

Reactions of $\text{Ru}_3(\text{CO})_{12}$ with 2-pentynal-diethyl-acetal. The crystal structure of $\text{Ru}_2(\text{CO})_6[\mu-\eta^4-\{\text{EtC}_2\text{C}(\text{H})(\text{OEt})_2\}\text{CO}\{\text{EtC}_2\text{C}(\text{H})(\text{OEt})_2\}]$ and its reactivity towards tetraethyl-orthosilicate

Giuliana Gervasio ^{a,*}, Domenica Marabello ^a, Enrico Sappa ^{*,b}, Andrea Secco ^b

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

^b Dipartimento di Scienze e Tecnologie Avanzate, Università del Piemonte Orientale, Spalto Marengo 33, I-15100 Alessandria, Italy

Received 10 March 2005; received in revised form 27 April 2005; accepted 3 May 2005

Available online 29 June 2005

Abstract

The title compound has been obtained in considerable yield by reacting $\text{Ru}_3(\text{CO})_{12}$ with 2-pentynal-diethyl-acetal [$\text{CH}_3\text{CH}_2\text{C}\equiv\text{C}(\text{H})(\text{OEt})_2$] (PDA) in hydrocarbon solvents. The X-ray analysis shows that the title complex belongs to the well known family of the *flyover* derivatives. Some X-ray structural studies have been reported, many years ago, on di-iron flyover complexes; in contrast only a few examples of diruthenium derivatives have been structurally characterized.

The complex contains ethoxy-groups which could potentially undergo hydrolysis in the presence of tetraethyl-orthosilicate (TEOS) in the presence of catalysts. Reactions of complex $\text{Ru}_2(\text{CO})_6[\mu-\eta^4-\{\text{EtC}_2\text{C}(\text{H})(\text{OEt})_2\}\text{CO}\{\text{EtC}_2\text{C}(\text{H})(\text{OEt})_2\}]$ with TEOS in the presence of HCl or of NaF (as catalysts) have been attempted. An inorganic-organometallic sol-gel material containing the skeleton of the complex has been obtained and characterized with IR-Raman, XRD on powders and SEM microscopy.

© 2005 Elsevier B.V. All rights reserved.

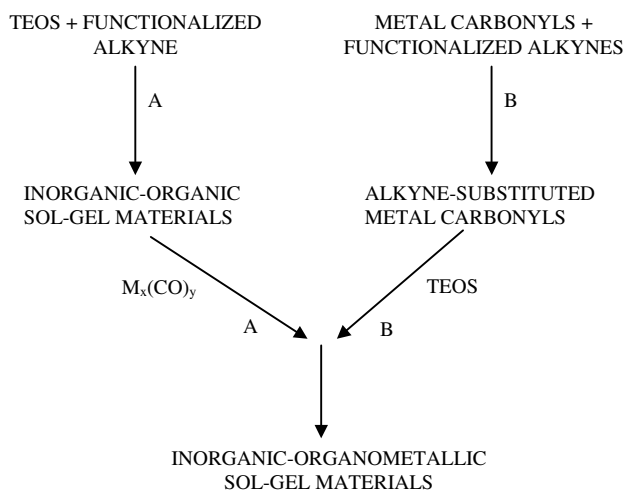
Keywords: Ruthenium flyover complexes; Crystal structure; Sol-gel Inorganic-organometallic materials

1. Introduction

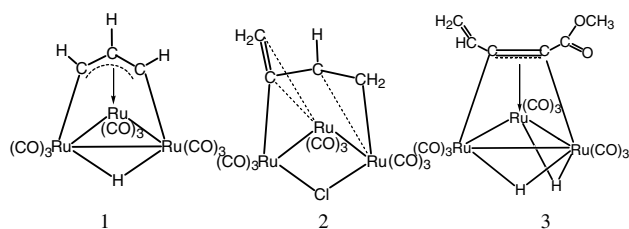
We are attempting the synthesis of inorganic-organometallic materials starting from tetraethoxysilane (TEOS) and alkynes bearing substituents which could participate to the hydrolytic reactions leading to solid hybrid materials. Once obtained, these materials would be reacted with metal carbonyls, which could interact with the alkyne $\text{C}\equiv\text{C}$ bonds and form organometallic systems (reaction pathway **A**). An alternative pathway (**B**) is represented by the synthesis of transition metal carbonyl complexes substituted with functionalized alkynes, to be reacted with TEOS (see Scheme 1).

