

The reaction of $\text{Ru}_3(\text{CO})_{12}$ with 1,4-dichloro-but-2-yne in basic methanolic solution. Synthesis and crystal structure of $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9\{\mu_3\text{-}\eta^2\text{-}[\text{H}_2\text{C}=\text{C}(\text{H})\text{C}\equiv\text{CC}(=\text{O})\text{OCH}_3]\}$

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Abstract

The title complex is obtained by reacting $\text{Ru}_3(\text{CO})_{12}$ with 1,4-dichloro-but-2-yne ($\text{ClCH}_2\text{C}\equiv\text{CCH}_2\text{Cl}$, DCB) in $\text{CH}_3\text{OH}/\text{KOH}$ solution (followed by acidification with HCl). The X-ray structure analysis shows that $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9\{\mu_3\text{-}\eta^2\text{-}[\text{H}_2\text{C}=\text{C}(\text{H})\text{CCC}(=\text{O})\text{OCH}_3]\}$ complex contains a “parallel” ene-yne acetyl substituent, $\text{H}_2\text{C}=\text{C}(\text{H})\text{C}\equiv\text{CC}(=\text{O})\text{OCH}_3$; the formation of such a ligand starting from DCB is – to our knowledge – unprecedented. The synthesis of complex $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9\{\mu_3\text{-}\eta^2\text{-}[\text{H}_2\text{C}=\text{C}(\text{H})\text{CCC}(=\text{O})\text{OCH}_3]\}$ occurs through the activation of CO and methanol. This process has been found for other reactions of functionalized alkynes with $\text{M}_3(\text{CO})_{12}$ carbonyls ($\text{M} = \text{Fe}, \text{Ru}$) under basic methanolic conditions.

The known hydridic cluster, $(\mu\text{-H})\text{Ru}_3(\text{CO})_9[\mu_3\text{-}\eta^3\text{-}(\text{MeCCHCH})]$ has been identified as the minor reaction product.
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Keywords: Triruthenium clusters; Parallel alkynes; Ene-yne ligands; Methanol and CO activation; Acetyl ligands; X-ray structure analysis

1. Introduction

We are currently exploring the chemistry of the metal carbonyl clusters $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Fe}, \text{Ru}$) towards functionalized alkynes. In particular, we have taken into account amino-alkynes, alkynols and alkyne-diols [1], such as but-2-yn-1,4-diol [$\text{HOCH}_2\text{C}\equiv\text{CCH}_2\text{OH}$, BUD]; we have found that the reactions of these ligands with $\text{Ru}_3(\text{CO})_{12}$ under alkaline conditions lead to the loss of the functionalities.

We have also found that BUD and 1,4-dichloro-but-2-yne (DCB) react with $\text{Fe}_3(\text{CO})_{12}$ losing, respectively, the OH or the chlorine substituents and forming the binuclear butatrienylic complex $\text{Fe}_2(\text{CO})_6[\text{H}_2\text{C}=\text{C}=\text{C}=\text{CH}_2]$ [2]. This prompted us to explore the reactivity of DCB towards $\text{Ru}_3(\text{CO})_{12}$ for a comparison with the

results already reported for BUD [1b]. We have found that DCB reacts with $\text{Ru}_3(\text{CO})_{12}$ in $\text{CH}_3\text{OH}/\text{KOH}$ to form, as the main product, $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9\{\mu_3\text{-}\eta^2\text{-}[\text{H}_2\text{C}=\text{C}(\text{H})\text{C}\equiv\text{CC}(=\text{O})\text{OCH}_3]\}$ [1b] in about 25% yields. Hypotheses on the reaction pathways leading to the vinyl-acetyl alkyne coordinated to the metals in complex **1** are discussed. CO and methanol activation is a common process under basic reaction conditions, however, different products can be obtained depending on the metal and on the reaction pathways.

