

Reaction of $\text{Ru}_3(\text{CO})_{12}$ with but-2-yn-1,4-diol in $\text{CH}_3\text{OH}/\text{KOH}$ solution. Crystal structure of $(\mu\text{-Cl})\text{Ru}_3(\text{CO})_9[\mu_3\text{-}\eta^4\text{-H}_2\text{CCC}(\text{H})\text{CH}_2]$

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Received 29 May 2003; accepted 18 September 2003

Abstract

The reaction of $\text{Ru}_3(\text{CO})_{12}$ with but-2-yn-1,4-diol ($\text{HOCH}_2\text{C}\equiv\text{CCH}_2\text{OH}$, BUD) in $\text{CH}_3\text{OH}/\text{KOH}$ followed by acidification with HCl leads to four products, one of which has been identified as the title complex $(\mu\text{-Cl})\text{Ru}_3(\text{CO})_9[\mu_3\text{-}\eta^4\text{-H}_2\text{CCC}(\text{H})\text{CH}_2]$. This is an open cluster containing a bridging Cl atom on the open side and a C_4H_5 moiety bound to all the metals. The structure of the complex has been determined by X-ray analysis.

The thermal reaction of $\text{Ru}_3(\text{CO})_{12}$ with BUD has been revisited for a comparison with the results in alkaline solution. The main product is the allylic derivative $\text{HRu}_3(\text{CO})_9[\text{HCCHCCHO}]$.

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Keywords: Alkyne-diols; Ruthenium carbonyl clusters; Hydrochloric acid; Dehydration and dehydroxylation reactions; Crystal structure

1. Introduction

We are synthesizing inorganic–organometallic materials by including alkynols or alkyne-diols into SiO_2 -based materials obtained through sol–gel procedures [1] and reacting these solids with $\text{Ru}_3(\text{CO})_{12}$ or other metal carbonyls. In order to characterize spectroscopically the materials, we are also synthesizing *models* of the alkyne–cluster interactions [2]. We are hence reacting alkynols and alkyne-diols with $\text{Ru}_3(\text{CO})_{12}$ in basic methanolic solutions, that is in conditions comparable with those occurring on silica surfaces where formation of cluster anions is likely to occur [3].

The reaction of $\text{Ru}_3(\text{CO})_{12}$ with BUD in $\text{CH}_3\text{OH}/\text{KOH}$ solution and subsequent acidification with HCl leads to four products, one of which is the title complex $(\mu\text{-Cl})\text{Ru}_3(\text{CO})_9[\mu_3\text{-}\eta^4\text{-H}_2\text{CCC}(\text{H})\text{CH}_2]$; this is an open Ru_3 cluster with a $\mu\text{-Cl}$ atom bridging the open side and a C_4H_5 ligand bound to all the metal atoms. Its structure has been determined using X-ray diffraction analysis. Hypotheses on its formation are discussed.

The thermal reaction of $\text{Ru}_3(\text{CO})_{12}$ with BUD has been revisited. The main product is the allylic cluster $(\mu\text{-H})\text{Ru}_3(\text{CO})_9[\text{HCCHCCHO}]$. The behaviour of BUD in alkaline and thermal conditions is compared with that of other alkynols used for forming inorganic–organometallic sol–gel systems.

2. Experimental

2.1. General experimental details. Analysis of the products

$\text{Ru}_3(\text{CO})_{12}$ (Strem Chemicals) and BUD (Lancaster Synthesis) were used as received; methanol, KOH (pellets) and HCl (concentrated, 37%) were laboratory grade chemicals. Solvents (heptane, toluene) were dehydrated over sodium. The reactions were performed under dry nitrogen in conventional three necked flasks equipped with gas inlet, cooler, mercury check valve and magnetic stirring.

The $\text{CH}_3\text{OH}/\text{KOH}$ solutions, after acidification to $\text{pH}=1$, were extracted with heptane: the extracts were brought to small volume under vacuum and

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chromatographed on t.l.c. plates (Merck Kieselgel P.F., eluent mixtures of hexane and diethyl ether in 90/10 v/v ratio). The reaction mixtures from the thermal reactions were filtered under N₂, brought to small volume under vacuum and chromatographed on t.l.c. plates.