Since now we have reacted $\text{Ru}_3(\text{CO})_{12}$ with several alkynols, alkyne-diols and chloro-alkynes: in particular, we have explored the reactions with but-2-yn-1,4-diol ($\text{HOCH}_2\text{C}\equiv\text{CCH}_2\text{OH}$, BUD), trimethylsilyl-propargyl alcohol ($\text{Me}_3\text{SiC}\equiv\text{CCH}_2\text{OH}$, TSPA) and 1,4-dichlorobut-2-yne ($\text{ClCH}_2\text{C}\equiv\text{CCH}_2\text{Cl}$, DCB) in $\text{KOH}/\text{CH}_3\text{OH}$ solution (followed by acidification with HCl). The main product of the reactions with TSPA was the allylic complex $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^3\text{-C}_3\text{H}_3)$ (complex **1**) [1] whereas from the reactions of BUD we obtained the butadienylic open cluster $(\mu\text{-Cl})\text{Ru}_3(\text{CO})_9[\mu_3\text{-}\eta^4\text{-H}_2\text{CCC}(\text{H})\text{CH}_2]$ (complex **2**) [2]; finally, when $\text{Ru}_3(\text{CO})_{12}$ was reacted with DCB, the complex $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9[\text{H}_2\text{C}=\text{C}(\text{H})\text{C}\equiv\text{C}(\text{O})\text{OCH}_3]$ (**3**) [3] containing a ene-yne bound in parallel fashion [4] was obtained. The structures found for complexes **1–3** are shown in Scheme 2.

* Corresponding authors. Tel.: +390116707504; fax: +390116707855.
E-mail address: giuliana.gervasio@unito.it (G. Gervasio).



Scheme 1.



Scheme 2.

During the formation of complexes **1**, **2** loss of the alkyne functionalities occurred; in the synthesis of **3** loss of chlorines and activation of CO and CH₃OH to form an acetato group was observed. These alkynes, therefore, cannot be used for the synthetic pathway **B**.

Here, we report on the reactions of Ru₃(CO)₁₂ with 2-pentynal-diethyl-acetal [CH₃CH₂C≡CC(H)(OEt)₂] (PDA) in hydrocarbon solvents. The main product obtained, in high yields, is the title complex (**4**) Ru₂(CO)₆[μ-η⁴-{EtC₂C(H)(OEt)₂}CO{EtC₂C(H)(OEt)₂}]; a minor complex (**5**) has been identified as the ferrole-like Ru₂(CO)₆(PDA)₂.

The reactions of Ru₃(CO)₁₂ with PDA in CH₃OH/KOH solution (followed by acidification with HCl) lead to the dihydride H₂Ru₃(CO)₉(CH₃CH₂C≡CCHO) with a parallel alkyne (complex **6**) and to the allylic, monohydridic HRu₃(CO)₉(HCCHCCH₂CH₃) (complex **7**). As discussed above the reactions under basic conditions result in the partial loss of functionalities.

The structure of complex **4** has been determined by an X-ray study. It belongs to the well known family of binuclear flyover complexes [5]. Only a few derivatives of this type have been reported and structurally characterized for ruthenium. During the synthesis of complex **4** the ligand PDA maintains its functionalities: it was therefore expected that the OEt groups could react with TEOS (especially under acidic or nucleophilic catalysis)

and that complex **4** could represent a good starting material for syntheses following pathway **B**. We have indeed obtained and characterized the expected inorganic-organometallic material.

2. Experimental

2.1. General experimental details, materials, analysis of the products

Ru₃(CO)₁₂ (Strem Chemicals), PDA and TEOS (Lancaster Synthesis) were commercial products and were used as supplied. Solvents were dehydrated over sodium. 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. Hydrocarbon solvents, KOH, HCl and methanol were laboratory grade chemicals supplied by Carlo Erba.

2.2. Analysis of the organometallic compounds

The reaction mixtures from the thermal reactions were filtered under N₂, brought to small volume under reduced pressure and separated on T.L.C. plates (Merck Kieselgel PF, eluent mixtures of hexane and diethyl ether). Elemental analyses were performed using the DiSTA facilities. The IR spectra were obtained on a Bruker Equinox 55 (KBr cell, 0.5 mm path length). The ¹H and ¹³C NMR spectra were obtained with a JEOL JNM 270/89 and a JEOL GX 270 spectrometers. The mass spectra were obtained with a Finnigan-Mat TSQ-700 mass spectrometer (Servizio di Spettrometria di massa, Dipartimento di Scienza e Tecnologia del Farmaco, Università di Torino).

2.3. Analysis of the sol-gel materials

The formation of the materials has been followed by IR-Raman using the following instruments: Bruker Equinox 55 with detectors MCT (working at 77 K) or pyroelectric DTGS (data elaboration through a Opus 4.0 software). The XRD analyses were performed with a ThermoARL (Lausanne) ARL X'TRA instrument (using the Cu Kα radiation). The SEM analyses were performed on a Cambridge Stereoscan S360 instrument equipped with a Oxford Instruments EDS and software Oxford INCA 200 (Dipartimento di Scienze della Terra, Università di Torino).