2. Experimental

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

$\text{Ru}_3(\text{CO})_{12}$ (Strem Chemicals) and DCB (Lancaster Synthesis) were used as received. Methanol, KOH

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(pellets) and HCl (37%) were laboratory grade chemicals. Solvents (hexane, heptane, toluene and diethylether) were dehydrated (over sodium when possible). The reactions were performed under dry nitrogen in conventional three necked flasks, equipped with gas inlet, cooler, mercury check valve and magnetic stirring.

The CH₃OH/KOH reaction solutions, after acidification, were extracted with organic solvents, brought to small volume under reduced pressure and chromatographed on t.l.c. plates [Kieselgel P.F. Merck, eluent a mixture of petroleum ether (40–70 °C) and diethylether in 90/10 v/v]. 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 ¹³C NMR spectra were obtained on a JEOL GX 270 spectrometer (Dipartimento di Chimica IFM, Università di Torino). The E.I. 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).

2.2. Reactions of Ru₃(CO)₁₂ with DCB in alkaline solution

In a typical reaction, 20 pellets of KOH (ca. 1.5 g) were dissolved in 200 cm³ of CH₃OH under N₂ at room temperature; 1.2 g (ca. 2 mmol) of Ru₃(CO)₁₂ were added and the suspension was stirred and heated at about 40 °C for 10 min, during which time the colour changed from orange to purple brown. DCB (2.0 cm³, ca. 15 mmol) was then added and warming was continued for 10–15 min. The suspension was allowed to cool and was acidified with HCl (37%) until pH 1 was obtained. A whitish precipitate (KCl) was observed. After filtering, the suspension was extracted four times with 50 cm³ of heptane/toluene (4/1 v/v); the deep yellow solution obtained was brought to small volume under reduced pressure and chromatographed on t.l.c. plates. Two bands were observed: light yellow (**2**, ca. 10%) and yellow (**1**, ca. 25%); small amounts of an orange crystalline deposit, identified as a mixture of complex **1** and of Ru₃(CO)₁₂ were also observed. The reaction was performed in similar conditions but using KOH dissolved in water–methanol (1/3 v/v) and slightly longer reaction times. Extraction with toluene–heptane gave a colourless solution which did not show any compound dissolved.

2.3. Complex 1

Calcd. C% 26.9 (27.0), H% 1.2 (1.3), Ru% 45.7 (45.6). IR (heptane): 2113 m, 2083 s, 2064 vs, 2050 s, 2019 s, 1987 m, 1714 m-s, cm⁻¹. ¹H NMR (CDCl₃, r.t.): 7.98 s (1H), 7.60 s (1H)(=CH₂, C₇), 6.25 d (1H, =CH, C₆), 4.98 s (3H, CH₃), -15.5 s(b), -19.5 s(b) (2H, hydrides). ¹³C

NMR: 52.6 s (CH₃), 120.4 s (=CH₂), 129 s (HC=), 144.5 s (C, alkyne), 176.0 s (C alkyne), 179.8 s (CO), 188.0–194.0 vb (CO, acetate?), 195.2 s (CO). E.I. mass spectrum: P⁺ = 670 *m/z*, loss of 9 CO followed by complex fragmentation. Very intense peak at *m/z* = 330 (Ru₃C₂).

2.4. Complex 2

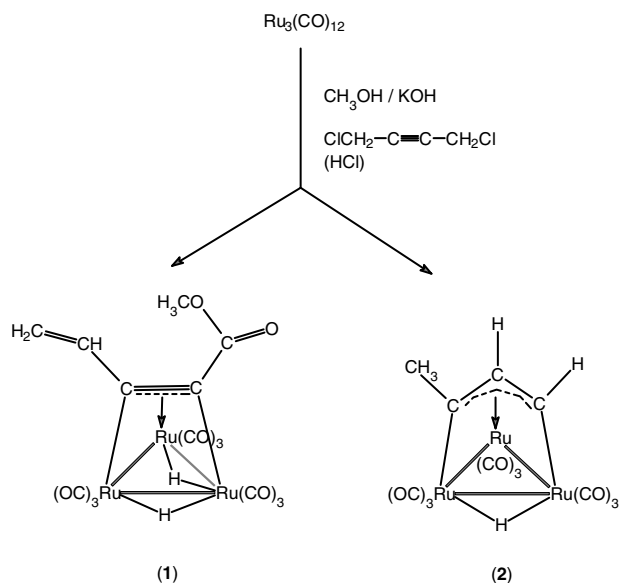
Calcd. C% 25.4 (25.6), H% 0.9 (1.0), Ru% 50.0 (49.6). IR (heptane): 2099 m-w, 2071 s, 2045 vs, 2028 s, 2018 m-s(sh), 2010 m-s(sh) cm⁻¹. ¹H NMR [3]: 8.55 d (1H, CH), 4.55 dd (1H, CH), 2.85 s (3H, CH₃), -20.39 s (1H, hydride). E.I. mass spectrum: P⁺ = 612 *m/z*, release of 9 CO; intense signal at 330 *m/z* (Ru₃C₂). Identification HRu(CO)₉ [MeC.CH.CH], see discussion below.

