

# Asymmetric acetylenic thioethers in ruthenium cluster chemistry

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Received 23 September 2003; accepted 13 November 2003

## Abstract

The compounds  $[\text{Ru}_3(\text{CO})_9(\mu, \eta^2\text{-SC}\equiv\text{CR})(\mu_3, \eta^2\text{-C}\equiv\text{CR}')]$  ( $\text{R} = \text{SiMe}_3$ ,  $\text{R}' = \text{Si}^i\text{Pr}_3$  (**1**);  $\text{R} = \text{Si}^i\text{Pr}_3$ ,  $\text{R}' = \text{SiMe}_3$  (**2**);  $\text{R} = \text{Si}^i\text{Pr}_3$ ,  $\text{R}' = \text{H}$  (**3**);  $\text{R} = \text{H}$ ,  $\text{R}' = \text{Si}^i\text{Pr}_3$  (**4**)) have been obtained by cleavage of one S–C bond of the thioethers  $^i\text{Pr}_3\text{SiC}\equiv\text{CSC}\equiv\text{CR}$  ( $\text{R} = \text{H}$ ,  $\text{SiMe}_3$ ) in the presence of  $\text{Ru}_3(\text{CO})_{12}$ . Thermal treatment of  $[\text{Ru}_3(\text{CO})_9(\mu, \eta^2\text{-SC}\equiv\text{CSi}^i\text{Pr}_3)(\mu_3, \eta^2\text{-C}\equiv\text{CH})]$  yields to the cluster  $[\text{Ru}_4(\text{CO})_9(\mu\text{-CO})_2(\mu_4\text{-S})(\mu_4\text{-}\eta^2\text{-C}(\text{H})\text{C})(\text{C}\equiv\text{CSi}^i\text{Pr}_3)]$  (**5**) which contains a bridging sulfur atom and a polycarbon chain as a consequence of the rupture of the S–C bond and a C–C coupling reaction. All derivatives have been characterized by spectroscopic data. An X-ray diffraction study was carried out on the species  $[\text{Ru}_3(\text{CO})_9(\mu, \eta^2\text{-SC}\equiv\text{CSi}^i\text{Pr}_3)(\mu_3, \eta^2\text{-C}\equiv\text{CSiMe}_3)]$  and of  $[\text{Ru}_3(\text{CO})_9(\mu, \eta^2\text{-SC}\equiv\text{CSi}^i\text{Pr}_3)(\mu_3, \eta^2\text{-C}\equiv\text{CH})]$ .

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**Keywords:** Ruthenium clusters; Alkyne thiolate clusters; Thioethers in cluster chemistry

## 1. Introduction

Transition metal chemistry with organosulfur compounds is a subject of interest due to its relevance from a biological, industrial and environmental point of view [1]. By contrast with the amount of coordination and organometallic compounds prepared using alkyl and aryl thiolate or thioether, work devoted to alkynyl groups is scarce [2]. On the other hand, in the last years, investigations on new materials that may exhibit relevant electrical and optical properties have focused the attention of the researchers on transition metal compounds with bridging polycarbon ligands bearing unsaturated C–C bonds, due to these may allow electronic communication between metal centres [3]. Among the different methods used for construction of these chains, the one based on C–C coupling reactions of vinyl or polyynyl groups is being developed [4].

Following our research field on ruthenium clusters containing acetylenic chains, in this paper we described the synthesis and characterization of the new clusters

$[\text{Ru}_3(\text{CO})_9(\mu, \eta^2\text{-SC}\equiv\text{CR})(\mu_3, \eta^2\text{-C}\equiv\text{CR}')]$  ( $\text{R} = \text{SiMe}_3$ ,  $\text{R}' = \text{Si}^i\text{Pr}_3$  (**1**);  $\text{R} = \text{Si}^i\text{Pr}_3$ ,  $\text{R}' = \text{SiMe}_3$  (**2**);  $\text{R} = \text{Si}^i\text{Pr}_3$ ,  $\text{R}' = \text{H}$  (**3**),  $\text{R} = \text{H}$ ,  $\text{R}' = \text{Si}^i\text{Pr}_3$  (**4**)) derived from the reaction of  $\text{Ru}_3(\text{CO})_{12}$  and the corresponding  $\text{RC}\equiv\text{CSC}\equiv\text{CR}'$ . Compounds **3** and **4** have also been obtained by desilylation reaction of **2** and **1**, respectively. The cluster  $[\text{Ru}_4(\text{CO})_9(\mu\text{-CO})_2(\mu_4\text{-S})(\mu_4\text{-}\eta^2\text{-C}(\text{H})\text{C})(\text{C}\equiv\text{CSi}^i\text{Pr}_3)]$  (**5**) has been generated from  $[\text{Ru}_3(\text{CO})_9(\mu, \eta^2\text{-SC}\equiv\text{CSi}^i\text{Pr}_3)(\mu_3, \eta^2\text{-C}\equiv\text{CH})]$  via a thermolytic reaction.