Elemental analyses were performed in the laboratories of the DiSTA (Università del Piemonte Orientale). The IR spectra were obtained on a Bruker Vector 22 (KBr cells, 0.5 mm path length). The ¹H NMR spectra were obtained on a JEOL GX 270 spectrometer. 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 in alkaline solution

In a typical reaction, 10–12 pellets of solid KOH (1.0 g ca) were added to cold methanol (100 ml): the solution was stirred for 5 min under N₂, then 0.5 g (1.65 mmol) of Ru₃(CO)₁₂ were added and the solution was warmed at 40 °C for 30 min. The colour changed from deep red to very deep brown. Solid BUD (10 pellets, 0.5 g ca, 5.8 mmol) was then added and warming was continued for 30 min. After cooling, the solution was acidified with concentrated aqueous HCl; an abundant whitish precipitate (KCl) was formed. This was filtered and the aqueous-methanolic solution extracted with heptane/benzene (90/10 v/v). The extract was purified on preparative t.l.c. plates; the following bands were collected; yellow **1** (5% ca), dark yellow **2** (10% ca), yellow **3** (20%) and deep yellow **4** (10%).

2.3. Complex 1

IR (heptane): 2080 s, 2066 vs, 2055 s, 2023 s, 1971 m-s, cm⁻¹. E.I. mass spectrum: P⁺ = 748, loss of 12 CO, intense peak at a 406 (Ru₄). Identification H₄Ru₄(CO)₁₂ (comparison with a known sample).

2.4. Complex 2

Calc: C 24.15, Cl 5.40, H 0.77. Found: C 24.3, Cl 5.3, H 0.8. IR (heptane): 2097 m, 2076 vs, 2044 vs, 2015 s, 1994 m-s, 1721 m-s, cm⁻¹. ¹H NMR (CDCl₃, r.t.): δ 4.13 (s, 1H), 4.07 (d, 1H, *J* = 2.08 Hz), 3.46 (s, 1H), 3.18 (t, 1H, *J* = 2.20 Hz, *J* = 2.20 Hz), 2.50 (d, 1H, *J* = 3.54 Hz). E.I. mass spectrum: decomposition.

2.5. Complex 3

Calc: C 24.88, H 0.79. Found: C 25.0, H 0.8. IR (CH₂Cl₂): 2106 m, 2081 vs, 2054 vs, 2023 vs(b), 1687 w, 1606 m-s, cm⁻¹. ¹H NMR (CDCl₃, r.t.): δ 9.98 (s, 1H), 8.64 (d, 1H), 7.75 (t, 1H, *J* = 0.8 Hz, *J* = 0.8 Hz), -20.86 (d, 1H: *J* = 0.5 Hz). E.I. mass spectrum: P⁺ = 626 *m/z*,

release of 10 CO, intense peak at 342 *m/z* (Ru₃C₃). Identification HRu₃(CO)₉[HCCHCCHO].

2.6. Complex 4

IR (CH₂Cl₂): 2096 m, 2068 vs, 2045 vs, 2028 vs, 2010 s(sh), 1605 m, cm⁻¹. ¹H NMR; 9.80 (s, 1H), 6.20(s, 1H). E.I. mass spectrum: P⁺ = 652 ca, apparent release of 12 fragments with 26–28 *m/z*. Tentatively identified as Ru₃(CO)₉(μ-CO)[C=C=C(H)(CHO)].

2.7. Reactions under thermal conditions

In a typical reaction 1.0 g of Ru₃(CO)₁₂ (3.2 mmol) and about 10 pellets of BUD (0.5 g ca, 5.8 mmol) were suspended in heptane, under N₂: BUD is very sparingly soluble in hydrocarbons and a vigorous agitation is needed. The suspension was brought to reflux and allowed to react for 6 min. A great amount of a brown precipitate was formed on the walls of the reaction vessel [this is nearly insoluble in all the organic solvents available: it is presumably a polymeric derivative]. t.l.c. separation showed the presence of the following bands: yellow (10%, **5**), purple (3%, unidentified), yellow (10%, **6**) and yellow-orange (30%, complex **3**) and decomposition. Similar results are obtained using toluene as a solvent for 3 min reflux.

2.8. Complex 5

IR (CH₂Cl₂): 2080 vs, 2053 vs, 2021 s(b) cm⁻¹. ¹H NMR; 5.60 (d, 2H: *J* = 2.5 Hz), 5.30 (d, 2H: *J* = 2.6 Hz), 3.25 (s,b, 2H,OH?). E.I. mass spectrum: P⁺ = 532, loss of 6 CO. Identification Ru₂(CO)₆(BUD)₂, ferrole.

