

# Carbon–carbon coupling reactions on triruthenium clusters: synthesis and structure of $\text{Ru}_3(\text{CO})_9[\mu_3-\eta^3\text{-PhCCCC(H)Ph}][\mu_2\text{-NS(O)MePh}]$ and $\text{Ru}_3(\mu_2\text{-CO})(\text{CO})_7[\mu_3-\eta^3\text{-PhCCCC(H)Ph}][\mu_3\text{-NS(O)MePh}]$

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## Abstract

The reaction of the electron-deficient cluster  $(\mu_2\text{-H})\text{Ru}_3(\text{CO})_9[\mu_3\text{-NS(O)MePh}]$  (**1**) with *para*-nitrotolane gives, with coupling of two alkyne units and elimination of the *para*-nitrophenyl fragment, the trinuclear complexes  $\text{Ru}_3(\text{CO})_9[\mu_3-\eta^3\text{-PhCCCC(H)Ph}][\mu_2\text{-NS(O)MePh}]$  (**2**) and  $\text{Ru}_3(\mu_2\text{-CO})(\text{CO})_7[\mu_3-\eta^3\text{-PhCCCC(H)Ph}][\mu_3\text{-NS(O)MePh}]$  (**3**). The resulting organic moiety, coordinated as  $\mu_3-\eta^3$ -5e-donor, is best considered as a butenyne ( $\text{PhC}\equiv\text{C}-\text{C}=\text{C}(\text{H})\text{Ph}$ ) ligand in **2** and as a butatriene ( $\text{PhC}=\text{C}=\text{C}=\text{C}(\text{H})\text{Ph}$ ) ligand in **3**. From the reaction mixture, the two isomeric vinyl complexes  $\text{Ru}_3(\mu_2\text{-CO})_2(\text{CO})_6[\mu_2-\eta^2\text{-PhC}=\text{C}(\text{H})(\text{C}_6\text{H}_4\text{-}p\text{-NO}_2)][\mu_3\text{-NS(O)MePh}]$  (**4a**) and  $\text{Ru}_3(\mu_2\text{-CO})_2(\text{CO})_6[\mu_2-\eta^2\text{-(C}_6\text{H}_4\text{-}p\text{-NO}_2)\text{-C}=\text{C}(\text{H})\text{Ph}][\mu_3\text{-NS(O)MePh}]$  (**4b**) complexes can also be isolated. © 1997 Elsevier Science S.A.

**Keywords:** Clusters; Ruthenium; Alkynes; Carbon–carbon coupling; Crystal structures

## 1. Introduction

Reactions involving carbon–carbon bond formation in transition metal clusters are of considerable interest because of their potential for generating new and unusual types of hydrocarbon fragments [1,2]. Reactions of this type are also considered as models for related processes occurring on metal surfaces [3–5]. In particular, alkynes can be coupled in the coordination sphere of transition metal clusters to give  $\text{C}_4$ ,  $\text{C}_6$ ,  $\text{C}_8$ , and  $\text{C}_{12}$  hydrocarbyls [6–37]. Thus, the cluster  $\text{Cp}'_2\text{Mo}_2\text{Co}_2(\text{CO})_4\text{S}_3$  reacts with phenylacetylene, in a first step to give the  $\mu_3-\eta^2$ -alkyne cluster  $\text{Cp}'_2\text{Mo}_2\text{Co}_2(\text{CO})_2\text{S}_3(\text{PhCCH})$  which, in a second step, adds another equivalent of phenylacetylene to give  $\text{Cp}'_2\text{Mo}_2\text{Co}_2(\text{CO})_2\text{S}_3(\text{CPhCHCHCPh})$  in which the two alkynes are coupled to give a cyclopentadiene unit [38]. On a  $\text{Ru}_4$  metal core, diphenylacetylene can be coupled to give a  $\text{C}_8$  hydrocarbyl: The cluster  $\text{Ru}_4(\text{CO})_8(\mu_4-$

$\text{PPh})[\eta^1, \eta^1, \eta^2, \eta^2\text{-(Ph)CC(Ph)C(Ph)C-}\eta^4\text{-CC(Ph)C(Ph)-C(Ph)}]$  is formed from the reaction of  $\text{Ru}_4(\text{CO})_{13}(\mu_3\text{-PPh})$  with  $\text{C}_2\text{Ph}_2$  [39].

In the preceding publication [40], we reported the reaction of the electron-deficient cluster  $(\mu_2\text{-H})\text{Ru}_3(\text{CO})_9[\mu_3\text{-NS(O)MePh}]$  (**1**) with non-functional alkynes to give various types of vinyl complexes. In an effort to generalize this concept, we extended this reaction also to functional alkynes. In this paper, we report the reaction of **1** with  $\text{PhC}\equiv\text{C}(\text{C}_6\text{H}_4\text{-}p\text{-NO}_2)$  to give  $\text{Ru}_3$  clusters containing  $\text{C}_4$  hydrocarbyl ligands resulting from the carbon–carbon coupling of two alkyne units.