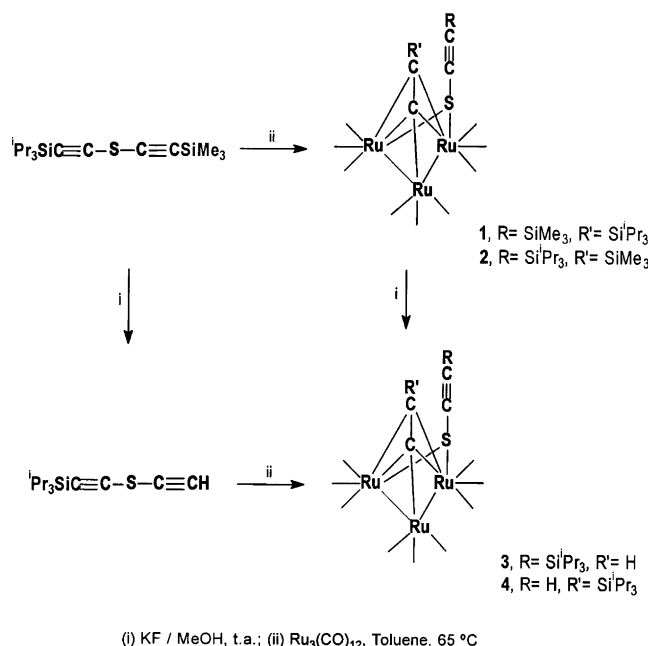
## 2. Results and discussion

The synthesis of compounds containing two redox active subunits joined by a polycarbon chain which permit the electronic transmission between them is a subject of interest in the last years [3,5]. Due to clusters acting as reservoirs of electrons, able to accept or release them, we planned to prepare ruthenium clusters connected to metal–ligand fragments by an unsaturated  $\text{C}_n$  chain. Previous results obtained in our laboratory [4d] on the symmetric thioether  $\text{S}(\text{C}\equiv\text{CSiMe}_3)_2$  with  $\text{Ru}_3(\text{CO})_{12}$  have showed that the heating of the

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compound  $[\text{Ru}_3(\text{CO})_9(\mu, \eta^2\text{-SC}\equiv\text{CSiMe}_3)(\mu_3, \eta^2\text{-C}\equiv\text{CSiMe}_3)]$  provokes the rupture of the S–C bond of the alkynylthiolate ligand as well as the formation of a diynyl ligand as a consequence of a C–C coupling reaction between the two acetylide groups, yielding the tetranuclear cluster  $[\text{Ru}_4(\text{CO})_9(\mu\text{-CO})_2(\mu_4\text{-S})(\mu_4\text{-}\eta^2\text{-C}(\text{SiMe}_3)\text{C})(\text{C}\equiv\text{CSiMe}_3)]$ . Taking all these into account, we decided to explore the behaviour of the asymmetric thioether  ${}^i\text{Pr}_3\text{SiC}\equiv\text{CSC}\equiv\text{CH}$  in order to prepare a cluster containing an unprotected acetylenic chain which allows a link to redox-active  $\text{ML}_n$  fragments. As compound  ${}^i\text{Pr}_3\text{SiC}\equiv\text{CSC}\equiv\text{CSiMe}_3$  is the starting material to synthesized  ${}^i\text{Pr}_3\text{SiC}\equiv\text{CSC}\equiv\text{C}$ , on the bases of our previous results using a symmetric thioether, we initially have study the behaviour of the former in order to find an alternative way to obtain a tetraruthenium cluster containing a  $\mu\text{-C}(\text{R})\text{CC}\equiv\text{CH}$  ligand. In fact the presence in the molecule of two different acetylide groups afford to isomers. A mixture of  $\text{Ru}_3(\text{CO})_{12}$  and an excess of the freshly prepared thioether  ${}^i\text{Pr}_3\text{SiC}\equiv\text{CSC}\equiv\text{CSiMe}_3$  was heated in toluene at 70 °C for 3 h. The product of the reaction was chromatographed affording a yellow band of  $[\text{Ru}_3(\text{CO})_9(\mu, \eta^2\text{-SC}\equiv\text{CSiMe}_3)(\mu_3, \eta^2\text{-C}\equiv\text{CSi}^i\text{Pr}_3)]$  (**1**) (isomer I) in trace amounts and a second orange band of  $[\text{Ru}_3(\text{CO})_9(\mu, \eta^2\text{-SC}\equiv\text{CSi}^i\text{Pr}_3)(\mu_3, \eta^2\text{-C}\equiv\text{CSiMe}_3)]$  (**2**) (isomer II) as the main product (Scheme 1). A hexane solution of **2** kept at –20 °C during 24 h gave suitable crystals for an X-ray diffraction study, confirming the structure which will be discussed in the following section.