2.9. Complex 6

Found: C 24.9, H 0.8. IR (heptane): 2110 w, 2087 m-s, 2045 vs, 2013 vs, 1998 s(sh), 1606 m, cm⁻¹. ¹H NMR; 9.99 (s, 1H), 8.65 (s, 1H), 2.35 (dd, 2H; *J* = 1.5 Hz, *J* = 1.6 Hz). E.I. mass spectrum: P⁺ = 440, release of 7 CO, intense peak at 240 *m/z* (Ru₂C₃).

2.10. Crystallography

The data collection was made on a Siemens P4 diffractometer equipped with a Bruker APEX CCD detector using graphite-monochromated Mo K α radiation (λ = 0.71073 Å). The complex **2** C₁₃H₅ClO₉Ru₃ crystallizes in triclinic P-1 space group, with *a* = 8.7098(7) Å, *b* = 9.8476(9) Å, *c* = 11.140(1) Å, α = 81.205(2)°, β = 76.824(2)°, γ = 83.951(2)°, *V* = 916.9(1) Å³, *M* = 643.83, *Z* = 2, *D_c* = 2.33 g cm⁻³, μ = 2.627 mm⁻¹. The red crystal used was prismatic of dimensions 0.06 × 0.20 × 0.22 mm. The θ range for measurement was 1.89–28.24°, 6677 reflections were measured at 293 K and 4197

were unique ($R_{\text{int}} = 0.027$). The intensities were corrected semi-empirically for absorption, based on symmetry equivalent reflections. The refinement of 250 parameters was made using full-matrix least-squares on F^2 . All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located on the last difference Fourier maps and were refined with U_{iso} 's set at 1.2 times U_{eq} of the corresponding C atom. The final parameters were: $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.0369$ for 3130 "observed" reflections having $F_o^2 > 2\sigma(F_o^2)$, $R_w = [\sum (wF_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2} = 0.0803$, Goodness-of-fit = $[\sum w(F_o^2 - F_c^2)^2 / (\text{no. of unique reflections} - \text{no. of parameters})]^{1/2} = 0.868$. Programs used were SHELXTL [4] for structure solution, refinement and molecular graphics, Bruker AXS SMART (diffractometer control), SAINT (integration), SADABS (absorption correction) [5].

3. Results and discussion

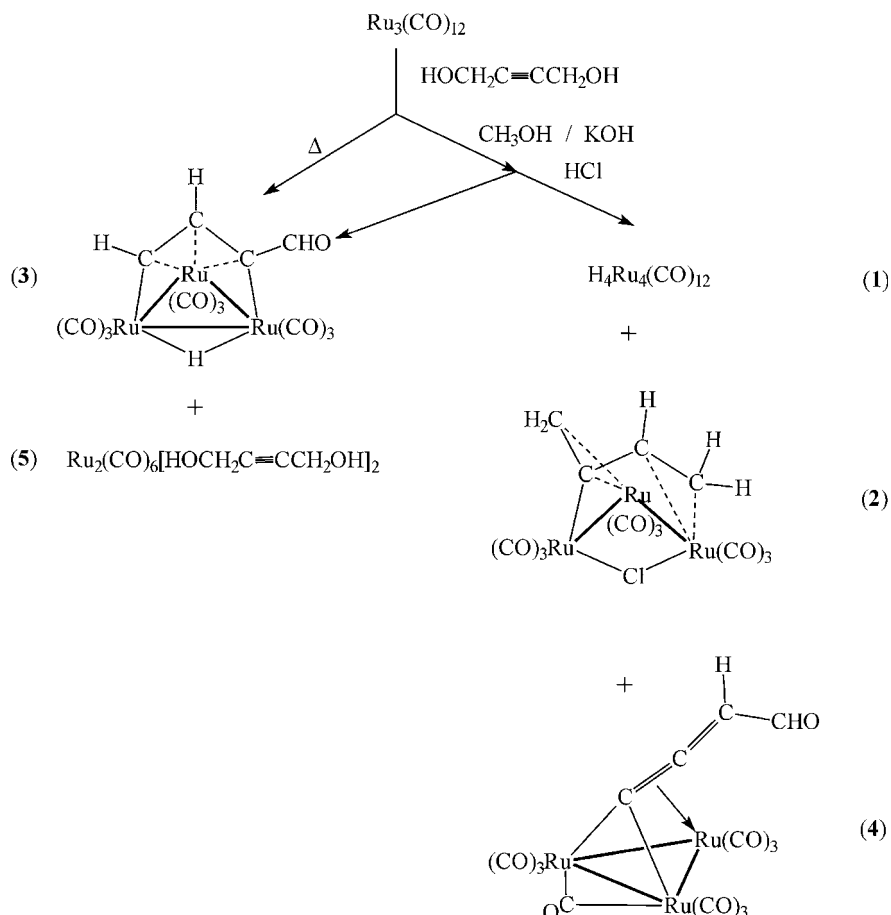
The reaction of $\text{Ru}_3(\text{CO})_{12}$ with BUD under basic conditions leads – after acidification with HCl – to $\text{H}_4\text{Ru}_4(\text{CO})_{12}$, to complex $(\mu\text{-Cl})\text{Ru}_3(\text{CO})_9[\mu_3\text{-}\eta^4\text{-}$