## 2. Results

### 2.1. Reaction of $(\mu_2\text{-H})\text{Ru}_3(\text{CO})_9[\mu_3\text{-NS(O)MePh}]$ (**1**) with $\text{PhC}\equiv\text{C}(\text{C}_6\text{H}_4\text{-}p\text{-NO}_2)$

The thermal reaction of the electron-deficient cluster  $(\mu_2\text{-H})\text{Ru}_3(\text{CO})_9[\mu_3\text{-NS(O)MePh}]$  (**1**) and the alkyne

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Table 1  
IR and NMR data of the complexes 2–4

Complexes	$\nu_{\text{CO}}$ [ $\text{cm}^{-1}$ ]	$\delta(^1\text{H})$ [ppm]
2 <sup>a</sup>	2070(vs), 2048(s), 2008(s)	2.94 ( $\text{C}_6\text{H}_5$ ) s; 7.09–8.54 ( $\text{C}=\text{C}(\text{Ph})\text{H}$ and $\text{C}_6\text{H}_5$ )
3 <sup>a</sup>	2080(m), 2040(vs), 2011(vs), 1974(m), 1805(w)	2.98 ( $\text{C}_6\text{H}_5$ ) s; 7.08–8.54 ( $\text{C}=\text{C}(\text{Ph})\text{H}$ and $\text{C}_6\text{H}_5$ )
4a + 4b <sup>b</sup>	2065(vw), 2057(w), 2039(s), 2015(s), 2005(sh), 1988(m), 1950(m), 1828(w)	3.192, 3.348 ( $\text{C}_6\text{H}_5$ ) s; 6.015, 6.237 ( $\text{C}=\text{C}\text{HPh}$ or $\text{C}=\text{C}\text{H}(\text{C}_6\text{H}_4\text{-}p\text{-NO}_2)$ ) s, 6.60–8.00 ( $\text{C}_6\text{H}_5$ and $\text{C}_6\text{H}_4\text{-}p\text{-NO}_2$ ) m

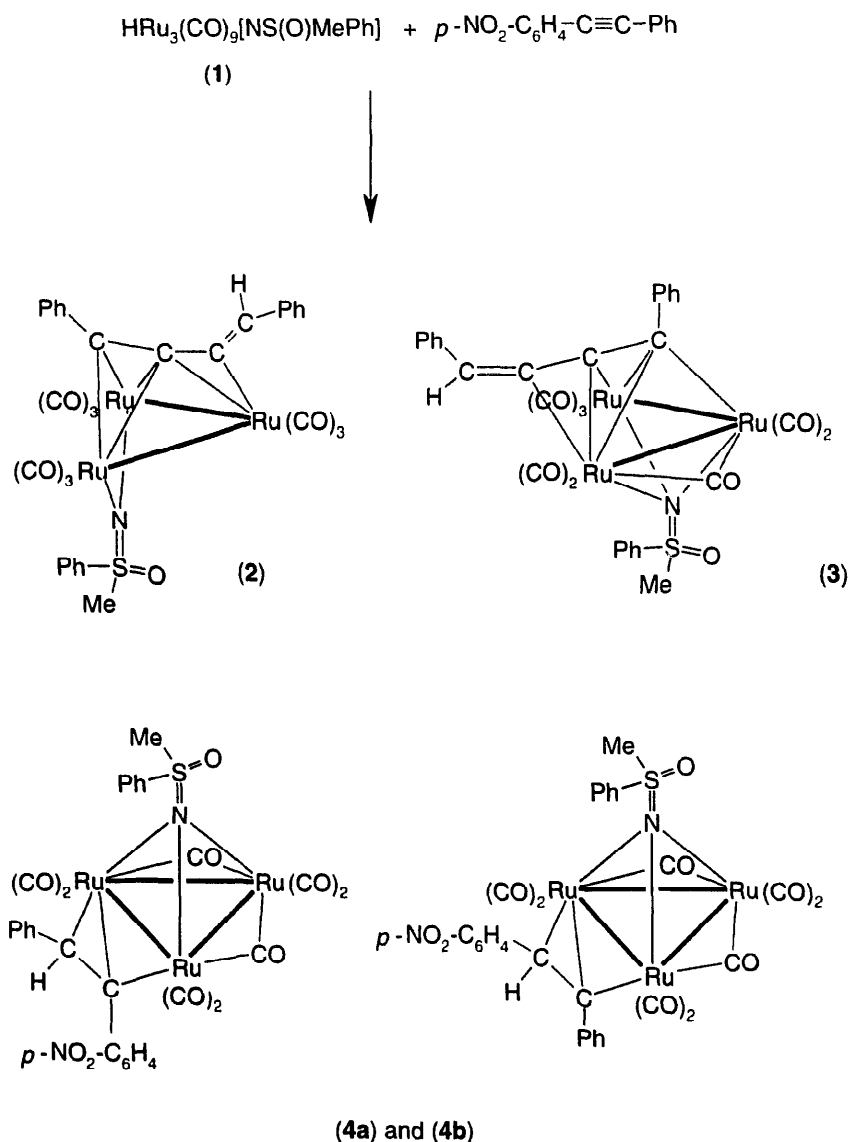
<sup>a</sup>In  $\text{CH}_2\text{Cl}_2$ .

<sup>b</sup>In cyclohexane solution.

<sup>c</sup>In a  $\text{CDCl}_3$  solution.