2.5. Crystallography of complex 1

The data collection was made on a Siemens P4 diffractometer equipped with a Bruker APEX CCD detector using graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). The complex **1** Ru₃C₁₅H₈O₁₁ crystallizes in monoclinic P2₁ space group, with $a = 9.076(1)$ Å, $b = 28.301(3)$ Å, $c = 9.218(1)$ Å, $\beta = 116.007(2)^\circ$, $V = 2128.0(5)$ Å³, $M = 667.43$, $Z = 4$, $D_c = 2.083$ g cm⁻³, $\mu = 2.15$ mm⁻¹. The yellow crystal used was prismatic of dimensions 0.14 × 0.16 × 0.24 mm. The θ range for measurement was 1.44–28.19°, 7259 reflections were measured at 293 K and 5382 were unique ($R_{\text{int}} = 0.025$). The intensities were corrected semi-empirically for absorption, based on symmetry equivalent reflections. The refinement of 542 parameters was made using full-matrix least-squares on F^2 . All non-hydrogen atoms were refined anisotropically, but two disordered oxygen atoms (O(3) in both molecules) that were isotropically refined with complementary occupation factors. Some hydrogen atoms were located on the last difference Fourier maps (e.g., the bridging H atoms) and others were calculated; they were refined with U_{iso} 's set at 1.2 or 1.5 times U_{eq} of the corresponding C atom. The hydride atoms H(1) and H(2) were refined. The final parameters were: $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.0327$ for 4981 “observed” reflections having $F_o^2 > 2\sigma(F_o^2)$, $R_w = [\sum (wF_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2} = 0.0670$, Goodness-of-fit = $[\sum w(F_o^2 - F_c^2)^2 / (\text{no. of unique reflections} - \text{no. of parameters})]^{1/2} = 1.033$. Programs used were SHELXTL [4] (structure solution, refinement and molecular graphics), Bruker AXSMART (diffractometer control), SAINT (integration) and SADABS (absorption correction) [5].

3. Results and discussion

The reaction of Ru₃(CO)₁₂ with DCB in CH₃OH/KOH (followed by acidification with HCl) is shown in



Scheme 1.

Scheme 1; it leads to complex **1** as the main product and to complex **2** as the minor product.

3.1. The synthesis of complexes **1** and **2**

The overall formation route leading to complex **1** requires – not necessarily in the order given below – the loss of the chlorines from DCB, uptake and shift of hydrogens on metal–metal bonds to form the hydride ligands and addition/insertion of a CO and of CH_3OH (which is splitted into H and CH_3O) to the coordinated four carbon-atom chain deriving from DCB. These steps will be separately discussed.

3.1.1. The loss of chlorine

Loss of chlorine occurs also in the formation of complex **2** as discussed below. Another example involving DCB is given by the reactions with $\text{Fe}_3(\text{CO})_{12}$ both under thermal and alkalyne conditions to give the butatrienyl complex $\text{Fe}_2(\text{CO})_6[\text{H}_2\text{C=C=C=CH}_2]$. Somewhat related to this behaviour is the recently reported synthesis of $\text{Ru}_3(\text{CO})_{12}$ from $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ in a reaction involving KOH and 2-ethoxyethanol, formation of formyl groups (WGSR reaction) and loss of chlorine [6]. In contrast, uptake of HCl in the reaction of $\text{Ru}_3(\text{CO})_{12}$ with BUD in conditions comparable with those used in this work leads to the open cluster $(\mu\text{-Cl})\text{Ru}_3(\text{CO})_9[\text{H}_2\text{CCC}(\text{H})\text{CH}_2]$ (**2c**) [1b] discussed below.