$\text{H}_2\text{CCC}(\text{H})\text{CH}_2]$ (**2**) and to the allylic $\text{HRu}_3(\text{CO})_9[\text{HCCHCCHO}]$ (**3**): complex **3** is also the major product of the reaction of $\text{Ru}_3(\text{CO})_{12}$ with BUD under thermal conditions (see Scheme 1). Hypotheses on the reaction pathways leading to these complexes are discussed below.

3.1. X-ray structure of complex **2**

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

The complex is an open cluster of three ruthenium atoms [$\text{Ru}(1)\text{--Ru}(2)$ 2.9675(6), $\text{Ru}(2)\text{--Ru}(3)$ 2.7544(5), $\text{Ru}(1)\cdots\text{Ru}(3)$ 3.7163(6) Å] to which a chlorine atom bridging the open $\text{Ru}(1)\text{--Ru}(3)$ edge is bound: the $\text{Ru}\text{--Cl}$ distances are $\text{Ru}(1)\text{--Cl}$ 2.435(1) Å; $\text{Ru}(3)\text{--Cl}$ 2.482(1) Å. Three terminal carbonyls are bound to each ruthenium atom; in the $(\text{CO})_3$ groups bound to $\text{Ru}(1)$ and $\text{Ru}(3)$ the $\text{Ru}\text{--C}_{\text{CO}}$ bond distances *trans* to Cl ligand are the shortest; in addition, two carbonyls deviate significantly from linearity ($\text{O}(13)\text{--C}(13)\text{--Ru}(1)$ 174.2(5)°, $\text{O}(23)\text{--C}(23)\text{--Ru}(2)$ 175.2(4)°). The four-carbon-atom organic moiety is bound to $\text{Ru}(1)$ *via* the $\text{C}(1)\text{--C}(2)$ bond $\{\text{H}_2\text{C}(1)\text{--C}(2)(\text{H})\}$ to $\text{Ru}(2)$ *via* $\text{C}(3)\text{--C}(4)$ $\{\text{C}(3)\text{--}$



Scheme 1.

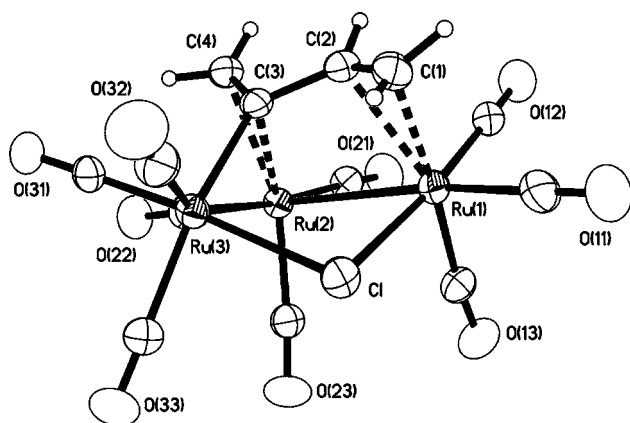


Fig. 1. ORTEP plot (30%) of complex $(\mu\text{-Cl})\text{Ru}_3(\text{CO})_9[\mu_3\text{-}\eta^4\text{-H}_2\text{CCC}(\text{H})\text{CH}_2]$ (**2**).