$\text{PhC}=\text{C}(\text{C}_6\text{H}_4\text{-}p\text{-NO}_2)$ , containing an electron-withdrawing group in one of the two aromatic substituents, affords in refluxing THF the two  $\text{C}_4$ -hydrocarbyl clusters  $\text{Ru}_3(\text{CO})_9[\mu_3\text{-}\eta^3\text{-PhCCCC(H)Ph}][\mu_2\text{-NS(O)MePh}]$  (2) and  $\text{Ru}_3(\mu_2\text{-CO})_7[\mu_3\text{-}\eta^3\text{-PhC-}$

$\text{CCC(H)Ph}][\mu_3\text{-NS(O)MePh}]$  (3). The reaction solution also contains the two isomeric vinyl complexes  $\text{Ru}_3(\mu_2\text{-CO})_2(\text{CO})_6[\mu_2\text{-}\eta^2\text{-PhCC(H)(C}_6\text{H}_4\text{NO}_2)]$  (4), which are presumably intermediates in the formation of 2 and 3. The products 2, 3 and 4 can



Scheme 1.

be separated from the reaction mixture by thin-layer chromatography—however, **4** does not resolve into the two isomers **4a** and **4b** clearly distinguishable in the NMR spectrum of **4**.

Compounds **2**, **3** and **4** were characterized by their analytical and spectroscopic data, **2** and **3** also gave suitable crystals for X-ray structure analysis. The IR spectrum of **2** exhibits three  $\nu_{\text{CO}}$  absorptions corresponding to only terminal CO ligands, whereas the IR spectrum of **3** presents four bands assigned to the terminal CO ligands and one absorption at  $1805\text{ cm}^{-1}$  which can be attributed to the bridging CO group (Table 1). The  $^1\text{H}$  NMR spectra of both **2** and **3** are very similar, showing the same pattern of signals but differing in the chemical shifts, in accordance with the molecular structures of **2** and **3** (Table 1).

The constitution of **4** is proposed on the basis of the spectroscopic and analytical data: In the FAB mass spectrum, the molecular peak is found at  $m/z$  908 ( $^{102}\text{Ru}$ ); in addition a complete fragmentation series corresponding to the subsequent loss of eight CO ligands is observed, all ions presenting the characteristic  $\text{Ru}_3$  isotope pattern. The infrared spectrum of **4** (Table 1) displays a  $\nu_{\text{CO}}$  pattern almost identical to that of the vinyl cluster  $\text{Ru}_3(\mu_2\text{-CO})_2(\text{CO})_6[\mu_3\text{-NS(O)MePh}](\mu_2\text{-}\eta^1,\eta^2\text{-PhCH}_2\text{C}=\text{CH}_2)$  characterized by X-ray crystallography (Ref. [40], see preceding paper); we therefore assign the absorption at  $1828\text{ cm}^{-1}$

to two bridging carbonyl ligands, being located over the two ruthenium–ruthenium bonds which are not bridged by the vinyl ligand. The  $^1\text{H}$  NMR spectrum of **4** (Table 1) clearly reveals the presence of two isomers by two signals for the vinyl hydrogen ( $\delta$  6.015 and 6.237 ppm) and two signals for the methyl substituent on the sulfur atom ( $\delta$  3.192 and 3.348 ppm). This is also reflected in the  $^{13}\text{C}$  NMR spectrum of **4** which shows the signals for the methyl substituent on the sulfur atom ( $\delta$  45.6 and 48.4 ppm) and two singlets at  $\delta$  67.8 and 72.0 ppm for the alkenyl carbon atoms ( $\text{C}=\text{CH}$ ).

We interpret these findings by the presence of two isomers which differ only in the orientation of the  $\mu_2\text{-}\eta^2$ -vinyl ligand:  $\text{Ru}_3(\mu_2\text{-CO})_2(\text{CO})_6[\mu_2\text{-}\eta^2\text{-PhCC(H)-(C}_6\text{H}_4\text{NO}_2)][\mu_3\text{-NS(O)MePh}]$  (**4a**) and  $\text{Ru}_3(\mu_2\text{-CO})_2(\text{CO})_6[\mu_2\text{-}\eta^2\text{-(C}_6\text{H}_4\text{NO}_2)\text{CC(H)Ph}][\mu_3\text{-NS(O)MePh}]$  (**4b**) (Scheme 1), but it is not possible to assign the NMR signals unambiguously to **4a** or **4b**.

## 2.2. Molecular structure of $\text{Ru}_3(\text{CO})_9[\mu_3\text{-}\eta^3\text{-PhCCCC(H)Ph}][\mu_2\text{-NS(O)MePh}]$ (**2**)

The molecular structure of **2** was confirmed by a single crystal X-ray structure analysis. Suitable crystals of **2** were grown at  $4^\circ\text{C}$  from a mixture of  $\text{CH}_2\text{Cl}_2$  and hexane. The unit cell contains two independent