3.1.2. The shift of hydrogen

The shift of hydrogen from organic moieties to metal–metal bonds (to form bridging hydrides) is a frequently found process [7]. If one considers, however, that, after the loss of chlorines, DCB will leave a $\text{H}_2\text{CC}\equiv\text{CCH}_2$ fragment and that in complex **1** five

hydrogens are present (two hydrides and three on the organic moiety, excluding the methyl group) one should conclude that: (i) the extra hydrogen could come from methanol as discussed below, (ii) the hydride could be formed upon shift of one hydrogen of the ligand and (iii) this process occurs together with multiple bond isomerization in the organic moiety. Indeed, the ligand of complex **1** is a *ene-yne*; thus, during the reaction a vinyl substituent (C(6)–C(7)) is formed and the C–C triple bond is shifted.

3.1.3. The activation of CO

Insertion of a CO into M–C or C–C bonds is also a known process. In particular, there are some examples of insertion of a *cluster-bound* carbonyl into organic moieties. One is represented by the thermal reactions of $\text{Ru}_3(\text{CO})_{12}$ with *t*-butyl-acetylene or with alkynols to form oxygenated heterocycles still coordinated to the cluster in a fully elucidated reaction sequence [8]. Addition of a phosphine at the ferrole-like derivative [9] $\text{Fe}_2(\text{CO})_6(\text{C}_2\text{Et}_2)_2$ results in the insertion of CO and formation of a ketonic flyover complex, a precursor of the formation of a tropone [10]. Finally, insertion of a CO during the oligomerization of isopropenylacetylene on $\text{Fe}_3(\text{CO})_{12}$ has been reported [11]; open cluster isomers were obtained. These contain a CO bound both to one iron atom and to a carbon of the organic moiety. Reverse reactions, that is splitting of alkynols into cluster-bound acetylides and ketones have also been observed, both for ruthenium [12] and for iron [13].

3.1.4. The activation of methanol

Addition and splitting of methanol to give cluster-bound $\mu\text{-OMe}$ and a hydrogenated substituent has been reported [14]. This kind of methanol activation has been found in other examples: (i) methanol may add to triruthenium clusters undergoing splitting into $\mu\text{-H}$ and $\mu\text{-OMe}$: further coupling of diynes with the bringing OMe leads to hydridic allylic derivatives with a five-carbon atom ligand [15]. It has also been shown that carbonylation of methanol on triiron-chalcogenide clusters involves heterolytic splitting of methanol and insertion of CO to form an acetyl group coordinated to one metal centre of an hydridic intermediate [16]. These results accord with our hypotheses on the formation of complex **1**.

3.1.5. Reaction pathways to complex **1**

We have previously found that the reaction of hex-1-en-3-yne $[\text{H}_2\text{C=CHC}\equiv\text{CEt}]$ with $\text{Fe}_3(\text{CO})_{12}$ yields the ferrole-like $\text{Fe}_2(\text{CO})_6[(\text{C}_2\text{Et}_2)\text{C}(\text{=O})\text{O}]$ carboxylato complex upon splitting of water into its three components favoured by the silica gel used for t.l.c. purification [17]. A comparable reaction sequence was found for the allenylidene complex $\text{Fe}_3(\text{CO})_9(\mu\text{-CO})[\text{C=C=C}(\text{H})\text{Ph}]$ to give the allenyl ferrole-like $\text{Fe}_2(\text{CO})_6[\text{Ph}(\text{H})\text{CCC}(\text{H})\text{-}]$

C(=O)OCH₃] (**3a**) where the CO presumably comes from the cluster and one hydrogen and the CH₃O group from addition and splitting of methanol [18]. We have found that this is a general process; we could indeed obtain the ferrole-like Fe₂(CO)₆[H₂CCC(H)C(=O)OCH₃] (**3b**) homologue of **3a** by reacting Fe₃(CO)₁₂ with propargyl alcohol or propargyl chloride in CH₃OH/KOH solution. The acetyl-substituted ferroleic complexes **3** mentioned above and their allenylidene precursors are shown in Scheme 2.

