55.67, H 3.26, Fe 19.24; found: C 55.8, H 3.3, Fe 19.1. (MW = 582).

*Complex **1b***

IR (cm^{-1}): 2050 (m b), 1970 (vs), 1900 (m b). ^1H NMR δ: 7.54 (m), 7.40 (m, 30H, Ph), 3.50 (s, 2H), 2.16 (s, 2H). ^{31}P NMR δ: 59.78 (s), 79.20 (s). CI-MS: M^+ = 842 *m/z* (exp. 844), loss of 5CO. Anal. calcd. (%): C 55.67, H 3.26, Fe 19.24; found: C 55.7, H 3.3, Fe 19.3. (MW = 844).

Reaction of complex 1 with CH_3OH under thermal conditions

Approximately 0.2 g of complex **1** (ca. 0.6 mmol) were dissolved in CH_3OH (10 cm^3), brought to reflux (3 min), and allowed to react for 15 min. The dark yellow suspension was brought to dryness under N_2 flow; after TLC purification, only parent **1** could be observed together with some decomposition.

Approximately 0.25 g of complex **1** (ca. 0.72 mmol) were dissolved in 10 cm^3 of CH_3OH (and 0.2 cm^3 of HCl were added), brought to reflux (5 min), and allowed to react for 13 min. No change in colour was observed. The suspension was dried under a nitrogen stream; TLC purification and spectroscopic analyses showed the presence of complex **1** only.

Reactions of 1a with methanol under thermal conditions

Approximately 25 mg of **1a** (crystals used for the X-ray study) were dissolved in 10 cm^3 of CH_3OH under N_2 and allowed to reflux for 5 min. No change in colour was observed. The mixture was brought to dryness under reduced pressure; after TLC separation, only one complex could be obtained (**1c**).

*Complex **1c***

IR (cm^{-1}): 2061 (m-s), 2018 (m-s), 1987 (vs), 1977 (s sh), 1946 (m). ^1H NMR δ: 7.70–7.28 (mm, Ph), 3.58 (s, 1H), 3.51 (s, 1H), 2.31 (s, 1H), 2.19 (s, 3H). CI-MS: M^+ = 584 *m/z*, loss of 6CO. Anal. calcd. (%): C 55.5, H 3.6, Fe 19.2; found: C 55.4, H 3.7, Fe 19.3.

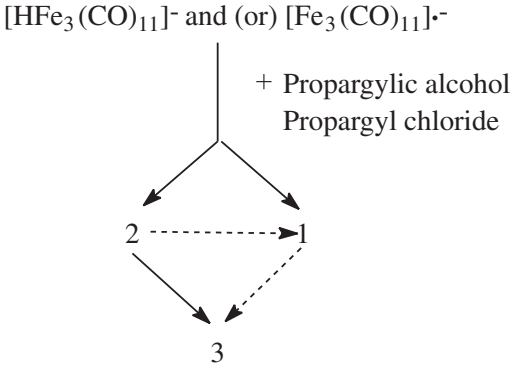
Reactions of 3 with triphenylphosphine

Approximately 0.5 g of complex **3** (ca. 1.3 mmol) were dissolved in heptane under N_2 and a 2:1 molar excess of PPh_3 was added. The suspension was brought to reflux (10 min) and allowed to reflux for 3 min. The colour of the clear solution turned from orange to red. TLC purification gave the following bands: dark yellow (**3**, ca. 10%), red (complex **3a**, ca. 40%) and impure PPh_3.

*Complex **3a***

IR (cm^{-1}): 2042 (vs), 1991 (vs), 1977 (s), 1963 (m), 1936 (m b). ^1H NMR δ: 7.55–7.25 (mm, Ph), 3.97 (s, 1H), 3.40 (s, 1H), 3.21 (s, 3H), 2.66 (s, 1H). ^{31}P NMR δ: 30.8 (s). Anal. calcd. (%): C 54.0, H 3.5, Fe 18.7; found: C 54.1, H 3.6, Fe 18.8.

Scheme 2.