The  ${}^1\text{H}$  NMR spectra of both isomers show the resonances corresponding to the  $\text{SiMe}_3$  [0.19 (**1**), 0.59 (**2**) ppm] and  $\text{Si}^i\text{Pr}_3$  [1.08 (**1**), 1.08 (**2**) ppm] groups as



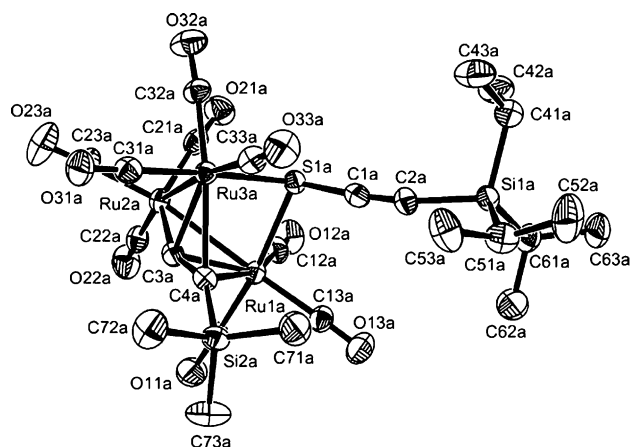
Scheme 1.

singlets. The carbonyl stretching frequencies observed in their IR spectra [2096 (w), 2068 (s), 2052 (s), 2021 (vs) and 1990 (w) (**1**); 2091 (w), 2072 (s), 2051 (s), 2018 (vs) and 1988 (w) (**2**)  $\text{cm}^{-1}$ ] exhibit a similar pattern to those reported for compounds  $[\text{Ru}_3(\text{CO})_9(\mu, \eta^2\text{-SC}\equiv\text{CSiMe}_3)(\mu_3, \eta^2\text{-C}\equiv\text{CSiMe}_3)]$  [**4d**],  $[\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)(\mu\text{-C}\equiv\text{CR})]$  [**6**] and  $[\text{Ru}_3(\text{CO})_9(\mu\text{-SC}_2\text{H}_5)(\mu_3, \eta^2\text{-C}\equiv\text{CR})]$  ( $\text{R} = \text{Me}$ ,  $\text{Ph}$ ) [**2h**].

The analogous reaction carried out using  ${}^i\text{Pr}_3\text{SiC}\equiv\text{CSC}\equiv\text{CH}$  instead afforded  $[\text{Ru}_3(\text{CO})_9(\mu, \eta^2\text{-SC}\equiv\text{CSi}^i\text{Pr}_3)(\mu_3, \eta^2\text{-C}\equiv\text{CH})]$  (**3**) and  $[\text{Ru}_3(\text{CO})_9(\mu, \eta^2\text{-SC}\equiv\text{CH})(\mu_3, \eta^2\text{-C}\equiv\text{CSi}^i\text{Pr}_3)]$  (**4**). The favouring of **2** and **3** over **1** and **4** (Scheme 1) may be due to steric reasons. In the  ${}^1\text{H}$  NMR spectrum of **3** and **4** the resonances of the  $\text{Si}^i\text{Pr}_3$  and  $\text{CH}$  groups appear as singlets at [1.13, 5.44 (**3**)], and [1.06, 2.99 (**4**) ppm], respectively. The IR  $\nu(\text{CO})$  bands of both sets of compounds were similar to the above mentioned. We also found that desilylation of compounds **1** and **2** produces **4** and **3**, respectively (Scheme 1).

X-ray diffraction studies have been carried out on compounds **2** and **3**. Plots of the molecular structures are shown in Figs. 1 and 2. Selected bond lengths and angles are given in Tables 1 and 2.