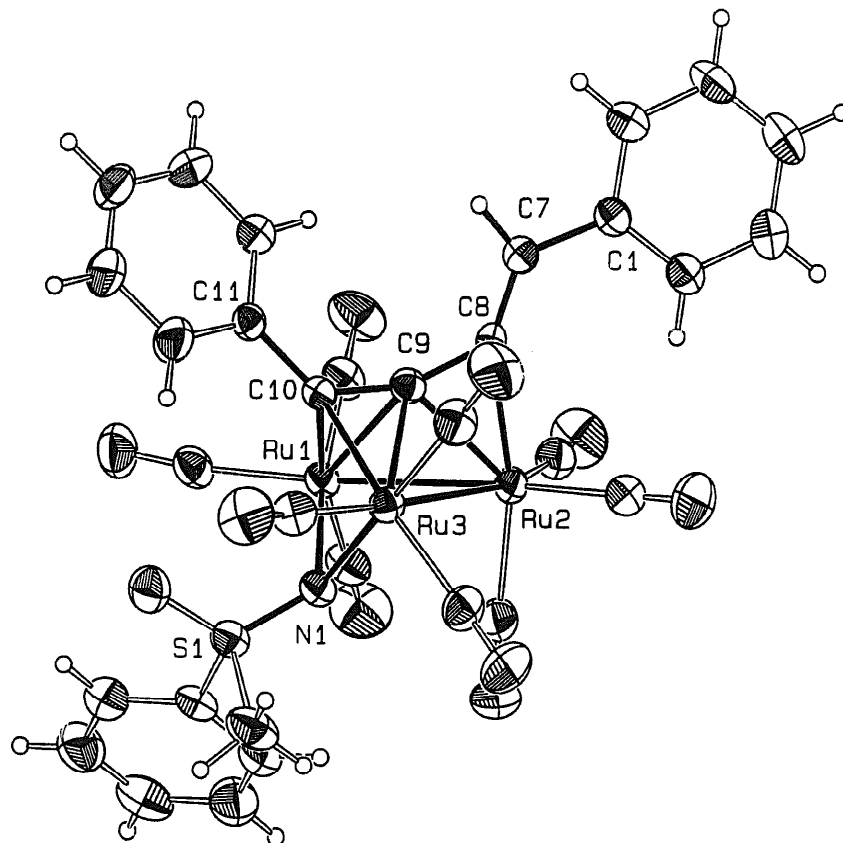


Fig. 1. ORTEP plot of **2** (Molecule A). Thermal ellipsoids are drawn at 40% of probability.

molecules of **2** which have the same constitution but differ in bond angles and bond lengths. The structure of the two molecules of **2** is presented in Figs. 1 and 2. Selected bond lengths and angles of the two molecules are listed in Table 2.

The organic fragment arising from the C–C coupling of two alkyne units is best described as a butenyne ligand  $\text{PhC}\equiv\text{C}-\text{C}=\text{C}(\text{H})\text{Ph}$ . Each of the three ruthenium atoms are bonded to three terminal CO groups. The nitrogen cap is bridging only the two ruthenium atoms Ru(1) and Ru(3) in a  $\mu_2$ -fashion [Ru(1)–N 2.166(5); Ru(3)–N 2.161(5) Å], in contrast to **1** where the nitrogen links the three metal centers in a  $\mu_3$ -mode. We also observe that in **2** the nitrogen–sulfur double bond is shorter [N(1)–S(1) 1.514(5) Å] than in **1** [N–S 1.566(7)], probably due to the coordination to only two metal atoms, the NS(O)MePh ligand still being a three-electron donor ligand. The  $\text{C}_4$  ligand is coordinated to the  $\text{Ru}_3$  framework by only three carbon atoms and acts as a five-electron ligand (Figs. 1 and 2). The carbon–carbon double bond of the vinyl part of the  $\text{C}_4$  ligand is not involved in the coordination. The carbon atom C(8) is  $\sigma$ -bonded to Ru(2) [Ru(2)–C(8) 2.095(6) Å] and donates one electron, whereas the C(9)–C(10) triple bond is  $\pi$ -bonding to both, Ru(1) and Ru(3) [Ru(1)–C(9) 2.339(5); Ru(1)–C(10) 2.234(6); Ru(3)–C(9) 2.326(6); Ru(3)–C(10) 2.202(5)] and acts as a four-electron donor. Compound **2** can be compared to  $\text{HOs}_3(\text{CO})_9(\mu_3-\eta^3-$

Table 2  
Selected bond lengths [Å] and bond angles [deg] for **2**

Molecule A		Molecule B	
C(7)–C(8)	1.328(8)	C(46)–C(47)	1.339(8)
C(7)–H(7)	0.98(6)	C(46)–H(46A)	0.99(5)
C(8)–C(9)	1.394(8)	C(47)–C(48)	1.383(8)
C(8)–Ru(2)	2.095(6)	C(47)–Ru(6)	2.082(6)
C(9)–C(10)	1.350(8)	C(48)–C(49)	1.341(8)
C(9)–Ru(2)	2.197(6)	C(48)–Ru(6)	2.207(6)
C(9)–Ru(3)	2.326(6)	C(48)–Ru(4)	2.342(6)
C(9)–Ru(1)	2.339(5)	C(48)–Ru(5)	2.358(6)
C(10)–C(11)	1.468(7)	C(49)–C(50)	1.483(8)
C(10)–Ru(3)	2.202(5)	C(49)–Ru(5)	2.187(6)
C(10)–Ru(1)	2.234(6)	C(49)–Ru(4)	2.212(6)
Ru(1)–Ru(2)	2.8644(7)	Ru(4)–Ru(6)	2.8570(7)
Ru(2)–Ru(3)	2.9030(7)	Ru(5)–Ru(6)	2.8908(8)
Ru(1)–Ru(3)	3.1703(2)	Ru(4)–Ru(5)	3.1654(2)
O(1)–S(1)	1.462(5)	O(2)–S(2)	1.461(5)
N(1)–S(1)	1.514(5)	N(2)–S(2)	1.516(5)
N(1)–Ru(3)	2.161(5)	N(2)–Ru(5)	2.163(5)
N(1)–Ru(1)	2.166(5)	N(2)–Ru(4)	2.170(5)
C(8)–C(7)–C(1)	129.2(6)	C(46)–C(47)–C(48)	134.4(6)
C(7)–C(8)–C(9)	133.5(5)	C(49)–C(48)–C(47)	162.0(6)
C(10)–C(9)–C(8)	158.4(6)	C(48)–C(49)–C(50)	130.5(5)
C(9)–C(10)–C(11)	131.7(5)	C(51)–C(50)–C(49)	122.0(6)

Estimated standard deviations in parentheses.