Table 1
Selected bond lengths (Å) and angles (°) for complex **2**

Ru(1)–C(12)	1.881(6)
Ru(1)–C(13)	1.911(5)
Ru(1)–C(11)	1.931(6)
Ru(1)–C(1)	2.257(5)
Ru(1)–C(2)	2.308(4)
Ru(1)–Cl	2.4354(13)
Ru(1)–Ru(2)	2.9675(6)
Ru(2)–C(22)	1.882(5)
Ru(2)–C(23)	1.909(5)
Ru(2)–C(21)	1.925(5)
Ru(2)–C(3)	2.211(4)
Ru(2)–C(4)	2.283(5)
Ru(2)–Ru(3)	2.7544(5)
Ru(3)–C(31)	1.848(6)
Ru(3)–C(32)	1.914(5)
Ru(3)–C(33)	1.977(5)
Ru(3)–C(3)	2.089(4)
Ru(3)–Cl	2.4821(13)
C(1)–C(2)	1.388(7)
C(2)–C(3)	1.454(6)
C(3)–C(4)	1.409(7)
Ru(3)–Ru(2)–Ru(1)	80.903(15)
Ru(1)–Cl–Ru(3)	98.16(4)
C(1)–C(2)–C(3)	127.5(5)
C(4)–C(3)–C(2)	112.2(4)
C(4)–C(3)–Ru(3)	120.9(3)
C(2)–C(3)–Ru(3)	126.0(4)

C(4)H₂} and to Ru(3) *via* C(3). The C(1)–C(2) [1.388(7) Å] and C(3)–C(4) [1.409(7) Å] bonds have formally a feature of elongated double bonds, whereas the former C≡C alkyne bond [C(2)–C(3) 1.454(6) Å] is close to a single bond between two formal sp² C atoms. Hence, the dehydroxylation of the BUD ligand has resulted in the formation of a “dienic” ligand in the place of the original internal alkyne.

This “dienic” ligand is bound to the cluster metals partly through π interactions, as shown by the Ru–C distances [Ru(1)–C(1) 2.257(5) Å, Ru(1)–C(2) 2.308(4)

Å; Ru(2)–C(3) 2.211(4) Å; Ru(2)–C(4) 2.283(5) Å]; the small value of the Ru(3)–C(3) distance [2.089(4) Å], the planarity of the Ru(3)C(2)C(3)C(4) moiety (mean deviation from planarity 0.032 Å) and the angles around C(3) allow to describe the Ru(3)–C(3) bond as a σ interaction. When considering the organic moiety as a 5 electron donor and the chlorine as a 3 electron donor, a total count of 50 electrons is obtained, in agreement with an *open* Ru₃ cluster.

3.2. The $\mu\text{-Cl}$ bridge. A comparison between **2** and the isomeric complex **7** ($\mu\text{-Cl}$)Ru₃(CO)₉($\mu_3\text{-}\eta^3\text{-MeC}_2\text{CH}_2$)

Triruthenium clusters containing $\mu\text{-Cl}$ bridges on open or closed Ru–Ru edges are known: most of them contain also other bridging ligands such as chlorine [6], sulphur [7], hydrogen [8], oxygen [9], phosphines [10] or phosphido groups [11], $\mu\text{-OH}$ [12] and $\mu\text{-AuL}$ [13]. In addition a number of homo- [14] and hetero-nuclear [15] tetrametallic complexes are known. Finally, pentanuclear [16] and more complex structures [17] such as Os₅(CO)₁₈(CNBu^t)₂Cl₂ (with *terminal* chlorines) [18] have been reported. Other reactions of Ru₃(CO)₁₂ with Cl[−] are known: these lead to different products, ranging from the [Ru₃(CO)₁₁Cl][−] anion [19] to binuclear [20] and cluster complexes [21] containing also organic moieties. Most of the above reactions occur under basic conditions and through metal carbonyl anions.

Chlorine-bridged triruthenium clusters containing hydrocarbyl ligands are not very common: one example is $(\mu\text{-Cl})\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}\equiv\text{CPh})$, an open cluster with a perpendicular acetylide obtained upon thermal activation of the C–Cl bond of PhC≡CCl [22]. Another example is the open cluster $(\mu\text{-Cl})\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}_2\text{Ph}_2)$ with a parallel alkyne, obtained using *halide promoted reactions*, that is starting from the cluster anion [Ru₃($\mu\text{-Cl}$)(CO)₁₀][−] already containing a chlorine bridge [23]. Using this method the synthesis of propargylic, allenyl and butatriene triruthenium complexes has been achieved. Among others, the allenyl $(\mu\text{-Cl})\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^3\text{-MeC}_2\text{CH}_2)$ complex (**7**) was obtained [24] and its structure studied by X-ray diffraction. The complex was obtained by reacting the tosyloxy alkyne MeC≡CCH₂OTs with [Ru₃($\mu\text{-Cl}$)(CO)₁₀][−]; interestingly its formula is *isomeric* with that of cluster **2**. The structures of the two complexes are compared in Fig. 2. The main differences involve the bonding and non-bonding Ru–Ru distances, owing to the different coordination of the organic ligand: the Ru₃ cluster in the allenyl compound, where only three carbon atoms interacts with metals, is smaller than in the butadienylic complex **2**, where a chain of four atoms is involved in the coordination to Ru₃. In complex **2** the chlorine atom is below the Ru₃ plane on the opposite side with respect to the organic ligand, while in the allenyl complex the chlorine atom is on the Ru₃ plane. These features con-