Compounds **2** and **3** consist of an open triangular arrangement. The overall structure shown for these compounds is analogous to that previously described for the cluster  $[\text{Ru}_3(\text{CO})_9(\mu, \eta\text{-SC}\equiv\text{CSiMe}_3)(\mu, \eta\text{-C}\equiv\text{CSiMe}_3)]$  [**4d**]. The alkynethiolate ligand bridges the two ruthenium atoms of the open edge of the  $\text{Ru}_3$  triangle and the acetylide group is  $\sigma, \pi$  coordinate to three atoms. Assuming that the  $\text{SC}\equiv\text{C}^i\text{Bu}$  and  $\text{C}\equiv\text{C}^i\text{Bu}$  fragments formally donate three and five electrons, respectively, each metal center is electronically precise giving a total count of 50 cluster valence electrons to the molecule. The Ru–Ru bond distances [2.8166(7), 2.8346(10) and 2.8319(11), 2.8274(10) Å] are similar to those exhibited by  $[\text{Ru}_3(\text{CO})_9(\mu, \eta\text{-SC}\equiv\text{CSiMe}_3)(\mu, \eta\text{-C}\equiv\text{CSiMe}_3)]$  [2.8397 (5) and 2.8204 (5) Å] [**4d**],  $[\text{Ru}_3$

Fig. 1. Molecular structure of compound **2**.

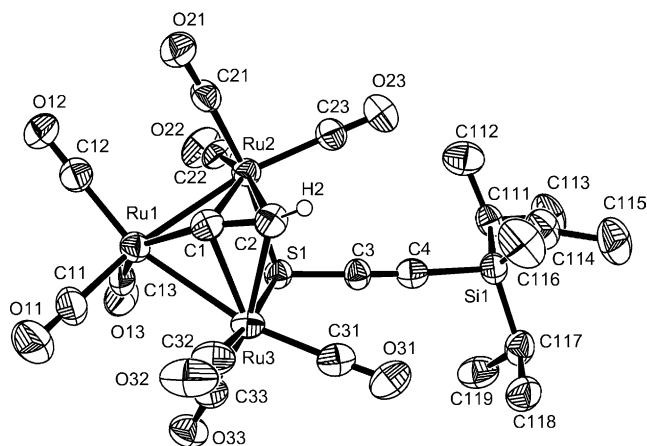


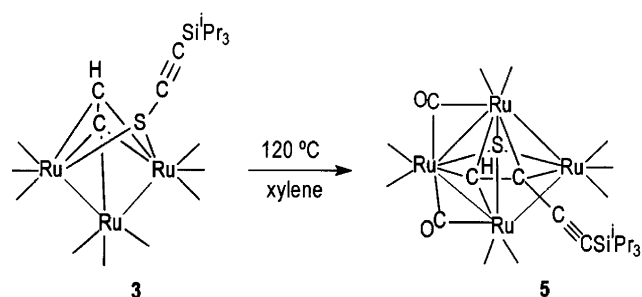
Fig. 2. Molecular structure of compound 3.

Table 1  
Selected distances (Å) and angles (°) of  $[\text{Ru}_3(\text{CO})_9(\mu, \eta^2\text{-SC}\equiv\text{CSi}^i\text{Pr}_3)(\mu_3, \eta^2\text{-C}\equiv\text{CMe}_3)]$

Ru(1)–C(4)	2.354(4)
Ru(1)–C(3)	2.241(4)
Ru(1)–Ru(2)	2.8166(7)
Ru(2)–C(3)	1.945(4)
Ru(1)–S(1)	2.4321(11)
Ru(3)–C(4)	2.345(4)
Ru(2)–Ru(3)	2.8346(10)
Ru(3)–C(3)	2.246(4)
Ru(3)–S(1)	2.4326(11)
C(3)–C(4)	1.290(6)
S(1)–C(1)	1.705(5)
C(1)–C(2)	1.205(6)
Ru(1)–Ru(2)–Ru(3)	3.05(2)
Ru(1)–S(1)–Ru(3)	87.48(4)
C(1)–C(2)–Si(2)	167.8(4)
C(1)–C(2)–S(1)	173.2(4)
C(4)–C(3)–Ru(2)	153.8(3)

Table 2  
Selected distances (Å) and angles (°) of  $[\text{Ru}_3(\text{CO})_9(\mu, \eta^2\text{-SC}\equiv\text{CSi}^i\text{Pr}_3)(\mu_3, \eta^2\text{-C}\equiv\text{CH})]$

Ru(1)–C(1)	1.934(8)
Ru(1)–Ru(3)	2.8319(11)
Ru(1)–Ru(2)	2.8274(10)
Ru(2)–C(1)	2.241(7)
Ru(2)–C(2)	2.287(8)
Ru(2)–S(1)	2.430(2)
Ru(3)–C(1)	2.235(7)
Ru(3)–C(2)	2.276(8)
Ru(3)–S(1)	2.4255(19)
C(3)–C(4)	1.197(10)
S(1)–C(3)	1.699(8)
C(1)–C(2)	1.288(11)
Ru(1)–Ru(2)–Ru(3)	71.90(3)
Ru(3)–S(1)–Ru(2)	86.36(6)
C(3)–C(4)–Si(1)	175.5(7)
C(4)–C(3)–S(1)	175.8(7)
C(1)–C(2)–Ru(1)	150.4(6)



Scheme 2.