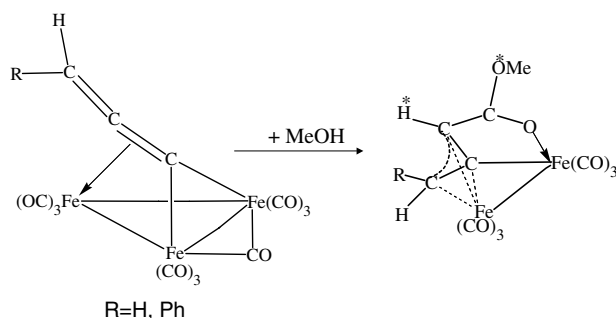
In the light of these results, we think that complex **1** is obtained starting from the anion [HRu₃(CO)₁₁][−] which is formed in alkaline solution [19].

After formation of the anion, a reaction sequence similar to that found for complexes **3** probably occurs, eventually via the intermediacy of a ene-yne (instead of an allenylidene) cluster intermediate. Complex **1**, however, is – to our knowledge – a rare example of a complex containing an acetyl group not bound to the cluster metals.

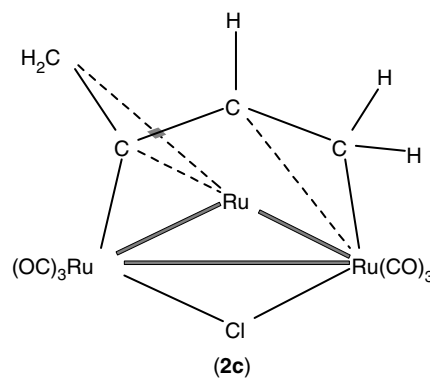
Finally, we have observed that the use of CH₃OH/H₂O instead of methanol only results in a total inhibition of the reaction. The reasons of this behaviour are unclear; it is possible that activation of water is more difficult than that of methanol, and that formation of COO containing complexes is therefore not allowed.

3.1.6. The synthesis of complex **2**

Complex **2** has been identified through IR and NMR spectroscopy and mass spectrometry as the already reported methyl-allyl derivative (μ-H)Ru(CO)₉{μ₃-η³-[MeC·CH·CH]} [20]; the identification has been confirmed by a comparison of the cell parameters. The structure of complex **2** is shown in Scheme 1. The complex is formed upon loss of chlorines from the DCB ligand and uptake of two hydrogens to form the bridging hydride and the C₄H₅ ligand. The origin of the two hydrogens is unclear: one could come from the [HRu₃(CO)][−] anion and the other both from addition of the (excess) HCl protons or from the water contained in the t.l.c. silica, as previously found [17]. In the light of the discussion above, complex **2** should be considered as a side-product of the reactions leading to complex **1**.



Scheme 2.



Scheme 3.

Loss of substituents has already been observed for trimethylsilyl-propargyl alcohol (TSPA) and diethylamino-1-propyne [1]; the main product of the reactions of these ligands with Ru₃(CO)₁₂ under basic methanolic solution was the hydridic allyl complex (μ-H)Ru₃(CO)₉[μ₃-η³-(HCCHCH)] (**2b**). In contrast, the reaction of the ruthenium carbonyl with BUD in the same conditions, lead to the chlorine-bridged (μ-Cl)Ru₃(CO)₉[μ₃-η⁴-(H₂CCCHCH₂)] (**2c**), an open cluster presumably obtained upon addition of HCl [1b]. Complex **2c** contains a C₄H₅ ligand “isomeric” with that found in **2**. This indicates that, whereas all the functionalized alkynes lose their functionalities under the reaction conditions described here, they can form a variety of hydrocarbyl ligands coordinated to clusters; the factors leading to the different ligands are not yet fully known. The structure found for complex **2c** is shown in Scheme 3.