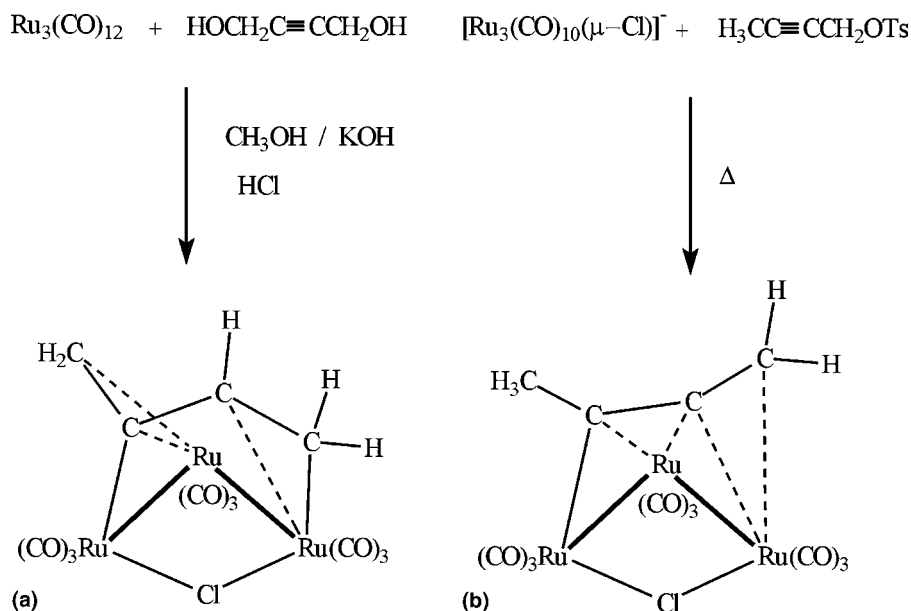


Fig. 2. The two isomers: (a) complex **2** $(\mu\text{-Cl})\text{Ru}_3(\text{CO})_9[\mu_3\text{-}\eta^4\text{-H}_2\text{CCC}(\text{H})\text{CH}_2]$, (b) complex **7** $(\mu\text{-Cl})\text{Ru}_3(\text{CO})_9[\mu_3\text{-}\eta^3\text{-MeC}_2\text{CH}_2]$ [24].

firm once more the great adaptability of the metal–metal bonds and the great influence of the organic ligands on the position of the bridging ligands.

A search in Cambridge Structural Databank (CSD) (release November 2002)[25] shows 36 clusters [26] containing one or more chlorine bridges over *open* or *closed* ruthenium clusters. The histogram (Fig. 3) reporting the 56 values of the Cl-bridged Ru–Ru bond distances shows a wide range of values from 2.758 to 3.680 Å (3.716 Å in complex **2**), with no significant maximum and with no interruption between the Ru–Ru