$(\text{CO})_9(\mu\text{-SC}_2\text{H}_5)(\mu_3, \eta^2\text{-C}\equiv\text{CR})$  [(R = CH<sub>3</sub>, 2.843(1) and 2.847(1) Å; R = Ph, 2.8391(8) and 2.8524(8) Å] [2h] and  $[\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)(\mu_3, \eta^2\text{-C}\equiv\text{C}^i\text{Bu})]$  [5a]. In addition the Ru–S distances [2.4321(11), 2.4326(11) and 2.430(2), 2.4255(19) Å] are comparable to values of 2.4353(7) and 2.4337(7) Å [4d].

Taking into account our experience in C–C coupling reactions between acetylide fragments to generate polycarbon chains, compound 3 was heated in xylene at 120 °C for 5 h affording complex 5 after chromatographic workup (Scheme 2). The new compound has been characterized by IR and NMR spectroscopy, analytical data and FAB mass spectrometry. The FAB mass spectrum gives the molecular ion at  $m/z$  951 together with several peaks due to CO loss. The IR spectrum of 5 shows the presence of both terminal and bridging CO groups and the pattern is analogous to the related compounds  $[\text{Ru}_4(\text{CO})_9(\mu\text{-CO})_2(\mu_4\text{-S})(\mu_4, \eta^3\text{-C}(\text{Me}_3\text{Si})\text{C}(\text{C}\equiv\text{CSiMe}_3))]$  [4d] and  $[\text{Ru}_4(\text{CO})_9(\mu\text{-CO})_2(\mu_4\text{-S})(\mu_4, \eta^2\text{-HC}\equiv\text{CPh})]$  [7]. Although suitable crystals for X-ray diffraction were not obtained, all spectroscopic and analytical data as well as the absence of a terminal acetylenic hydrogen in the <sup>1</sup>H NMR spectrum suggest the formula  $[\text{Ru}_4(\text{CO})_{10}(\mu_4\text{-S})(\mu_4, \eta^2\text{-CHC}(\text{C}\equiv\text{CSi}^i\text{Pr}_3))]$  for this cluster.

Attempts to join compound 5 to  $\text{ML}_n$  fragments failed; however, this compound is of interest as an acetylenic cluster stabilized by sulfur.

### 3. Experimental

#### 3.1. General information

All reactions were carried out under argon atmosphere using Schlenk techniques. Solvents were dried according to standard methods. IR spectra were recorded on a Perkin–Elmer 1600 FTIR spectrophotometer using NaCl cells. <sup>1</sup>H NMR was registered on a Bruker AMX-300 instrument in CDCl<sub>3</sub>. Elemental analyses were performed on a Perkin–Elmer 240-B microanalyzer. FAB<sup>+</sup> mass spectra were carried out on a WG AutoSpec spectrometer, using 3-nitrobenzyl

alcohol as matrix.  ${}^i\text{Pr}_3\text{SiC}\equiv\text{CSC}\equiv\text{CSiMe}_3$  and  ${}^i\text{Pr}_3\text{SiC}\equiv\text{CSC}\equiv\text{CH}$  were prepared as previously reported [8].

### 3.2. Reaction of $\text{Ru}_3(\text{CO})_{12}$ with ${}^i\text{Pr}_3\text{SiC}\equiv\text{CSC}\equiv\text{CSiMe}_3$

A mixture of  $\text{Ru}_3(\text{CO})_{12}$  (0.100 g, 0.156 mmol) and an excess of  ${}^i\text{Pr}_3\text{SiC}\equiv\text{CSC}\equiv\text{CSiMe}_3$  (0.097 g, 0.313 mmol) in toluene (20 cm<sup>3</sup>) was heated at 70 °C. After stirring for 3 h at this temperature, the solvent was removed under vacuum and the residue chromatographed on silica gel. Elution with *n*-hexane gave first a pale yellow band of  $[\text{Ru}_3(\text{CO})_9(\mu, \eta^2\text{-SC}\equiv\text{CSiMe}_3)(\mu_3, \eta^2\text{-C}\equiv\text{CSi}^i\text{Pr}_3)]$  (**1**) in trace amounts and a second orange band which afforded by dryness  $[\text{Ru}_3(\text{CO})_9(\mu, \eta^2\text{-SC}\equiv\text{CSi}^i\text{Pr}_3)(\mu_3, \eta^2\text{-C}\equiv\text{CSiMe}_3)]$  (**2**) as yellow solid (0.074 g, 55% yield). Crystals suitable for X-ray study of isomer **2** were obtained from *n*-hexane at 20 °C.