3.2. The structure of complex **1**

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

The complex is formed by a scalene triangle of ruthenium atoms, each coordinated by three terminal CO groups. Two bridging hydrides span the Ru(2)–Ru(3) and the Ru(1)–Ru(3) edges of the cluster. H(1) is nearly coplanar with the cluster plane (7° and 16° deviation from Ru₃ plane for molecule A and B, respectively), whereas the Ru(1)H(2)Ru(3) plane forms an angle of 107° (molecule A) or of 127° (molecule B) with the cluster plane. The different disposition of the two hydrides is common for these clusters, and depends on the steric requirement of organic ligand; in fact the hydride is on the plane of cluster where the ligand is far (H(1)) and it is on the opposite side of the ligand with respect Ru₃ where hindered by the ligand (H(2)) [1a].

The organic moiety may be formally represented as σ and π bound to the cluster in a *parallel* fashion; the elongated C(1)≡C(2) bond is parallel to the Ru(2)–Ru(3) cluster edge and the above alkyne bears a vinyl H₂C(7)=C(6)H substituent on C(1) and a C(3)-(=O)OMe (acetyl) substituent on C(2).

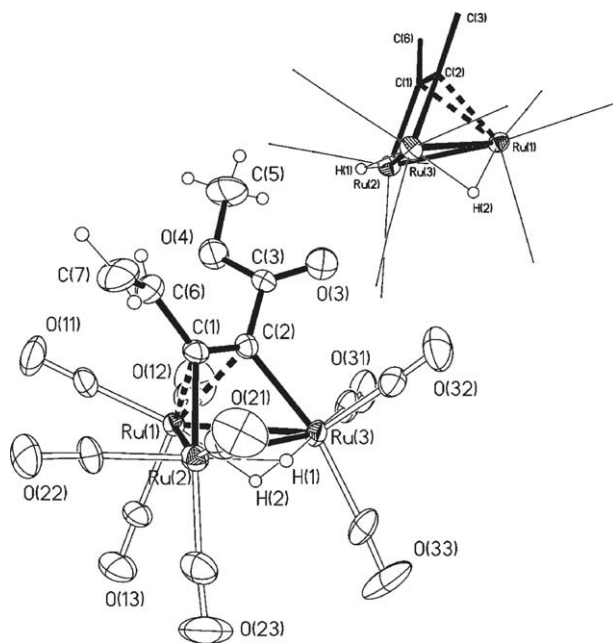


Fig. 1. ORTEP plot (30% probability) of one of the two independent molecules of complex **1** ($(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9\{\mu_3\text{-}\eta^2\text{-}[\text{H}_2\text{C}=\text{C}(\text{H})\text{C}\equiv\text{CC}(\text{=O})\text{OCH}_3]\}$). Top right the scheme of the molecule showing the disposition of the hydride atoms.

Table 1

Selected bond lengths (Å) and angles (°) for complex **1** ($(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9\{\mu_3\text{-}\eta^2\text{-}[\text{H}_2\text{C}=\text{C}(\text{H})\text{C}\equiv\text{CC}(\text{=O})\text{OCH}_3]\}$)