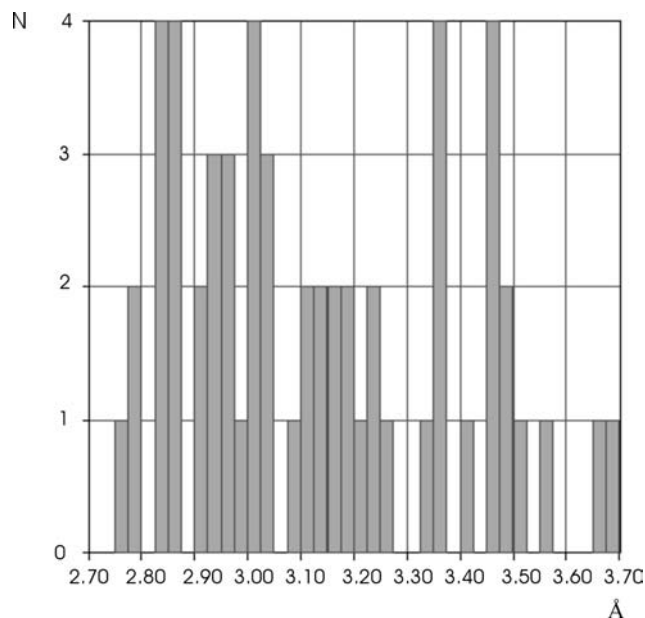


Fig. 3. Histogram reporting the number of structures (N) versus $(\mu\text{-Cl})\text{Ru}\text{-Ru}$ distance (Å).

bonds considered *closed* and *open* (around 3.10 Å). Normally the existence or not of a direct Ru–Ru bond is attributed on the basis of electron count (48 and 50 electrons for a *closed* or *open* cluster, respectively) and around the value of 3.10 Å both situations may overlap. This smoothing trend is due probably to the great variety of geometries of the complexes, always containing also other bridging ligands of various nature.

An analogous research on the values of Ru–Cl bond distances shows mostly a range between 2.40 and 2.50 Å with some values shorter (2.31–2.36 Å) and longer (2.51–2.59 Å).

3.3. Crystal packing

The molecules related by inversion centres are packed on one side *via* Cl···Cl van der Waals interactions (3.59 Å) and on the other side *via* weak O···H bonds (H(2)···O(21) 2.71 Å, C–H···O 160°, and H(4A)···O(21) 2.77 Å, C–H···O 150°) [27]. The short Cl···Cl contact give rise also to a short Cl···O(33) contact (3.43 Å). These interactions generate a chain of molecules oriented along the $[\bar{1}\bar{1}\bar{1}]$ direction. The chains are then linked mainly through O···O bonds and via H(1B)···O(33) interaction (2.81 Å, C–H···O 102°). Among the ruthenium complexes containing bridging chlorine, only $(\mu\text{-Cl})\text{Ru}_3(\text{CO})_9[\mu\text{-AuPH}(\text{Bu}^t)_2]$ [15] contains a short intermolecular Cl···Cl contact (3.475 Å).

3.4. The dehydroxylation of BUD and the synthesis of complex **2**

Cluster **2** is obtained upon loss of two OH from BUD and addition of HCl. Direct (and reversible) HCl

addition has been evidenced for mononuclear [28] and cluster [29] osmium derivatives. However, the more interesting reaction – for this discussion – is the addition of aqueous HCl to a C=CH₂ vinylidene ligand bound to a penta-ruthenium cluster to give a μ -Cl bridge and a μ_3 -CCH₃ [16].

In the case of **2** the addition of HCl or of Cl⁻ may occur only upon acidification with HCl. It is therefore presumable that the first reaction step is the formation (in KOH/CH₃OH solution) of the known anion [HRu₃(CO)₁₁]⁻ [30] which reacts easily with alkynes. The anion could give migratory insertion of BUD into the Ru–H bond; the loss of the OH groups would then occur to form water using the anionic hydride or in a second moment, in the presence of H⁺ from HCl. The latter could then react with the resulting cluster as previously discussed. It has also been shown that alkynols, under protonating conditions undergo dehydration, a well known reaction [3]: the formation of **4**, tentatively identified as the allenylidene derivative Ru₃(CO)₉(μ -CO)[C=C=C=(H)(CHO)] would indicate that this reaction also occurs.

Reactions of alkyne diols with clusters, under thermal conditions are known. In particular BUD reacts with H₂Os₃(CO)₁₀; the ligand coordinates first in parallel way to give Os₃(CO)₉(μ -CO)(HOCH₂C₂CH₂OH) then undergoes loss of CO and of water to form the hydridic allenyl (μ -H)Os₃(CO)₉[(CHO)C=C=CH₂] and allyl (μ -H)Os₃(CO)₉[(CHO)CC(H)C(H)] derivatives [31]. As further discussed below, Ru₃(CO)₁₂ behaves in the same way. The related alkyne HC≡CCH₂CH₂OH reacts with Os₃(CO)₁₀(MeCN)₂ to form a complex containing a parallel alkynol which isomerizes to an hydrido-acetylide derivative; prolonged thermolysis of the latter derivative results in a migration of the OH hydrogen on a cluster edge and cyclization of the ligand to form a cluster bound furfuryne coordinated in parallel way [32]. The same heterocycle, coordinated again in parallel fashion is obtained under forcing conditions when reacting BUD with a cyclopentadienyl tricobalt cluster [33].