X-ray structure analysis for complex 1a

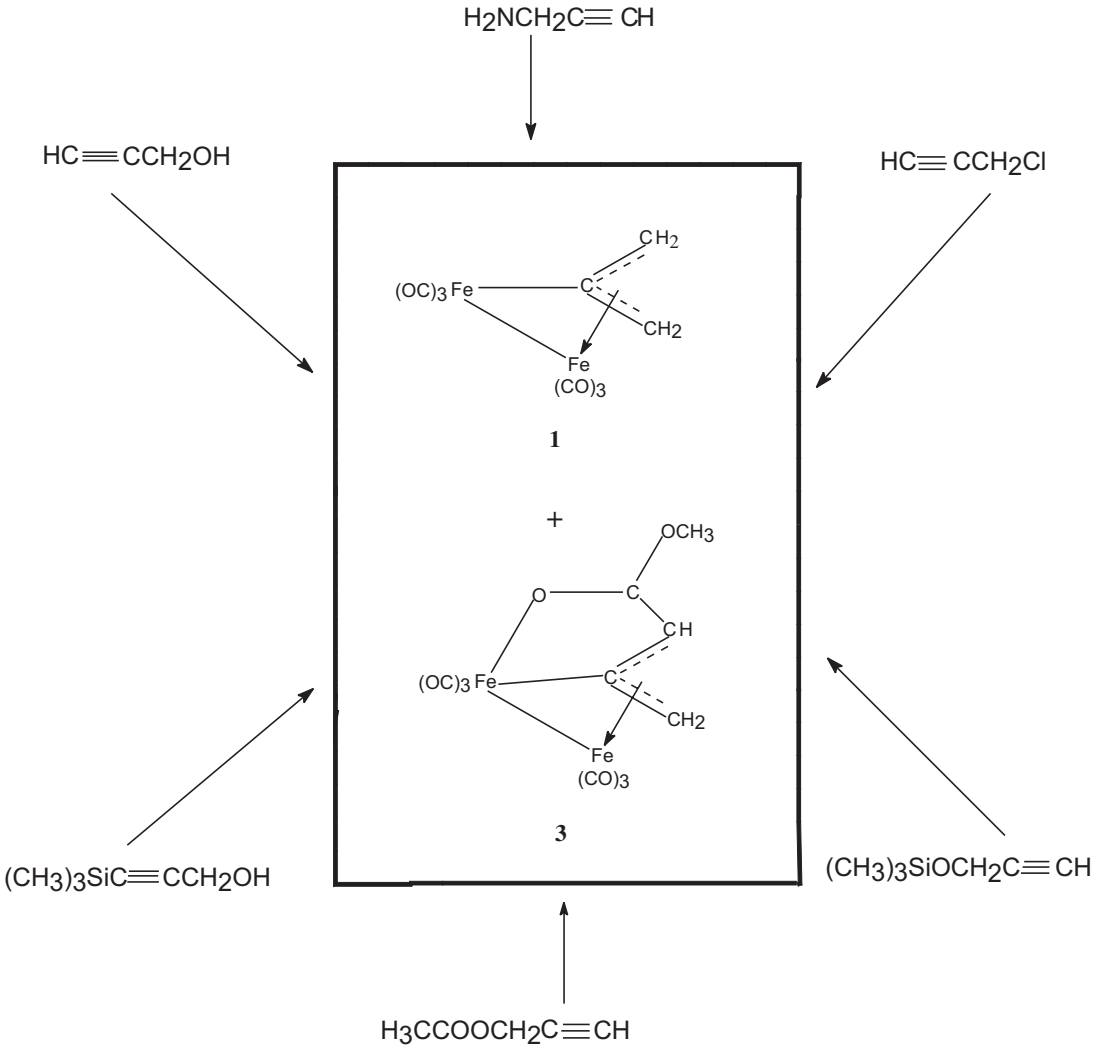
The reflection data were collected on a Siemens P4 diffractometer equipped with a Bruker APEX CCD detector using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The complex **1a** ($C_{27}H_{19}Fe_2O_6P$) crystallized from *n*-heptane in a monoclinic $P2_1/n$ space group, with a = 12.7888(15) Å, b = 9.3735(10) Å, c = 21.4652(26) Å, β = 92.163(2)°, V = 2571.3(5) $Å^3$, MW = 582.09, Z = 4, Dcalcd. = 1.504 g cm^{-3}, μ = 1.230 mm^{-1}. The red crystal used was prismatic and had dimensions of 0.08 × 0.10 × 0.20 mm^3. The θ range for measurement was 1.90°–28.32°; 23 563 reflections were measured at 293 K and 5444 were unique (R_{int} = 0.077). The intensities were corrected semi-empirically for absorption, based on symmetry equivalent reflections. The refinement of 325 parameters was made using full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were calculated and refined with U_{iso} set at 1.2 times U_{eq} of the corresponding C atom. The final parameters were: $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.0732$ for 2975 "observed" reflections having $F_o^2 > 2\sigma(F_o^2)$, $Rw = [\Sigma(wF_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2} = 0.127$, goodness-of-fit = $[\Sigma w(F_o^2 - F_c^2)^2/(\text{No. of unique reflections} - \text{No. of parameters})]^{1/2} = 0.959$. Programs used were SHELXTL (9) for structure solution, refinement, and molecular graphics, Bruker AXS SMART (diffractometer control), SAINT (integration), and SADABS (absorption correction) (10). The high R values are due to the poor quality of crystals; the intensity measurements were repeated on other crystals with the same results. Therefore, the calculated hydrogen atom positions must be considered with caution.