	Molecule A	Molecule B
Ru(1)–Ru(2)	2.724(1)	2.723(1)
Ru(1)–Ru(3)	2.826(1)	2.821(1)
Ru(2)–Ru(3)	2.967(1)	2.963(1)
Ru(1)–C(1)	2.330(7)	2.317(7)
Ru(1)–C(2)	2.204(7)	2.196(7)
Ru(2)–C(1)	2.079(8)	2.065(8)
Ru(3)–C(2)	2.112(8)	2.098(7)
C(1)–C(2)	1.372(11)	1.383(11)
C(1)–C(6)	1.460(11)	1.480(11)
C(2)–C(3)	1.476(11)	1.513(13)
C(3)–O(3)	1.22(2)	1.18(2)
C(3)–O(4)	1.299(11)	1.286(13)
O(4)–C(5)	1.443(11)	1.476(14)
C(6)–C(7)	1.283(15)	1.300(15)
Ru(2)–Ru(1)–Ru(3)	64.61(3)	64.59(3)
Ru(1)–Ru(2)–Ru(3)	59.38(2)	59.31(2)
Ru(1)–Ru(3)–Ru(2)	56.01(3)	56.11(3)
C(1)–Ru(2)–Ru(3)	68.4(3)	68.7(2)
C(2)–Ru(3)–Ru(2)	66.5(2)	66.4(2)
C(2)–C(1)–C(6)	122.5(7)	121.7(8)
C(2)–C(1)–Ru(2)	111.2(6)	110.7(5)
C(6)–C(1)–Ru(2)	126.3(7)	127.6(6)
C(1)–C(2)–C(3)	124.4(8)	124.5(7)
C(1)–C(2)–Ru(3)	112.8(6)	113.2(6)
C(3)–C(2)–Ru(3)	120.3(7)	119.3(6)
O(3C)–C(3)–O(4)	122.8(9)	118.7(15)
O(3C)–C(3)–C(2)	118.6(11)	124.4(14)
O(4)–C(3)–C(2)	115.3(9)	114.4(9)
C(3)–O(4)–C(5)	117.2(9)	114.6(10)
C(7)–C(6)–C(1)	126.8(10)	125.8(11)

Trinuclear clusters bearing a parallel acetylene are quite common in alkyne-cluster chemistry; in a relatively recent review [21] we could report 59 X-ray structural determinations for such complexes. In more recent times at least other 25 structural determinations have been reported. The clusters with parallel alkynes may be divided in “sub-classes” as follows: (i) triangular clusters without bridging ligands, (ii) triangular clusters with bridging hydrides [22], (iii) triangular clusters with bridging CO’s, (iv) triangular clusters with CO and other bridging groups, (v) triangular clusters with $\mu\text{-PPH}_2$ bridges, (vi) open triangular clusters and (vii) polynuclear clusters with alkynes bound parallel on triangular faces.

Among these sub-classes, that of the clusters with two bridging hydrides is one of the more represented, with at least 18 structure determinations (13 of ruthenium-based clusters). These structures are apparently quite “rigid”, that is they do not differ very much in the bonding parameters and in the position of the hydrides with respect to the organic moiety. Therefore, the interest for complex **1** is mostly due to its significance in the organometallic-mediated stoichiometric syntheses reported in this work.

4. Conclusions

The main product of the reaction reported in this work is complex **1**. Its formation occurs through a complex reaction pattern involving several steps, that is: loss of chlorine and oxidative addition of the alkyne with shift of hydrogen and of the multiple bonds to form a ene-yne ligand, addition of a CO to the organic moiety, attack and splitting of methanol into CH_3O to form the $\text{C}(\text{=O})\text{OCH}_3$ acetyl group and H (to form, presumably, one of the hydrido ligands).

Under the modellistic profile [23] it is of interest a comparison of the above reactions with the methylene-to-acetyl conversion observed on dppm-bridged heteronuclear Rh/Os complexes using $\text{CF}_3\text{SO}_3\text{H}$ as a protonating agent and involving the insertion of a coordinated CO into the M–C bond; these reactions have been considered models for the oxygenate formation by bimetallic Fischer–Tropsch catalysts [24].

As discussed above, there are literature examples for the formation of $\text{C}(\text{=O})\text{OR}$ groups coordinated to metals. The reactivity observed for $\text{M}_3(\text{CO})_{12}$ clusters ($\text{M} = \text{Fe}, \text{Ru}$) in $\text{CH}_3\text{OH}/\text{KOH}$ solution indicates that activation of CO and methanol is a general trend which could be exploited in metal promoted stoichiometric organic syntheses.

Thus, the reaction reported here represents a further example of the wide potential of alkyne-cluster chemistry under basic methanolic conditions.

Acknowledgements

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