2.4. Syntheses in hydrocarbon solution

In a typical synthesis 1.2 g (ca. 2 mmol) of ruthenium carbonyl was suspended in heptane under N₂ and 3 cm³ of PDA (ca. 20 mmol) was added. The suspension was brought to reflux and allowed to react for 7 min. The

red-orange suspension was filtered under N_2 and brought to small volume under reduced pressure. T.L.C. yielded two bands: lemon yellow (**4**, 60%), orange yellow (**5**, 5%) and decomposition. Unreacted liquid PDA was collected with **4** and then eliminated.

2.4.1. Complex **4** $Ru_2(CO)_6[\mu-\eta^4-\{EtC_2C(H)(OEt)_2\}-CO\{EtC_2C(H)(OEt)_2\}]$

Found for $Ru_2C_{25}H_{37}O_{11}$: C% 44.2 (44.12), H% 4.8 (4.70) (in parentheses, calculated values). IR (heptane); 2088 m-s, 2059 vs, 2019 vs, 2013 s(sh), 2000 m-s(sh), 1673 m, cm^{-1} . 1H NMR ($CDCl_3$, r.t.): [6] 5.06 t [1H, CH], 4.84 t [1H, CH], 3.90 dddd [2H, CH_2 (OEt)], 3.73 m [5H, Et on C_1], 3.54 m [5H, Et on C_4], 2.96 m [2H, CH_2 (OEt)], 2.40 m [2H, CH_2 (OEt)], 1.75 m [2H, CH_2 (OEt)], 1.20 m [12 H, CH_3 (OEt)]. Some attributions can be reversed. ^{13}C NMR ($CDCl_3$, r.t.): 14.9 m, 15.2 s, 15.3 s*, 20.2 s, 22.5*, 25.6*, 42.6, 60.4*, 67.7 d, 65.4 [CH_3 and CH_2 carbons: * denotes lower intensity, thus, presumably CH_2 signals]; 91.3 s [$C-H$], 102.5 m [ring carbons]; 186.1 [1 CO], 196.3 [1 CO] [equatorial CO's], 1.94.0 dd (4 CO) [axial CO's], 199.8 s (1 CO) [ring CO]. E.I. mass spectrum: P^+ m/z = 712 (weak), loss of two CO, then loss of m/z = 46 [CH_3CH_2OH], loss of one CO, loss of m/z = 42 [CH_3CHO], then loss of 4 CO. Intense doubly charged ions.

2.4.2. Complex **5** $Ru_2(CO)_6[CH(OEt)_2C(Et)-CCH(OEt)_2C(Et)]$

Found for $Ru_2C_{23}H_{32}O_{11}$: C% 44.1 (44.18), H% 5.0 (4.90). IR: 2064 s, 2040 vs, 2026 s, 1998 m-s, cm^{-1} . 1H NMR: 6.01 t [1H, CH], 5.90 t [1H, CH], 4.10 qq [2H, CH_2 (OEt)], 3.90 m [5H, Et], 3.55 [5H, Et], 3.0 qq [2H, CH_2 (OEt)], 2.55 qq [2H, CH_2 (OEt)], 2.10 qq [2H, CH_2 (OEt)], 1.80 tt [6H, CH_3 , (OEt)], 1.34 tt [6H, CH_3 (OEt)]. EI-MS: P^+ = 684 m/z , loss of 76 m/z (Et_2O), loss of a second Et_2O , then release of 6 CO.

2.5. Reaction of $Ru_3(CO)_{12}$ with PDA in CH_3OH/KOH solution

In a typical reaction 20 pellets of KOH (ca. 1.0 g) were dissolved in 150 cm^3 of methanol under N_2 and 1.2 g of $Ru_3(CO)_{12}$ was added: the suspension was stirred and warmed at about 40 °C for 20 min. After this time, 3.0 cm^3 of PDA was added and warming was allowed for 20 min. After cooling the reaction mixture was acidified with HCl (37%) to pH 1. A white precipitate of KCl was deposited. After filtering, the solution (dark yellow) was extracted two times with 75 cm^3 of heptane. The light yellow solution was brought to small volume under reduced pressure: an orange residual of $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$ was filtered off. The solution was chromatographed. The following bands were observed on the t.l.c. plates: light yellow (**6**, 15%), yellow (**7**, 10%) and decomposition.

2.5.1. Complex **6** $H_2Ru_3(CO)_9[EtC_2CHO]$

Found for $Ru_3C_{14}H_8O_{10}$: C% 26.2 (26.17), H% 1.3 (1.25). IR: 2113 w, 2094 m, 2072 s, 2042 vs, 2032 s(sh), 2010 s, 1993 m-s, cm^{-1} . 1H NMR: 9.90 s (1H, CH O), 1.60 s (2H, CH_2), 1.40 dt (3H, CH_3), -16.57 s(b) (1H, hydride), -20.40 s(b) (1H, hydride). EI-MS: P^+ = 658 m/z , loss of 9 CO.