**1**: IR (*n*-hexane, cm<sup>-1</sup>): 2096 (w), 2068 (s), 2052 (s), 2021 (vs), 1990 (w). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 1.08 (s, 21H, Si<sup>*i*</sup>Pr<sub>3</sub>), 0.19 (s, 9H, SiMe<sub>3</sub>).

**2**: IR (*n*-hexane, cm<sup>-1</sup>): 2091 (w), 2072 (s), 2051 (s), 2018 (vs), 1988 (w). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 1.08 (s, 21H, Si<sup>*i*</sup>Pr<sub>3</sub>), 0.59 (s, 9H, SiMe<sub>3</sub>). *Anal.* Calc. for  $\text{Ru}_3\text{SSi}_2\text{O}_9\text{C}_{25}\text{H}_{30}$  (Found): C, 34.68 (34.90); H, 3.49 (3.48)%.

### 3.3. Reaction of $\text{Ru}_3(\text{CO})_{12}$ with ${}^i\text{Pr}_3\text{SiC}\equiv\text{CSC}\equiv\text{CH}$

$\text{Ru}_3(\text{CO})_{12}$  (0.100 g, 0.156 mmol) in toluene (20 cm<sup>3</sup>) was heated at 60 °C and then an excess of  ${}^i\text{Pr}_3\text{SiC}\equiv\text{CSC}\equiv\text{CH}$  (0.041 g, 0.172 mmol) added and the mixture was stirred for 5 h. Due to the thermal decomposition of the thioether, additional portions of the ligand were required until the reaction was complete as indicated by the IR spectrum. Elution with *n*-hexane afforded a yellow band of  $[\text{Ru}_3(\text{CO})_9(\mu, \eta^2\text{-SC}\equiv\text{CSi}^i\text{Pr}_3)(\mu_3, \eta^2\text{-C}\equiv\text{CH})]$  (**3**) (0.043 g, 35% yield). Further elution with the same solvent gave trace amounts of a yellow band containing  $[\text{Ru}_3(\text{CO})_9(\mu, \eta^2\text{-SC}\equiv\text{CH})(\mu_3, \eta^2\text{-C}\equiv\text{CSi}^i\text{Pr}_3)]$  (**4**).

**3**: IR (*n*-hexane, cm<sup>-1</sup>): 2087 (w), 2077 (vs), 2054 (vs), 2019 (vs), 1990 (m). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 5.44 (s, 1H, CCH), 1.13 (s, 21H, Si<sup>*i*</sup>Pr<sub>3</sub>). *Anal.* Calc. for  $\text{Ru}_3\text{SSiO}_9\text{C}_{22}\text{H}_{22}$  (Found): C, 33.29 (33.40); H, 2.79 (2.68)%.

**4**: IR (*n*-hexane, cm<sup>-1</sup>): 2098 (w), 2076 (s), 2054 (s), 2021 (vs), 1992 (w). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 2.99 (s, 1H, SCCH), 1.08 (s, 21H, Si<sup>*i*</sup>Pr<sub>3</sub>).

### 3.4. Synthesis of compound $[\text{Ru}_4(\text{CO})_9(\mu\text{-CO})_2(\mu_4\text{-S})(\mu_4\text{-}\eta^2\text{-C(H)C})(\text{C}\equiv\text{CSiMe}_3)]$ (**5**)

$[\text{Ru}_3(\text{CO})_9(\mu, \eta^2\text{-SC}\equiv\text{CSi}^i\text{Pr}_3)(\mu_3, \eta^2\text{-C}\equiv\text{CH})]$  (0.127 g, 0.15 mmol) was heated at 120 °C in xylene (20 cm<sup>3</sup>) for 5 h.

Then the solvent was removed under vacuum. Column chromatography on silica gel, using *n*-hexane as eluent, yielded a yellow band containing  $[\text{Ru}_4(\text{CO})_9(\mu\text{-CO})_2(\mu_4\text{-S})(\mu_4, \eta^2\text{-C(H)C})(\text{C}\equiv\text{CSi}^i\text{Pr}_3)]$  as the main product.

IR (*n*-hexane, cm<sup>-1</sup>): 2095 (w), 2062 (s), 2044 (vs), 2039 (sh), 2007 (m), 1995 (w), 1860 (w). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 4.26 [s, 1H, C(H)C], 0.92 [s, 21H, Si<sup>*i*</sup>Pr<sub>3</sub>]. *Anal.* Calc. for  $\text{Ru}_4\text{SSiO}_{11}\text{C}_{24}\text{H}_{22}$  (Found): C, 30.32 (30.35); H, 2.31 (2.58)%.