$\text{H}_2\text{CC}\equiv\text{C}-\text{Me}$ ), which is the only complex presenting the same CCC coordination mode, according to the interpretation of the spectroscopic data, since no crystal

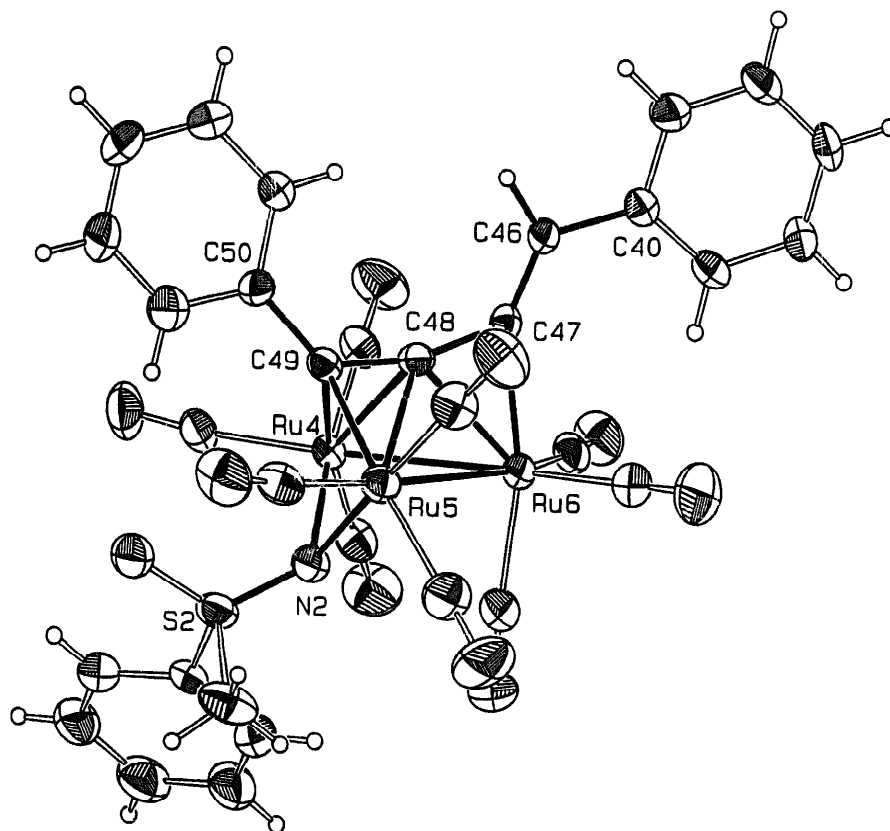


Fig. 2. ORTEP plot of **2** (Molecule B). Thermal ellipsoids are drawn at 40% of probability.

structure analysis is available [41]. The short distance between Ru(2) and C(9) [Ru(2)–C(9) 2.1972(1) Å] is presumably due to a geometric arrangement of the C<sub>4</sub> chain with respect to the Ru<sub>3</sub> core. This description of the C<sub>4</sub> ligand as a  $\sigma,\pi,\pi$ -donor is however, an oversimplification because of the mixing of the  $\sigma$  and  $\pi$  contributions of each metal-ligand interaction [42,43].

The electron count of **2** being 50e is in accordance with an open M<sub>3</sub> triangle. We therefore consider the Ru(1)···Ru(3) vector as an open edge, even if the distance is shorter [Ru(1)···Ru(3) 3.1703(2) Å] than in open Ru<sub>3</sub> clusters (average Ru···Ru 3.430 Å). The C(8)C(9)C(10) angle is 158.4°(6), confirming the description of a butenynyl fragment; for a allenyl (butatrienyl) moiety, the average CCC angle is normally between 138°(2) and 152°(1) [42].

### 2.3. Molecular structure of Ru<sub>3</sub>( $\mu_2$ -CO)(CO)<sub>7</sub>[ $\mu_3$ - $\eta^3$ -PhCCCC(H)Ph][ $\mu_3$ -NS(O)MePh] (**3**)

The molecular structure of **3** was confirmed by a X-ray structure analysis of a suitable crystal obtained by room temperature crystallization from a mixture of CH<sub>2</sub>Cl<sub>2</sub> and hexane. The molecular structure of **3** is depicted in Fig. 3, selected bond lengths and angles are presented in Table 3.