Results and discussion

Spectroscopic characterization of complexes 5–7

Complex **5** is obtained only from the isomeric ligands trimethylsilyl propargyl alcohol and propargyloxytrimethylsilane. The analytical and spectroscopic data (except for the ^1H NMR) are closely comparable with those of complex **4**. However, in view of the high complexity of the NMR spectrum, we cannot provide a structure. Complex **5** has an isomeric formula with respect to **4** (elemental analysis and mass spectrum) and the NMR spectrum could indicate that "**5**" is a nonseparated mixture of the two isomers. Attempts

Scheme 3.



at obtaining crystals suitable for X-ray analysis were unsuccessful.

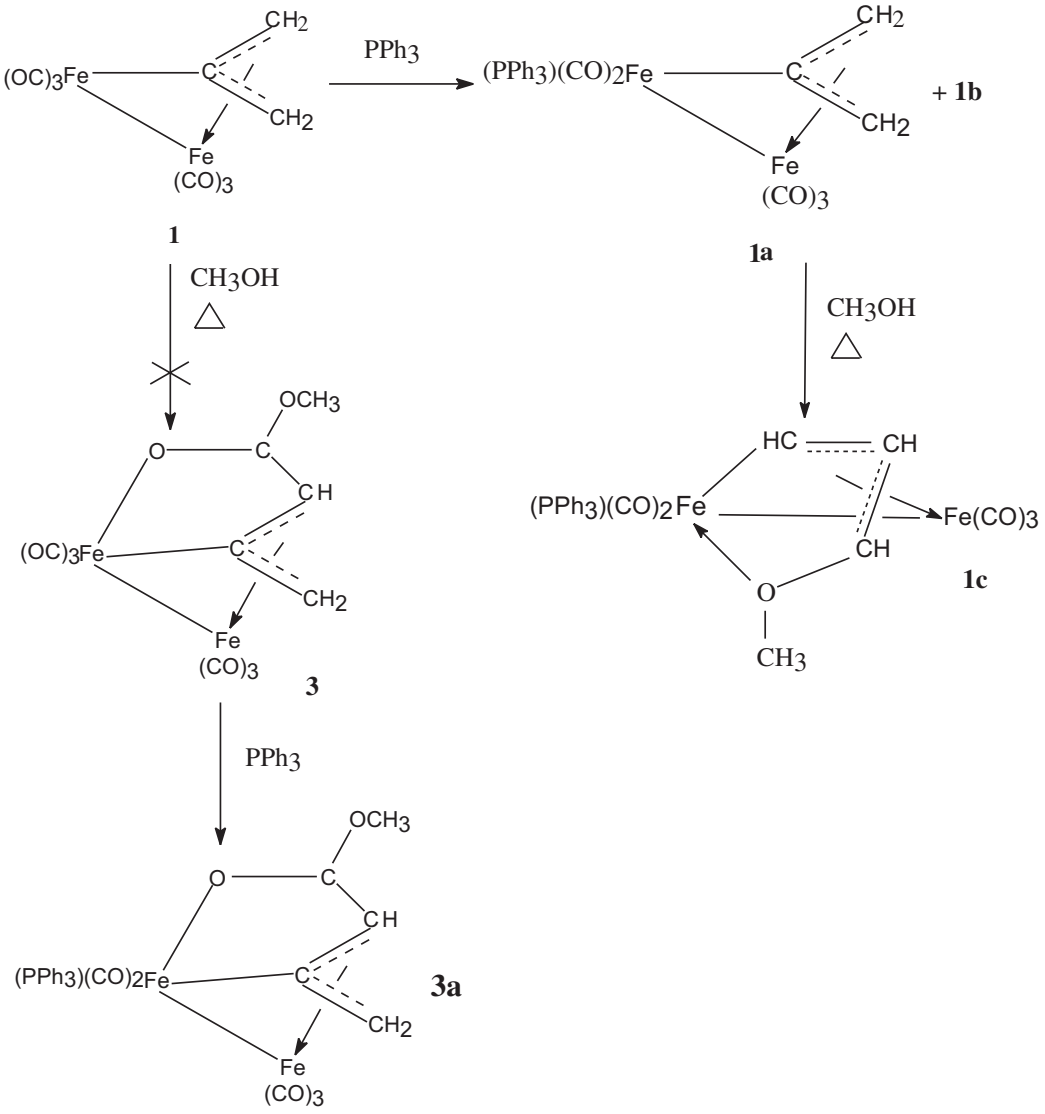
Complexes **6** and **7** are the homologues of **1** and **3**, respectively, and contain a phenyl at the site of one of the hydrogens of the C_3 part of the organic ligand. The complexes are obtained from 3-phenyl-2-propyn-1-ol, which apparently behaves like the other alkynes, but does not lose the phenyl group. Complex **7** shows the same analytical data, but a different NMR with respect to the complex reported in ref. 7. Again, it could be an isomer obtained by a different position of the phenyl group in the structure.