The formation of **2** requires the formal double loss of OH. Examples of dehydroxylation of cluster bound alkynols are known: one of them occurs – for triruthenium derivatives – in basic methanolic solution [34]. To our knowledge, however, the double loss of OH observed in this reaction is unprecedented.

3.5. Characterization of other reaction products. Thermal reaction of Ru₃(CO)₁₂ with BUD

H₄Ru₄(CO)₁₂ has also been obtained from the reactions of the ruthenium carbonyl with BUD in methanolic solution. It has been identified by IR spectrophotometry and mass spectrometry. Its presence indicates that, besides the dehydroxylation and dehydration reactions,

also formation and recombination of metal fragments occurs; this is probably the result of the protonation of [HRu₃(CO)₁₁]⁻ not concerning BUD.

In methanolic solution, two other products were obtained: one of which, complex **4** has been tentatively identified as the allenylidene Ru₃(CO)₉(μ -CO)[C=C=C=(H)(CHO)] resulting from dehydration of coordinated BUD: the other one (complex **3**) has been identified (through IR and ¹H spectroscopies and mass spectrometry) as the allylic HRu₃(CO)₉[HCCHCHO].

Complex **3** also is obtained upon dehydration of BUD, a well known process. It is the main product of the thermal reaction of Ru₃(CO)₁₂ with BUD. This reaction had been reported by Deeming and coworkers [31]: we have revisited it in order to compare the results with those obtained under basic conditions. We could characterize the ferrole-like Ru₂(CO)₆(BUD)₂: in addition, we obtained complex **6** whose analytical and spectroscopic data would agree with the formulation as the allenyl derivative (μ -H)Ru₃(CO)₉[H₂C=C=C(H)CHO]: however, the mass spectrum gives a “parent ion” at 440 *m/z* corresponding to the formula Ru₂(CO)₇(C₃H₄) indicating that decomposition occurs. Thus, the identification of complex **6** is not certain: attempts at obtaining X-ray grade crystals are in progress.

3.6. A comparison with the behaviour of other functionalized alkynes

In the reactions of BUD with Ru₃(CO)₁₂ both under alkaline and under thermal conditions, products containing organic moieties which have totally (e.g., complex **2**) or partially (e.g., complex **3**) lost the OH functionalities were obtained. The same is observed for the MeC≡CCH₂OTs alkyne during the formation of complex **7**. We have recently reported the reactions of diethylamino-propyne [HC≡CCH₂NEt₂, DAP] with Ru₃(CO)₁₂ under thermal conditions and those of trimethylsilyl propargyl alcohol [(HO)CH₂C≡C(SiMe₃), TSPA] with Ru₃(CO)₁₂ both under thermal and under alkalyne conditions [35]. From these reactions – among others – the allylic derivatives (μ -H)Ru₃(CO)₉[HCCHCH] (**8**) and (μ -H)Ru₃(CO)₉[HCCHC(CH₂OH)] (**9**) were obtained: these correspond, once again to the total or partial loss of the functionalities of the alkyne ligands.

4. Conclusions

When considering the results obtained in this work or reported in the literature [24,34] one is allowed to think that the loss of the functionalities of the alkynes, especially in the reactions with KOH/CH₃OH (followed by acidification) is a general trend. Protonation reactions would be responsible of the observed results. In account

of the present observations, one may reasonably expect that the OH functionalities of the cluster-bound alkynes might be lost during the cluster incorporation into silica. However, loss of water and OH was expected, and has been found, when BUD alone was reacted with tetraethoxysilane [36].

The attempts at obtaining clusters modelling the surface-alkyne–metal carbonyl interactions have lead, in the case of BUD to the unexpected new complex **2**: it is obtained upon loss of two OH from the parent ligand and formal addition of HCl. Both processes have already been reported in the literature, but this is – to our knowledge – the first example for them occurring during the same reaction. Thus, the combination of two known reaction pathways may lead to a new structure isomeric with that of the recently reported complex **7**. This behaviour indicates that there are still many aspects of the chemistry of akynols towards clusters to be discovered.

Acknowledgements

Financial support to this work was obtained from MIUR (Rome) and Università del Piemonte Orientale under the Cofin 2000 programme.

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