The three ruthenium atoms in **3** form an open tri-

Table 3  
Selected bond lengths [Å] and bond angles [deg] for **3**

C(8)–C(9)	1.407(5)	N(1)–Ru(1)	2.129(3)
C(8)–C(11)	1.497(5)	N(1)–Ru(3)	2.165(3)
C(8)–Ru(3)	2.227(4)	N(1)–Ru(2)	2.228(3)
C(8)–Ru(1)	2.314(4)	O(1)–S	1.445(3)
C(8)–Ru(2)	2.319(4)	Ru(1)–Ru(2)	2.7164(5)
C(9)–C(10)	1.336(6)	Ru(1)–Ru(3)	2.8290(5)
C(9)–Ru(3)	2.099(4)	Ru(2)–Ru(3)	3.4324(3)
C(9)–Ru(2)	2.250(4)		
C(10)–C(17)	1.326(6)	C(9)–C(8)–C(11)	121.1(3)
C(10)–Ru(2)	2.286(4)	C(10)–C(9)–C(8)	139.7(4)
C(17)–H(17)	0.99(4)	C(17)–C(10)–C(9)	150.5(4)
N(1)–S	1.554(3)	C(10)–C(17)–C(18)	122.4(4)

Estimated standard deviations in parentheses.

gle [Ru(1)–Ru(2) 2.7164(5); Ru(1)–Ru(3) 2.8290(5); Ru(2)···Ru(3) 3.4324(3) Å], all ruthenium–ruthenium distances being different. Two of the three ruthenium atoms, Ru(1) and Ru(2), are bonded to two terminal CO groups, whereas Ru(3) is bonded to three terminal CO ligands. A carbonyl group bridges the Ru(1)–Ru(2) edge and lies in the same plane as the metal framework (dihedral angle 175.7°). The position of the carbonyl ligand is not symmetrical between both ruthenium atoms, and C(29) is closer to Ru(1) than to Ru(2) [Ru(1)–C(29)

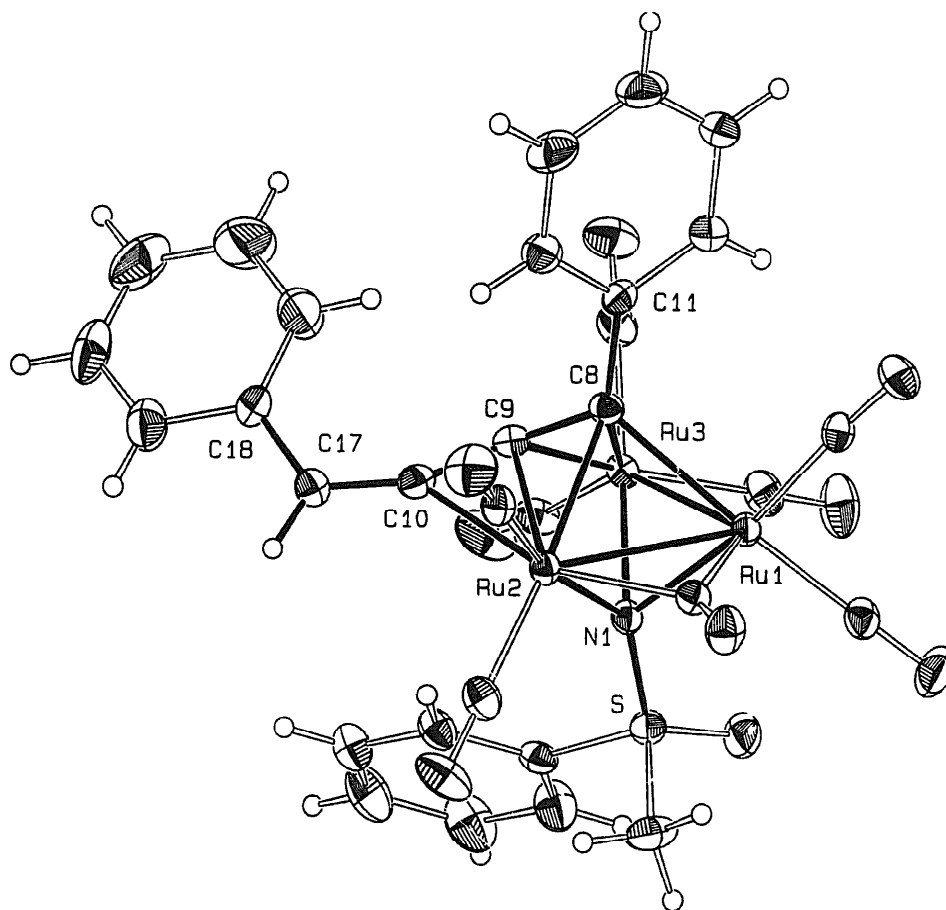


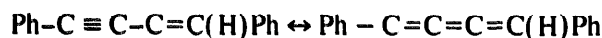
Fig. 3. ORTEP plot of **3**. Thermal ellipsoids are drawn at 40% of probability.

2.0208(2); Ru(2)–C(29) 2.1199(2) Å]. We also observed that the nitrogen cap is asymmetrically coordinated to the Ru<sub>3</sub> core, all the Ru–N bond lengths being different [Ru(1)–N 2.129(3); Ru(2)–N 2.228(3); Ru(3)–N 2.165(3) Å].