Reactions leading to complexes 1 and 3

As previously discussed, the reactions of $Fe_3(CO)_{12}$ with propargylic alcohol and propargyl chloride give, as the main products, complexes **1**, **3**, and **4** and much smaller amounts of the allenylidene complex **2**[7]. No unequivocal evidence, both for the structure of **1** and for its role in the reaction pathways leading to **3**, was obtained. As shown in Scheme 2, two hypotheses can be advanced: (*i*) **1** would be a fragmentation product derived from **2**; however, complex **2** was obtained in yields not allowing a reactivity study, only from the reactions of propargylic alcohol and propargyl chloride. It was observed only in trace amounts in other reactions leading to medium yields of **1**. This could represent indirect evidence for **2** being a labile intermediate in the formation of **1** (as a by-product) and of **3** in a direct reaction. (*ii*) An alternative possibility could be that **1** is an intermediate in the formation of **3**.

The formation of complexes **1** and **3** has been therefore taken into account. The results show that complexes **1** and **3** are obtained in medium yields starting from propargylic alcohol, propargyl chloride, trimethylsilyl propargyl alcohol, propargyloxytrimethylsilane, monopropargylamine, and propargyl acetate (see Table 1). These alkynes can release -C≡CCH_2OH or HC≡CCH_2-, three-carbon atom fragments that could rearrange (and uptake hydrogen atoms) to form the H_2C=C=CH_2 ligand observed in **1** and **1a**. In contrast, complexes **1** and **3** are not obtained from trimethylsilyl acetylene and 1,1-diphenyl-2-propyn-1-ol, which can release only C_2 fragments. The reaction of $Fe_3(CO)_{12}$ with 1,1-diphenyl-2-propyn-1-ol in the same conditions reported for the other alkyne ligands yields only two products in trace amounts (not collected). The reaction of $Fe_3(CO)_{12}$ with trimethylsilyl acetylene gives mostly $Fe_3(CO)_{12}$ and very small yields of a orange, yellow, and red bands showing IR

Scheme 4.



and NMR spectra different from those of **1** and of **3**. The "parent" alkynes forming complexes **1** and **3** are shown in Scheme 3.

Interestingly, 3-phenyl-2-propyn-1-ol, which would not easily release the C_6H_5 substituent, gives complexes **6** and **7**, which are the phenyl-containing homologues of **1** and **3**.