2.5.2. Complex **7** $HRu_3(CO)_9[HCC(H)CET]$

Found for $Ru_3C_{14}H_8O_9$: C% 19.8 (19.08), H% 1.5 (1.41). IR: 2095 w, 2069 vs, 2058 vs, 2045 s(sh), 2023 vs, 1989 m, cm^{-1} . 1H NMR: 2.53 q (2H, CH_2), 1.37 s (1H), 1.28 s (1H), 0.85 s (3H, CH_3). EI-MS: P^+ = 626 m/z , loss of 9 CO.

2.6. Reaction of complex **4** with TEOS

To a solution of 5 cm^3 of TEOS (ca. 2.5 mmol) in 10 cm^3 of water/ethanol (1:1 V/V), 0.75 g of complex **4** (ca. 1 mmol) was added, while stirring at 50 °C under air. The colour of the mixture slowly turned from dark-yellow to brown-yellow. Gelation started to occur after 6 h, while the formation of a yellow-brown coarse powder occurred only after 2 days. The solid material was extracted with heptane: a very pale yellow solution containing only trace amounts of a mixture of $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$ (as shown by the IR spectrum) was obtained. In the IR spectrum of the material after gelation carbonyl absorptions at 2088 m, 2060 vs, 2021 vs(b) and 1761 cm^{-1} typical of **4** were still present in high intensity. The Raman spectrum could not be properly registered because of fluorescence due to the presence of the metal.

The XRD spectrum indicates that the material is amorphous. The SEM results are discussed below.

2.7. Reaction of PDA with TEOS

About 5.0 cm^3 of PDA was reacted with 14.4 cm^3 of TEOS dissolved in about 6.0 cm^3 of water and 6.0 cm^3 of ethanol: 3 cm^3 of an aqueous solution of NaF (0.01 M) was added. The molar ratio PDA/TEOS was 1:2. Gelation started after 1 h and after 1 day a light brown powder was obtained. The IR Raman spectrum [7] showed the following signals: 2972 m, 2931 s, 2876 m-s (PDA ethyls), 2309 w, 2246 m ($C\equiv C$), 1452 m (Si-OC $2H_5$, PDA C-C), 1092 m (Si-OC $2H_5$, Si-O-Si), 882 m (Si-O-C), cm^{-1} .

In the XRD spectrum a broad signal was observed. Again this indicates that the material is amorphous.

2.8. X-ray structural analysis of complex **4**

The reflection data were collected on a Siemens P4 diffractometer equipped with a Bruker APEX CCD detector using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The complex **4** $C_{25}H_{32}O_{11}Ru_2$

crystallizes in orthorhombic $P2_12_12_1$ space group, with $a = 9.686(2)$ Å, $b = 13.797(2)$ Å, $c = 22.147(4)$ Å, $V = 2959.6(10)$ Å³, $M = 710.65$, $Z = 4$, $D_c = 1.598$ g cm⁻³, $\mu = 1.07$ mm⁻¹. The red crystal used was prismatic of dimensions $0.06 \times 0.12 \times 0.14$ mm. The θ range for measurement was 1.89 – 28.24° ; 9907 reflections were measured at 293 K and 5678 were unique ($R_{\text{int}} = 0.056$). The intensities were corrected semi-empirically for absorption, based on symmetry equivalent reflections. The refinement of 343 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: $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.0615$ for 3763 “observed” reflections having $F_o^2 > 2\sigma(F_o^2)$, $R_w = [\sum (wF_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2} = 0.130$, Goodness-of-fit = $[\sum w(F_o^2 - F_c^2)^2 / (\text{no. of unique reflections} - \text{no. of parameters})]^{1/2} = 0.963$. Programs used were SHELXTL [8] for structure solution, refinement and molecular graphics, Bruker AXS SMART (diffractometer control), SAINT (integration), SADABS (absorption correction) [9].