The coordination of the C<sub>4</sub> fragment in **3** is different from that in **2**, inasmuch as it is best described as butatrienyl ligand PhC=C=C=C(H)Ph, although it also acts as a 5e-donor and it is also coordinated by three carbon atoms. The double bond C(10)=C(17) does not interact with any ruthenium as in **2** [Ru(1)–C(17) 5.5385(5); Ru(2)–C(17) 3.3886(4); Ru(3)–C(17) 4.2806(5) Å]. In a first approximation, we can consider the C<sub>4</sub> ligand to be  $\sigma$ -bonded by C(8) to Ru(1) and Ru(2) ('shared  $\sigma$ -bond') [Ru(1)–C(8) 2.3136(2); Ru(2)–C(8) 2.3186(2) Å] and  $\pi$ -bonded by C(8)=C(9) to Ru(3) [Ru(3)–C(8) 2.2275(2); Ru(3)–C(9) 2.0989(3)], and  $\pi$ -bonded by C(9)=C(10) to Ru(2) [Ru(2)–C(9) 2.2501(2); Ru(2)–C(10) 2.2857(3)]. A comparison of the butatrienyl ligand in **3** with allenyl complexes such as Ru<sub>3</sub>(CO)<sub>9</sub>[ $\mu_3$ - $\eta^3$ -EtCCC(H)CH<sub>3</sub>] [44] or Ru<sub>3</sub>(CO)<sub>8</sub>[ $\mu_3$ - $\eta^3$ -CH<sub>2</sub>CC('Pr)]( $\mu_2$ -PPh<sub>2</sub>) [45] reveals the C(8)C(9)C(10) angle of 139.7°(4) to be similar to the corresponding allenyl angles of 143.7°(3) [45] or 142.3°(6) [44].

### 3. Discussion

Despite the different coordination of the C<sub>4</sub> ligand in **2** and **3**, the nature of the C<sub>4</sub> hydrocarbyl fragment is the same. The two ligands can in fact be considered as two mesomeric representations of the same hydrocarbyl radical.



In both, **2** and **3**, the C<sub>4</sub> hydrocarbyl ligand is coordinated to the Ru<sub>3</sub> framework by only three carbon atoms, the C=C(H)Ph double bond of the ligand is not interacting with a metal atom. The main difference between clusters **2** and **3** is the electron-deficient character of **3** (48e), while **2** is electron-precise comprising 50e.

It is interesting to note that the C<sub>4</sub> hydrocarbyl ligands in **2** and **3**, formed by a carbon–carbon coupling of two C<sub>2</sub> units, can obviously not be generated from the corresponding C<sub>4</sub> hydrocarbon. The reaction of Ru<sub>3</sub>(CO)<sub>12</sub> with the enyne PhC≡C–CH=C(H)Ph leads to the formation of three isomeric binuclear complexes Ru<sub>2</sub>(CO)<sub>6</sub>[C<sub>4</sub>Ph<sub>2</sub>(CH=CHPh)<sub>2</sub>] as well as to two trinuclear clusters Ru<sub>3</sub>(CO)<sub>6</sub>( $\mu$ -CO)<sub>2</sub>[C<sub>4</sub>Ph<sub>2</sub>(CH=CHPh)<sub>2</sub>] and Ru<sub>3</sub>(CO)<sub>8</sub>[ $\mu_3$ - $\eta^1, \eta^1, \eta^4, \eta^2$ -C<sub>4</sub>Ph<sub>2</sub>(CH=CHPh)<sub>2</sub>], none of which contains a C<sub>4</sub> hydrocarbyl ligand [46].

The isolation and characterisation of the vinyl complex **4** (two isomers **4a** and **4b**) from the reaction mixture would suggest that the C–C coupling of the two

alkyne units on the Ru<sub>3</sub> core implies insertion of the alkyne into the ruthenium-hydrido bond in **1** to give a vinyl complex followed by the coordination of a second alkyne to give an alkyne-vinyl complex in which the C–C coupling takes place. However, the reaction of **4** (isomer mixture) with *para*-nitrotolane under the same reaction conditions did not yield **2** or **3**. We therefore rule out the intermediacy of **4a** or **4b** in the formation of **2** and **3**.

### 4. Experimental

All manipulations were carried out in a nitrogen atmosphere, using standard Schlenk techniques. The organic solvents were distilled over appropriate drying agents [47], saturated with nitrogen prior to use. The NMR spectra were recorded using a Varian Gemini 200 BB instrument or a Bruker AMX 400 at 297 K. The IR spectra were recorded using a Perkin-Elmer FTIR 1720X spectrophotometer (4000–400 cm<sup>-1</sup>). Microanalytical data were obtained from the Mikroelementaranalytisches Laboratorium der ETH Zürich. The mass spectrum was recorded by Professor T.A. Jenny, University of Fribourg (Switzerland). The starting compounds ( $\mu_2$ -H)Ru<sub>3</sub>(CO)<sub>9</sub>[ $\mu_3$ -NS(O)MePh] (**1**) [48] and PhC=C(C<sub>6</sub>H<sub>4</sub>-*p*-NO<sub>2</sub>) were synthesized according to published methods [49]. Methyl phenyl sulfoximine (racemate) was obtained from Professor Carsten Bolm, RWTH Aachen (Germany).

#### 4.1. Reaction of ( $\mu_2$ -H)Ru<sub>3</sub>(CO)<sub>9</sub>[ $\mu_3$ -NS(O)MePh] (**1**) with PhC=C(C<sub>6</sub>H<sub>4</sub>-*p*-NO<sub>2</sub>)