### 3.5. Crystal data for complexes **2** and **3**

For the two compounds data were collected on a IPDS STOE diffractometer using a graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 170 K for **2** and at 293 K for **3**. Crystal data and structure refinement parameters for compounds **2** and **3** are listed in Table 3. Final unit cell parameters were obtained by means of a least-squares refinement of a set of 8000 well measured reflections, and crystal decay was monitored during the data collection. No significant fluctuation of intensities were observed during the measurement. Structures were solved by Direct Methods using SIR92 [9], and refined by least-squares procedures on a  $|F|^2$  with the aid of SHELXL97 [10] included in the programs package WinGX version 1.63 [11]. The atomic scattering factors were taken from International Tables for X-Ray Crystallography [12]. All hydrogen atoms were located on a difference Fourier maps, and refined by using a riding model, with a Uiso fixed at 20% higher than Uiso of the

Table 3  
Crystal data, data collection and structure refinement for compounds **2** and **3**

	<b>2</b>	<b>3</b>
Formula	$\text{C}_{25}\text{H}_{30}\text{O}_9\text{SSi}_2\text{Ru}_3$	$\text{C}_{22}\text{H}_{22}\text{O}_9\text{SSiRu}_3$
Molecular weight	865.94	793.76
<i>T</i> (K)	170(2)	293(2)
Grid crystal size (mm)	0.27 × 0.22 × 0.07	0.50 × 0.45 × 0.25
Colour	light yellow	pale yellow
Crystal form	plate	parallelepiped
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	$Pbca$
<i>a</i> (Å)	25.220(5)	16.053(5)
<i>b</i> (Å)	9.121(2)	16.088(5)
<i>c</i> (Å)	29.700(6)	22.600(5)
$\beta$ (°)	101.15(3)	
<i>V</i> (Å <sup>3</sup> )	6703(2)	5837(3)
<i>Z</i>	8	8
$\mu$ (mm <sup>-1</sup> )	1.512	1.807
2 $\theta$ Range (°)	3.3–52.1	2.9–48.4
Reflections measured	43 953	35 140
Reflections unique	10 834	4620
$R_{\text{int}}$	0.0484	0.1146
<i>R</i>	0.0283	0.0444
$R_w$	0.0596	0.0990
Goodness-of-fit	0.934	0.924
$\rho_{\text{max}} - \rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.720 and -0.378	0.512 and -0.608

C(sp<sup>2</sup>) to which they were connected and 50% higher for hydrogens attached to C(sp<sup>3</sup>) atoms. All non-hydrogen atoms were anisotropically refined and in the last cycles of refinement a weighting scheme was used, where weights are calculated from the following formula:  $w = 1/[\sigma_2(F_o^2) + (aP)^2 + bP]$ , where  $P = (F_o^2 + 2F_c^2)/3$ . Criteria for a satisfactory complete analysis were the ratio of rms shift to standard deviations being less than 0.1 and also no significant residual electronic densities on final difference maps. Drawings of molecules are performed with the program ORTEP32 [13] with 50% probability displacement ellipsoids for non-hydrogen atoms.

#### 4. Supplementary material

Crystallographic data for the structures reported on this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 219311 for compound **2** and No. 219312 for compound **3**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033); e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk) or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

#### Acknowledgements

Financial support was generously provided by MCYT, Spain (Project BQU 2001/0216).