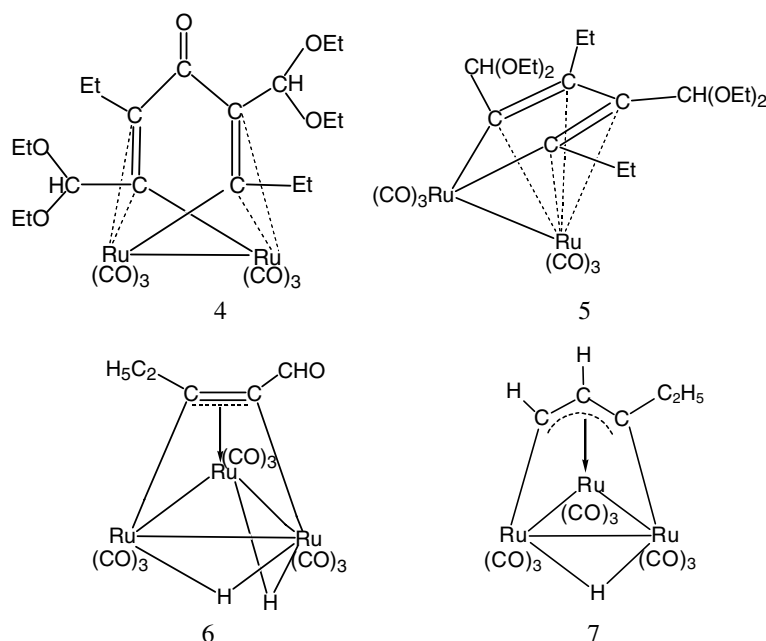
3. Results and discussion

The reactions of $\text{Ru}_3(\text{CO})_{12}$ with PDA under thermal conditions lead to the formation in good yields of complex **4** as the major product and of cluster **5** in smaller amounts. This has been identified as $\text{Ru}_2(\text{CO})_6\text{L}_2$ “ferrole” (L = PDA) [5]; this kind of complexes may exist

in three geometrical isomers. On the basis of the ¹H NMR we propose the isomer shown in Scheme 3. The ferrole-type complexes are among the more common products of the thermal reactions of $\text{M}_3(\text{CO})_{12}$ carbonyls with differently substituted alkynes [5].

The reactions in KOH/CH₃OH (followed by acidification) lead to medium yields of complexes **6** and **7**. Complex **6** has been identified as the dihydride $\text{H}_2\text{Ru}_3(\text{CO})_9(\text{CH}_3\text{CH}_2\text{C}\equiv\text{CCHO})$ with a parallel alkyne; this kind of structural arrangement is quite common for ruthenium–alkyne derivatives [4]. Complex **7** has been identified as the monohydric, allylic $\text{HRu}_3(\text{CO})_9(\text{HCCHCCH}_2\text{CH}_3)$, homologue of complex **1**. These complexes are also well known in alkyne cluster chemistry [10]; for example, the structure of the methyl-substituted homologue has been reported [11]. The structure of complex **4** and the proposed structures for complexes **5**, **6**, **7** are shown in Scheme 3.

The reactions of $\text{Ru}_3(\text{CO})_{12}$ with PDA under basic methanolic conditions lead to complexes **6** and **7**, which contain ligands derived from PDA after loss of part of the functionalities, in particular the EtO groups. Thus, once again, the reactions under basic conditions (where it is probable that anions such as $[\text{HRu}_3(\text{CO})_{11}]^-$ are formed) lead to the loss of functional groups as observed for complexes **1** and **2**. It seems, therefore, that this is a general trend for functionalized alkynes under these reaction conditions. It is also interesting to note that the observed loss of OEt functionalities could indicate that similar behaviour also occurs during the reactions with TEOS discussed below.



Scheme 3.

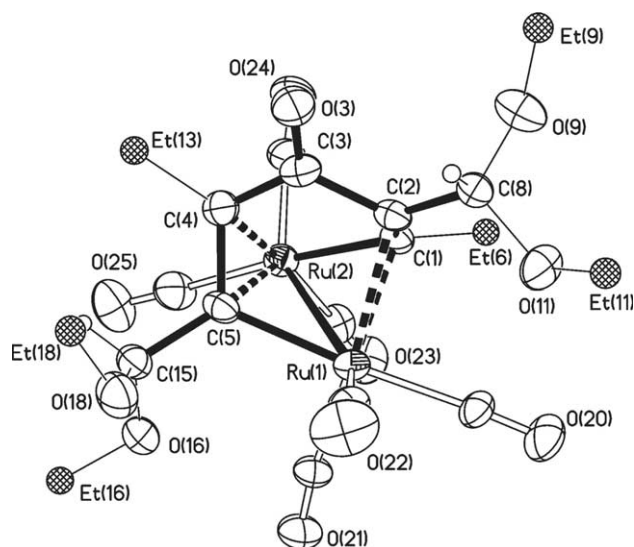


Fig. 1. ORTEP plot of $\text{Ru}_2(\text{CO})_6[\mu-\eta^4\text{-}\{\text{EtC}_2\text{C}(\text{H})(\text{OEt})_2\}\text{CO}\{\text{EtC}_2\text{C}(\text{H})(\text{OEt})_2\}]$ (**4**).

3.1. Synthetic pathways to complex **4**

Flyover complexes homologues of **4** were obtained when $\text{Fe}_3(\text{CO})_{12}$ was reacted under thermal conditions with alkynes; these complexes are formed after relatively long reaction times. In some instances, however, they can be formed when phosphine substitution for CO's on ferrole-like structures $[\text{Fe}_2(\text{CO})_6\{\text{RC}_2\text{R}'\}_2]$ is attempted using Me_3NO as a promoter [12]; further reactions of the flyover complexes with Me_3NO lead to cyclopentenones and quinones. A similar reactivity trend is observed when $\text{Ru}_3(\text{CO})_{12}$ is reacted with PDA in hydrocarbons; the flyover complex **4** is obtained in high yields together with the ferrole complex **5**.