It is also worth noting that **1** and **3** are obtained from monopropargylamine: this also indicates that the NH_2 functionality can be lost. Finally, complex **3** is also obtained from propargyl acetate. Mathieu and co-workers (11) have described the synthesis of the acetate open-cluster derivative $Fe_3(CO)_{10}(PPh_2)[CHCCHC(OCH_3)O]$ containing a heterocyclic ring comparable with that of **3**. The complex was obtained from $[HFe_3(CO)_{11}]^-$ and $(CH_3COO)CH_2C{\equiv}CPPh_2$.

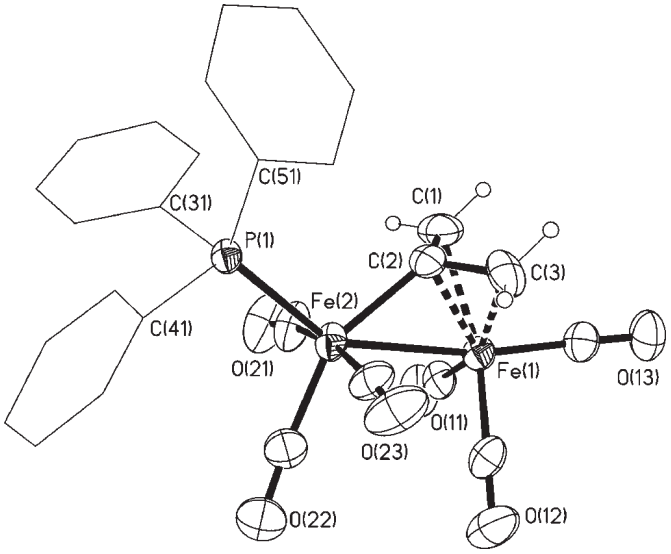
It is also interesting to observe that **1** (and **3**) are obtained when reacting propargylic alcohol and propargyl chloride both with $Fe_3(CO)_{12}$ and with $Fe(CO)_5$ in basic methanolic conditions. The intermediacy of the $[HFe_3(CO)_{11}]^-$ anion in these reactions can be hypothesized on the grounds of the following observations: (*i*) its formation from $Fe_3(CO)_{12}$ in the reaction conditions adopted was reported in the literature (1); (*ii*) its presence during the synthesis of $Fe_3(CO)_{12}$ starting from $Fe(CO)_5$ is well-established (12). It is also possible that, in the above reaction conditions, the radical anion $[Fe_3(CO)_{11}]^{\cdot-}$ (13) is present.

Reactions leading to 1a and 1b — Proposed structure of complex 1 on the basis of the X-ray structure of complex 1a

The reaction of complex **1** with triphenylphosphine leads to the monosubstituted **1a**, whose structure is discussed in the following, and to the disubstituted complex **1b** presumably bearing the two phosphine ligands on different iron atoms, as indicated by the ^{31}P NMR spectrum.

Complex **1**, when dissolved in heptane, heptane–toluene, or other solvents and kept at –30 °C, gives large and well-formed orange "crystals"; however, when the solvent is removed, even at low temperature, the crystals collapse quickly forming a thick oil. For **1** a structure is therefore proposed on the basis of analytical and spectroscopic data and on the

Fig. 1. ORTEP plot of $Fe_2(CO)_6(PPh_3)[\mu\text{-}\eta^3\text{-}(H_2CCCH_2)]$ (complex **1a**) with thermal ellipsoids (30% probability).



following observations: (*i*) **1** is formed from several alkynes that can loose a three-carbon atom fragment; (*ii*) in a recent report propargylic alcohol has been shown to react with triruthenium benzoquinoline complexes releasing a (coordinated) C_3H_4 unit (14), albeit different from that proposed for **1**; (*iii*) complex **1** shows a ^1H NMR spectrum indicating the presence of two nonequivalent CH_2 groups. Mass spectra of samples coming from reactions with different alkynes all showed a $P^+ = 348$ *m*/*z* corresponding to $Fe_2(CO)_7(C_3H_4)$. In the light of the structure of **1a** discussed in the following, we now think that the more probable structure is that shown in Scheme 3.

Reactions of complexes 1 and 1a with CH_3OH

Complex 1

These reactions have shown that under thermal conditions complex **1** does not react very easily with methanol. Only trace amounts of complex **3** were observed. Thus, complex **1** should be considered a side product, rather than an intermediate, in the formation of **3**.