A solution of ( $\mu_2$ -H)Ru<sub>3</sub>(CO)<sub>9</sub>[ $\mu_3$ -NS(O)MePh] (**1**) (200 mg, 0.28 mmol) and PhC≡C(C<sub>6</sub>H<sub>4</sub>-*p*-NO<sub>2</sub>) (188 mg, 0.84 mmol) in THF (40 ml) was heated in a pressure Schlenk tube to 50°C for 6 h. After evaporation of the solvent the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and separated by thin-layer chromatography (first: aluminum oxide, CH<sub>2</sub>Cl<sub>2</sub>/hexane 1:1; second: silica gel CH<sub>2</sub>Cl<sub>2</sub>/cyclohexane 1:1). From the first main band (red) **2** was extracted with CH<sub>2</sub>Cl<sub>2</sub> and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane at 4°C, **3** was extracted from the second main band (red–orange) with CH<sub>2</sub>Cl<sub>2</sub> and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane at room temperature. The third main band (orange) contained **4** as the isomer mixture **4a** and **4b**, which was extracted with CH<sub>2</sub>Cl<sub>2</sub> and obtained as a brownish powder. All compounds were dried in vacuo. **2**: yield 36 mg, 14%. Anal. Found **2**: C, 43.94; H, 2.22; N, 1.78. C<sub>32</sub>H<sub>19</sub>NO<sub>10</sub>SRu<sub>3</sub>(0.5 C<sub>6</sub>H<sub>14</sub>), Calc. C, 43.98; H, 2.74; N, 1.47%. **3**: yield 27 mg, 11%. Anal. Found **3**: C, 45.34; H, 2.95; N, 1.53. C<sub>31</sub>H<sub>19</sub>NO<sub>9</sub>SRu<sub>3</sub>(0.75 C<sub>6</sub>H<sub>14</sub>), Calc. C, 45.33; H, 2.95; N, 1.47%. **4**: yield 17 mg, 7%. Anal. Found **4**: C, 44.34;

Table 4  
Crystallographic and refinement data for **2**, **3**

Compound	<b>2</b>	<b>3</b>
Empirical formula	C <sub>32</sub> H <sub>19</sub> NO <sub>10</sub> Ru <sub>3</sub> S	C <sub>31</sub> H <sub>19</sub> NO <sub>9</sub> Ru <sub>3</sub> S · CH <sub>2</sub> Cl <sub>2</sub>
Formula weight (g mol <sup>-1</sup> )	912.79	969.71
Temperature (K)	293(2)	293(2)
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>a</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> , <i>b</i> , <i>c</i> (Å)	19.649(2), 29.004(2), 11.7751(8)	10.0921(11), 16.326(2), 21.525(3)
$\alpha$ , $\beta$ , $\gamma$ (°)	90, 90.026(7), 90	90, 99.763(12), 90
Volume (Å <sup>3</sup> )	6710.5(10)	3495.1(7)
<i>Z</i>	8	4
<i>D</i> <sub>calc</sub> /g cm <sup>-3</sup>	1.807	1.843
Absorption coefficient (Mo K $\alpha$ , mm <sup>-1</sup> )	1.306	1.397
<i>F</i> (000)	3568	1896
Crystal size	0.57 × 0.53 × 0.30	0.53 × 0.30 × 0.30
$\theta$ Scan range (°)	2.07 to 25.50	2.11 to 25.52
<i>h</i> , <i>k</i> , <i>l</i> ranges	-23 to 23, 0 to 35, 0 to 14	-12 to 12, 0 to 19, 0 to 26
Reflections collected	12476	6517
Independent reflections	12476	6517
Reflections observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	10047	5833
Data/restraints/parameters	12473/0/936	6510/0/455
Goodness of fit on <i>F</i> <sup>2</sup>	1.155	1.144
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0492, <i>wR</i> 2 = 0.0856	<i>R</i> 1 = 0.0322, <i>wR</i> 2 = 0.0742
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0691, <i>wR</i> 2 = 0.0930	<i>R</i> 1 = 0.0386, <i>wR</i> 2 = 0.0804
Largest diff. peak and hole (e Å <sup>-3</sup> )	1.054 and -0.473	0.885 and -0.444
Empirical absorption correction	DIFABS	-
Transmission factors: min/max	0.758/1.156	-

H, 3.27; N, 2.91. C<sub>29</sub>H<sub>18</sub>N<sub>2</sub>O<sub>11</sub>SRu<sub>3</sub>(1.5 C<sub>6</sub>H<sub>14</sub>), Calc. C, 44.92; H, 3.57; N, 2.75%. Mass spectrum (FAB) *m/z*: 4 908 (M<sup>+</sup>) (<sup>102</sup>Ru).

#### 4.2. X-ray structure analysis of **2** and **3**

Suitable crystals of **2**, **3**, were obtained as indicated in Section 4. Intensity data were collected on a Stoe-Siemens AED2 4-circle diffractometer at room temperature (Mo-K $\alpha$  graphite monochromated radiation,  $\lambda$  = 0.71073 Å;  $\omega/2\theta$  scans). Table 4 summarizes the crystallographic and selected experimental data for **2** and **3**. The structures were solved by direct methods using the program SHELXS-86 [50]. The refinement, using weighted full matrix least-square on *F*<sup>2</sup>, was carried out using the program SHELXL-93 [51]. For **2**, an empirical absorption correction was applied using [DIFABS] [52]. Complex **3** crystallizes with a molecule of CH<sub>2</sub>Cl<sub>2</sub> per unit cell. The hydrogen atoms of the C<sub>4</sub> hydrocarbyl chains of **2** and **3** were located from difference maps and refined isotropically. The methyl, and phenyl hydrogens of **2** and **3** were included in calculated positions and refined as riding atoms using the SHELXL 93 default parameters. The figures were drawn with ZORTEP [53] (thermal ellipsoids, 40% probability level). Full tables of atomic parameters and bond lengths and angles may be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cam-

bridge CB2 1EZ (UK) on quoting the full journal citation.

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