The reactivity of some di-iron flyover derivatives has been studied: for example photochemistry and photocatalysis experiments have been performed for several $\text{Fe}_2(\text{CO})_6[(\text{RC}_2\text{R}')_2(\text{CO})]$ complexes [13] and HPLC separation experiments have been attempted for $\text{Fe}_2(\text{CO})_6[(\text{RC}_2\text{R}')_2(\text{CO})]$ ($\text{R} = \text{R}' = \text{Ph}$, Me ; $\text{R} = \text{Ph}$, $\text{R}' = \text{Me}$) isomers [14].

3.2. The molecular structure of complex **4**

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

Complex **4** shows a flyover structure [5] with an organic moiety formed by two alkyne molecules with a CO inserted: a number of di-iron complexes including structural studies are reported in the literature [15]. There is also a unique example where the organic ligand is formed by three alkynes with an alkyne inserted at the place of CO [16].

Contrasting with iron, there is only a small number of diruthenium-containing flyover complexes whose structures have been studied by X-ray diffractometry:

Table 1
Selected bond lengths (Å) and angles (°) for complex **4**

Ru(1)–Ru(2)	2.7103(12)
Ru(1)–C(1)	2.198(8)
Ru(1)–C(2)	2.288(7)
Ru(1)–C(5)	2.087(10)
Ru(2)–C(1)	2.069(10)
Ru(2)–C(4)	2.257(9)
Ru(2)–C(5)	2.234(9)
C(1)–C(2)	1.410(11)
C(2)–C(3)	1.504(13)
C(3)–O(3)	1.207(9)
C(3)–C(4)	1.496(14)
C(4)–C(5)	1.442(11)
C(2)–C(1)–Ru(2)	116.4(7)
C(4)–C(3)–C(2)	115.5(7)
C(5)–C(4)–C(3)	109.8(8)
C(4)–C(5)–Ru(1)	114.2(7)

$\text{Ru}_2(\text{CO})_6[(\text{C}_2\text{Ph}_2)_2\text{CO}]$ [17] (**4a**), $\text{Ru}_2(\text{CO})_6[\{\text{HC}_2(\text{C}_3\text{H}_7)\}(\text{C}_2\text{Ph}_2)(\text{CO})]$ [18] (**4b**), $\text{Ru}_2(\text{CO})_6[\{\text{C}(\text{C}\equiv\text{CPh})=\text{CPh}\}_2(\text{CO})]$ [19] (**4c**), $\text{Ru}_2(\text{CO})_4(i\text{-Pr-Pyca})[\{\text{C}(\text{C}(\text{O})\text{OMe})=\text{C}(\text{C}(\text{O})\text{OMe})\}_2(\text{CO})]$ (**4d'**) and $\text{Ru}_2(\text{CO})_4(t\text{-Bu-Pyca})[\{\text{C}(\text{C}(\text{O})\text{OMe})=\text{C}(\text{C}(\text{O})\text{OMe})\}_2(\text{CO})]$ [20] (**4d''**) (Pyca = pyridine-2-carbalimine). The main structural parameters of the complexes are closely comparable.

It has also been found that there are some triruthenium structures containing flyover ligands [18]: these do not release ketones, but undergo cluster demolition with loss of metal fragments and of dppm ligands. This indicates a great stability of the binuclear flyover structures: it is therefore presumable that these are still maintained during the reactions with TEOS.

3.3. Reactions of complex **4** with TEOS

Complex **4** has been reacted with TEOS using NaF as a catalyst to favour the hydrolytic reactions leading to sol-gel systems. We have found, indeed, that a sol-gel material is formed. This has been characterized by XRD: the material is amorphous. The SEM analysis indicates that the material is composed of small chips showing a very porous texture: this is of some interest in view of possible catalytic applications. Some examples of the SEM images obtained are shown in Fig. 2.

Extraction of the material with heptane indicated that complex **4** is strongly bound and not only adsorbed into the silica network. The IR spectra also support this hypothesis. Therefore, the above results indicate that complex **4** has undergone condensation with TEOS, forming a sol-gel material (**M-1**) in which the complex is presumably bound as shown in Fig. 3.