Complex 1a

From this reaction, one can see that complex **1a** can add methanol, giving, however, a complex (**1c**) different from **3a**. For complex **1c**, we propose the structure shown in Scheme 4 on the basis of the analytical and spectroscopic results and by analogy with the previous reports of Mathieu and co-workers (11). Thus, complex **1a** is not an intermediate in the formation of the phosphine-substituted **3a**.

Reaction of complex 3 with PPh_3

The monosubstituted complex **3a** was isolated and characterized using spectroscopy; complex **3a** probably follows the behaviour of other ferrole-like complexes, where the phosphine substitution for CO occurs first at the iron atom σ bound to the organic ring (15).

Table 2. Some relevant bond distances (Å) and angles (°) for complex **1a**, $Fe_2(CO)_6(PPh_3)[\mu\text{-}\eta^3\text{-}(H_2CCCH_2)]$.

Bond distances (Å)	
Fe(1)—C(2)	1.952(5)
Fe(1)—C(3)	2.120(5)
Fe(1)—C(1)	2.123(6)
Fe(1)—Fe(2)	2.6479(10)
Fe(2)—C(2)	1.977(5)
Fe(2)—P(1)	2.2514(14)
P(1)—C(51)	1.824(4)
P(1)—C(31)	1.824(5)
P(1)—C(41)	1.835(5)
C(1)—C(2)	1.448(8)
C(2)—C(3)	1.384(8)
Bond angles (°)	
C(3)-C(2)-C(1)	112.5(6)
C(3)-C(2)-Fe(2)	119.4(5)
C(1)-C(2)-Fe(2)	117.9(5)

The crystal structure of 1a

The structure of **1a** is shown in Fig. 1 and significant distances and angles are given in Table 2. The complex is formed by two nonequivalent iron atoms, with an Fe—Fe distance of 2.648(1) Å.

The C_3H_4 ligand is coordinated both to Fe(1), as a formal $3e^-$ donor, and to Fe(2), as a formal $1e^-$ donor. Six COs are terminally bound to Fe(1) and to Fe(2), which is also bound to the PPh_3 ligand disposed cis with respect to C(2), in the less sterically and electronic demanding situation. When considering the C_3H_4 as a four-electron donor and the presence of an Fe—Fe bond, each iron atom would reach the 18-electron configuration. The Fe(2)-C(1)-C(2)-C(3) moiety deviates from planarity with a mean deviation of 0.10 Å. The Fe—C bond distances and their geometry agree with a formal description of a π interaction of Fe(1) with C(1)—C(2) and with C(2)—C(3) elongated double bonds and with a Fe(2)—C(2) σ interaction. This situation corresponds to a π-allyl moiety where a hydrogen atom is substituted by an iron atom. Allyl groups coordinated in this way are commonly found, especially in the nickel triad chemistry. Complex **1a** has been very presumably obtained upon simple substitution of a phosphine for a CO, suggesting a similar formula for **1**.[3]

Conclusions

The results obtained allow the unequivocal characterization of complex **1**. We have found that **1** is a by-product in the synthesis of **3**; it is presumably a fragmentation product of the allenylidenic complex **2**. Complex **1** does not react with methanol to give **3**. In contrast, **1a** gives a product (**1c**)

[3] Supplementary data for this article are available on the journal Web site (http://canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 5001. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 273281 contains the crystallographic data for this manuscript. These data can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

containing the fragments of methanol, albeit coordinated differently than in **3** or **3a**.

These results confirm the mechanism already proposed for the formation of **3** (see Scheme 2), that is, the intermediacy of complex **2** only. Formation of complexes containing methoxycarbonyl groups upon activation of CO under basic methanolic conditions seems to be a general trend. For example, recently we have observed that $Ru_3(CO)_{12}$ reacts with 1,4-dichloro-but-2-yne in basic methanolic conditions forming the complex $H_2Ru_3(CO)_9[H_2C{=}CC{\equiv}CC(=O)OCH_3]$ (16); the formation of this complex requires loss of chlorine and activation of CO. In our opinion, the mechanisms leading to this type of complex deserve further efforts towards being fully understood, especially in view of organometallic-mediated organic syntheses.

Last but not least, from the reactions described in this paper, complex **1a** was obtained. The structure of this complex is unprecedented and shows, once again, that alkynol-cluster chemistry may lead to unprecedented bonding modes for hydrocarbyls on metal clusters.

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