#### References

- [1] (a) R. Cammack (Ed.), *Iron–Sulfur Proteins*, *Advances in Inorganic Chemistry*, vol. 38, 1992;
- (b) R.A. Sanchez-Delgado, *J. Mol. Catal.* 86 (1994) 287;
- (c) T.B. Rauchfuss, *Prog. Inorg. Chem.* 39 (1991) 259.
- [2] (a) M. Herres, O. Walter, H. Lang, R. Hosch, J. Hahn, *J. Organomet. Chem.* 466 (1994) 237;
- (b) G. Schmidt, N. Schittenhelm, U. Behrens, *J. Organomet. Chem.* 95 (1995) 496;
- (c) H. Zhang, A.W.M. Lee, W.-Y. Wong, M.S.M. Yuen, *J. Chem. Soc., Dalton Trans.* (2000) 3675;
- (d) W. Weigand, *Z. Naturforsch., Teil B* 46 (1991) 1333;
- (e) W. Weigand, C. Robl, *Chem. Ber.* 126 (1993) 1807;
- (f) W. Weigand, M. Weishaupl, C. Robl, *Z. Naturforsch., Teil B* 51 (1996) 501;
- (g) I. Ara, E. Delgado, J. Fornies, E. Hernández, E. Lalinde, N. Mansilla, M.T. Moreno, *J. Chem. Soc., Dalton Trans.* (1998) 3199;
- (h) S. Jeannin, Y. Jeannin, F. Robert, C. Rosenberger, *Inorg. Chem.* 33 (1994) 243;
- (i) C. Rosenberg, N. Steunou, S. Jeannin, Y. Jeannin, *J. Organomet. Chem.* 494 (1995) 17.
- [3] (a) I.R. Whittall, A.M. McDonagh, M.G. Humphrey, M. Samoc, *Adv. Organomet. Chem.* 42 (1998) 291;
- (b) S.R. Marder, in: D.W. Bruce, D. O'Hare (Eds.), *Inorganic Materials*, Wiley, Chichester, 1996, p. 121;
- (c) N.J. Long, *Angew. Chem., Int. Ed. Engl.* 34 (1995) 21;
- (d) M.I. Bruce, P.J. Low, N.N. Zaitseva, S. Kahlal, J.-F. Halet, B.W. Skelton, A.H. White, *J. Chem. Soc., Dalton Trans.* (2000) 2939;
- (e) P.J. Low, R. Rousseau, P. Lam, K.A. Udachin, G.D. Enright, J.S. Tse, D.D.M. Wayner, A.J. Carty, *Organometallics* 18 (1999) 3897;
- (f) M.I. Bruce, B.W. Skelton, A.H. White, N.N. Zaitseva, *J. Organomet. Chem.* 650 (2002) 188.
- [4] (a) A.J. Carty, G. Hogarth, G.D. Enright, G.J. Frapper, *J. Chem. Soc., Chem Commun.* (1997) 1883;
- (b) Y. Chi, A.J. Carty, P. Blenkinsop, E. Delgado, G.D. Enright, W. Wang, S.-M. Peng, G.-H. Lee, *Organometallics* 15 (1996) 5269;
- (c) E. Delgado, Y. Chi, W. Wang, G. Hogarth, P. Low, G.D. Enright, S.-M. Peng, G.-H. Lee, A.J. Carty, *Organometallics* 17 (1998) 2936;
- (d) M.I. Alcalde, A.J. Carty, Y. Chi, E. Delgado, B. Donnadiu, E. Hernández, K. Dallmann, J. Sánchez-Nieves, *J. Chem. Soc., Dalton Trans.* (2001) 2502.
- [5] (a) F. Paul, C. Lapinte, *Coord. Chem. Rev.* 180 (1998) 431;
- (b) J.M. Tour, *Acc. Chem. Rev.* 33 (2000) 791.
- [6] (a) A.J. Carty, S.A. MacLaughlin, N.J. Taylor, *J. Organomet. Chem.* 204 (1981) C27;
- (b) A.A. Cherkas, J.F. Corrigan, S. Doherty, S.A. MacLaughlin, F. van Gastel, N.J. Taylor, A.J. Carty, *Inorg. Chem.* 32 (1993) 1662;
- (c) F. van Gastel, L. Agocs, A.A. Cherkas, J.F. Corrigan, S. Doherty, R. Ramachandran, N.J. Taylor, A.J. Carty, *J. Cluster Sci.* 2 (1991) 131.
- [7] R.D. Adams, J.E. Babin, M. Tasi, T.A. Wolfe, *Organometallics* 6 (1987) 2228.
- [8] A.W.M. Lee, A.B.W. Yeung, M.S.M. Yuen, H. Zhang, X. Zhao, W.Y. Wong, *Chem. Commun.* (2000) 75.
- [9] (a) SIR 92 – a program for crystal structure solution. A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* 26 (1993) 343;
- (b) SIR 97. A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst.* 32 (1999) 115.
- [10] G.M. Sheldrick, *SHELX97* [includes *SHELXS97*, *SHELXL97*, *CIF-TAB*] – Programs for Crystal Structure Analysis (Release 97-2), Institut für Anorganische Chemie der Universität Tammanstrasse 4, D-3400 Göttingen, Germany, 1998, p. >ttingen.
- [11] WinGX-1.63. Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-Ray Diffraction Data L. Farrugia, *J. Appl. Crystallogr.* 32 (1999) 837.
- [12] *International tables for X-Ray crystallography*, 1974, vol. IV, Kynoch Press, Birmingham, England.
- [13] ORTEP32 for Windows. L.J. Farrugia, *J. Appl. Crystallogr.* 30 (1997) 565.