The ligand PDA has also been reacted with TEOS under nucleophilic catalytic conditions for comparison. In this case, also, a sol-gel material (**M-2**) derived from the condensation of the PDA ligand and of TEOS is obtained. As for the ruthenium-containing material above, the

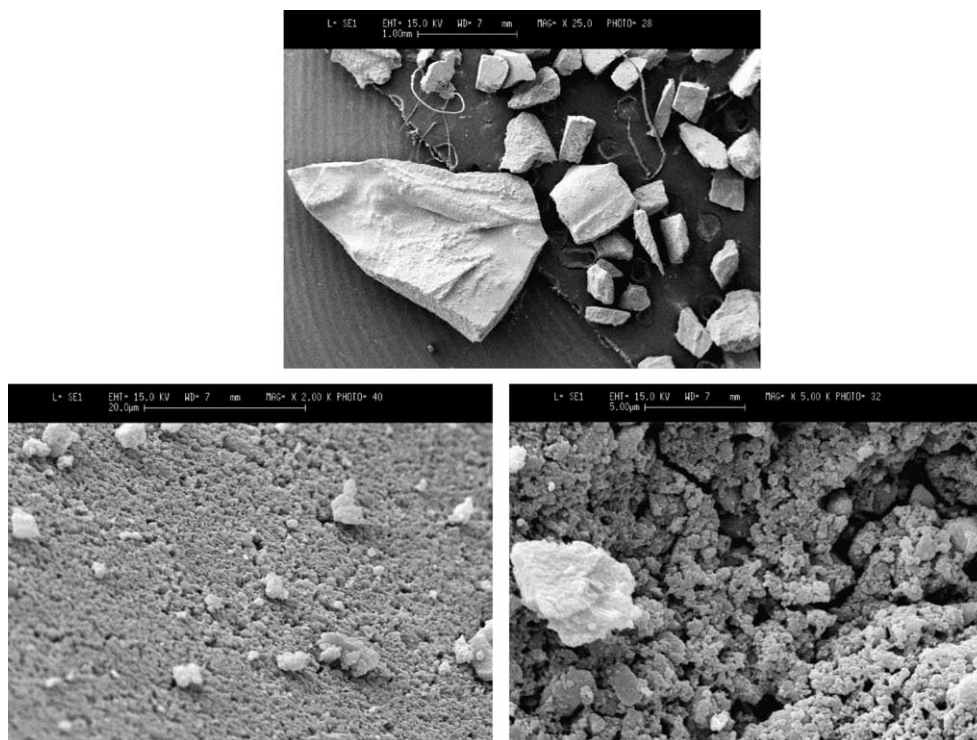


Fig. 2. SEM images (at 25, 2000 and 5000 magnitudes) of the sol-gel material obtained from the reaction of TEOS and Ru₃PDA.

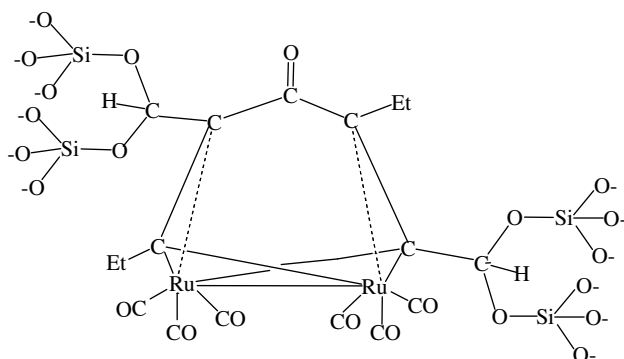


Fig. 3. Proposed structure of the sol-gel material obtained from the reaction of TEOS and Ru₃PDA.

IR-Raman spectra show the presence of Si–O–Si and of Si–O–C bands, indicating that condensation between the (coordinated or) free ligand and tetraethoxysilane has occurred. The IR-Raman signals typical of ethyl groups observed in materials **M-1** and **M-2** are presumably due to the ethyl (rather than to the ethoxy) groups of the ligand PDA. In addition, the spectroscopic results for the material obtained by reacting PDA and TEOS indicate that the triple C≡C bond of the alkyne is still present.

4. Conclusions

We have found that most of the alkynes reacted with Ru₃(CO)₁₂ undergo loss of functionalities especially

when the reactions are performed under basic methanolic conditions. This also happens during the reactions of PDA. Contrasting with this behaviour, PDA reacts thermally with the ruthenium carbonyl without loss of functionalities, to give complex **4** in good yields. Complex **4** is one of the few examples of structural determination for ruthenium derivatives belonging to the family of the binuclear flyover complexes. It is quite stable and this has allowed us the reactions with TEOS: a sol-gel material has been obtained and characterized. This contains (modified) cluster **4** condensed with the silica obtained from TEOS. Thus, the proposed route **B** to organometallic-inorganic sol-gel materials can effectively occur. Also, the condensation of ligand PDA and TEOS indicates that route **A** could be attempted. The sol-gel materials will be tested in solid-gas catalysis [21].

Acknowledgement

Financial support to this work has been obtained from the Università del Piemonte Orientale and from MIUR (Rome) under the PRIN 2003 program.

References

- [1] G. Gervasio, D. Marabello, P. King, E. Sappa, A. Secco, J. Organomet. Chem. 671 (2003) 137.

- [2] G. Gervasio, D. Marabello, E. Sappa, A. Secco, *J. Organomet. Chem.* 689 (2004) 35.
- [3] G. Gervasio, D. Marabello, E. Sappa, A. Secco, *J. Organomet. Chem.* 690 (2005) 1594.
- [4] S. Deabate, R. Giordano, E. Sappa, *J. Cluster Sci.* 8 (1997) 407.
- [5] E. Sappa, *J. Organomet. Chem.* 573 (1999) 139.
- [6] The ^1H NMR of the PDA ligand in the same solvent is: 5.24 t (1H, CHO), 3.71 m (CH_2), 3.54 m (CH_2), 2.24 q (CH_2), 1.22 t (CH_3 , OEt), 1,12 t (CH_3).
- [7] For comparison, the IR Raman of PDA is: 2977 m, 2928 vs, 2885 s (Et, EtO), 2246 m-s ($\text{C}\equiv\text{C}$), 1457 m (C–C, Et) cm^{-1} and that of TEOS is: 2972 m, 2931 vs, 2891 s, 2768 w, 2721 w (Et, OEt), 1452 w (C–C Et), 1092 w, 650 w, cm^{-1} .
- [8] G.M. Sheldrick, SHELXTL, Version 5.1, Bruker AXS Inc., Madison, WI, 1997.
- [9] SMART, SAINT, SADABS, XPREP Software for CCD diffractometers, Bruker AXS Inc., Madison, WI.
- [10] S. Doherty, J.F. Corrigan, A.J. Carty, E. Sappa, *Adv. Organomet. Chem.* 37 (1995) 39.
- [11] K. Rao, R.J. Angelici, V.G. Young Jr., *Inorg. Chim. Acta* 198–200 (1992) 211.
- [12] (a) G. Gervasio, R. Giordano, E. Sappa, M. Costa, G. Predieri, A. Tiripicchio, *J. Cluster Sci.* 4 (1993) 33;
(b) R. Giordano, E. Sappa, D. Cauzzi, G. Predieri, A. Tiripicchio, *J. Organomet. Chem.* 511 (1996) 263.
- [13] D. Osella, M. Botta, R. Gobetto, R. Amadelli, V. Carassiti, *J. Chem. Soc., Dalton Trans.* (1988) 2519.
- [14] D. Osella, O. Gambino, C. Nervi, M. Ravera, *J. Organomet. Chem.* 433 (1992) 287.
- [15] (a) R.J.P. Corriu, J.J.E. Moreau, *J. Chem. Soc., Chem. Commun.* (1980) 278;
(b) F.A. Cotton, D.L. Hunter, J.M. Troup, *Inorg. Chem.* 15 (1976) 63;
(c) D. Osella, M. Botta, R. Gobetto, R. Amadelli, V. Carassiti, *J. Chem. Soc., Dalton Trans.* (1988) 2519;
(d) E. Sappa, D. Cauzzi, G. Predieri, A. Tiripicchio, M. Tiripicchio Camellini, *J. Organomet. Chem.* 412 (1991) C-14;
(e) M.H. Carre, J.J.E. Moreau, *Inorg. Chem.* 21 (1982) 3099;
(f) R.C. Pettersen, C.G. Cash, *Inorg. Chim. Acta* 34 (1979) 261, see also Ref. [9].
- [16] (a) J. Piron, P. Piret, J. Meunier-Piret, M. van Meerssche, *Bull. Soc. Chim. Belg.* 78 (1979) 121;
(b) P. Piret, J. Meunier-Piret, M. van Meerssche, G.S.D. King, *Acta Crystallogr.* 19 (1965) 78.
- [17] A.J. Blake, P.J. Dyson, S.L. Ingham, B.F.G. Johnson, C.M. Martin, *Organometallics* 14 (1995) 862.
- [18] S. Rivomanana, C. Mongin, G. Lavigne, *Organometallics* 15 (1996) 1195.
- [19] M.I. Bruce, N.N. Zaitseva, B.W. Skelton, A.H. White, *Inorg. Chim. Acta* 250 (1996) 129.
- [20] F. Muller, G. van Koten, L.H. Polm, K. Vrieze, M. Zoutberg, D. Heijdenrijk, E. Kragten, C.H. Stam, *Organometallics* 8 (1989) 1340.
- [21] (a) See for example: M. Castiglioni, S. Deabate, E. Garrone, R. Giordano, B. Onida, G. Predieri, E. Sappa, *J. Cluster Sci.* 8 (1977) 381;
(b) C. Allasia, M. Castiglioni, R. Giordano, E. Sappa, F. Verre, *J. Cluster Sci.* 11 (2000) 493.