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Triruthenium clusters containing vinyl ligands: synthesis and structure of $Ru_3(\mu_2\text{-}CO)_2(CO)_6[\mu_3\text{-}NS(O)MePh](\mu_2\text{-}\eta^1,\eta^2\text{-}PhCH_2C{=}CH_2)$, $Ru_3(\mu_2\text{-}CO)(CO)_7[\mu_3\text{-}NS(O)MePh](\mu_3\text{-}\eta^1,\eta^2\text{-}Pr^nC{=}CHPr^n)$, $Ru_3(\mu_2\text{-}CO)(CO)_7[\mu_3\text{-}NS(O)MePh](\mu_3\text{-}\eta^1,\eta^2\text{-}PhC{=}CHBu^n)$, and $(\mu_2\text{-}H)Ru_3(CO)_6(\mu_2\text{-}\eta^1,\eta^2\text{-}PhC{=}CHPh)(\mu_3\text{-}\eta^1,\eta^2\text{-}PhC{\equiv}CPh)[\mu_3\text{-}\eta^1,\eta^2\text{-}NS(O)Me(C_6H_4)]$

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Abstract

The electron-deficient cluster $(\mu_2\text{-}H)Ru_3(CO)_9[\mu_3\text{-}NS(O)MePh]$ (**1**) reacts with the terminal alkyne $PhCH_2C{\equiv}CH$ to give the vinyl complex $Ru_3(\mu_2\text{-}CO)_2(CO)_6[\mu_3\text{-}NS(O)MePh](\mu_2\text{-}\eta^1,\eta^2\text{-}PhCH_2C{=}CH_2)$ (**2**). The analogous reaction with internal alkynes ($RC{\equiv}CR'$) affords the clusters $Ru_3(\mu_2\text{-}CO)(CO)_7[\mu_3\text{-}NS(O)MePh](\mu_3\text{-}\eta^1,\eta^2\text{-}RC{=}CHR')$ (**3**: R = R′ = Pr^n; **4**: R = Ph; R′ = Bu^n) in which the vinyl ligand has opened a Ru–Ru bond upon coordination the Ru_3 framework. In the case of diphenylacetylene, reaction with two equivalents of the alkyne, yields the vinyl–alkyne cluster $(\mu_2\text{-}H)Ru_3(CO)_6(\mu_2\text{-}\eta^1,\eta^2\text{-}PhC{=}CHPh)(\mu_3\text{-}\eta^1,\eta^2\text{-}PhC{\equiv}CPh)[\mu_3\text{-}\eta^1,\eta^2\text{-}NS(O)Me(C_6H_4)]$ (**5**) with *ortho*-metallation of the phenyl substituent of the sulfoximido cap. © 1997 Elsevier Science S.A.

Keywords: Clusters; Ruthenium; Alkynes; Vinyl ligands; Crystal structures

1. Introduction

The vinyl ligand, $-CH{=}CH_2$, and its derivatives have received much attention in coordination chemistry because of the synthetic potential of this function for vinylation processes such as the Heck Reaction [1]. Cluster complexes containing vinyl ligands have been discussed [2] as intermediates in catalytic processes such as alkene isomerisation [3], alkene hydrogenation [4], alkyne hydrogenation [5–7], and alkyne–alkene codimerization [8].

There are several coordination modes of the vinyl ligand in cluster chemistry, and for trinuclear clusters, three types of vinyl coordination have been found so far (Scheme 1). If the vinyl group is coordinated in a terminal fashion ('end-on') to the metal center, it is only σ-bound and acts as one-electron donor (type A). Only one example of this type is reported in the literature: the complex $Ru_3(CO)_9(\mu_3\text{-}ampy)(\eta^1\text{-}PhCCHPh)$ (ampyH = 2-amino-6-methylpyridine) was fully characterized [5]. Unfortunately, no structural information is available for this complex, but the η^1-coordination is confirmed by the NMR data. This compound is only accessible from the corresponding $\mu_2\text{-}\eta^1,\eta^2$-vinyl complex $Ru_3(CO)_8(\mu_3\text{-}ampy)(\mu_2\text{-}\eta^1,\eta^2\text{-}PhCCHPh)$ by reaction with carbon monoxide, the latter complex being an example for type B (π-'side-on') [5]. If the vinyl ligand is coordinated in a $\mu_2\text{-}\eta^1,\eta^2$-fashion (σ-'end-on' to one metal center and π-'side-on' to another metal center) according to type B, it acts as a three-electron

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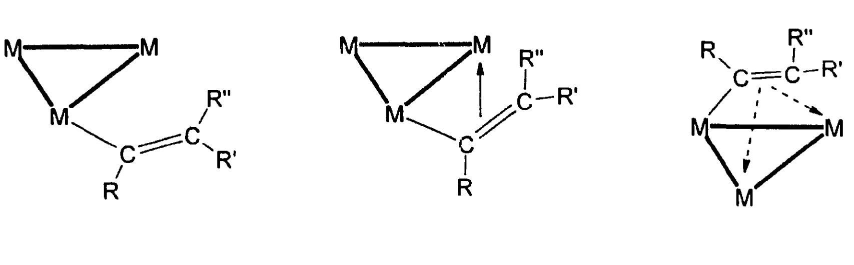


(A) (B) (C)

Scheme 1.

donor. Numerous examples of this type are known, the first compounds to be characterized being (μ_2-H)$Os_3(CO)_9$(μ_2-η^1,η^2-CHCHR) (R = Ph, Me, Et, *t*Bu) and (μ_2-H)$Os_3(CO)_9$(μ_2-η^1,η^2-CRCHR′) (R = Ph, R′ = Ph, Me, Et) [9]. Complexes of this type are accessible either by alkyne insertion into metal–hydrogen bonds or by C–H activation of an alkene on a metal cluster [10].

In type C, the vinyl ligand, while still being a three-electron donor, is coordinated in a μ_3-η^1,η^2-fashion (σ-'end-on' to one metal center and π-'side-one' to the other two metal centers). This coordination has been found in (μ_2-H)$Os_3(CO)_{10}$(μ_3-η^1,η^2-CF_3CCHCF_3) [11,12] and in (η^5-C_5Me_5)$WRu_2(CO)_7$(μ_2-NPh)(μ_3-η^1,η^2-CF_3CCHCF_3) [13]. The complex $Ru_3(CO)_8$(μ_3-η^1,η^2-$HNNMe_2$)(μ_3-η^1,η^2-$PhCCH_2$) [14] can be classified as type C, in as much as the vinyl group also acts as a three-electron donor coordinated to the three metal centres in a μ_3-η^1,η^2-fashion, but differs in as much as the vinyl cap bridges an open Ru_3 framework and not a closed trinuclear metal core.

In this paper, we report the synthesis and structural characterization of some new trinuclear vinyl complexes by the reaction of the electron-deficient cluster (μ_2-H)$Ru_3(CO)_9$[μ_3-NS(O)MePh] [15] with terminal and internal alkynes.

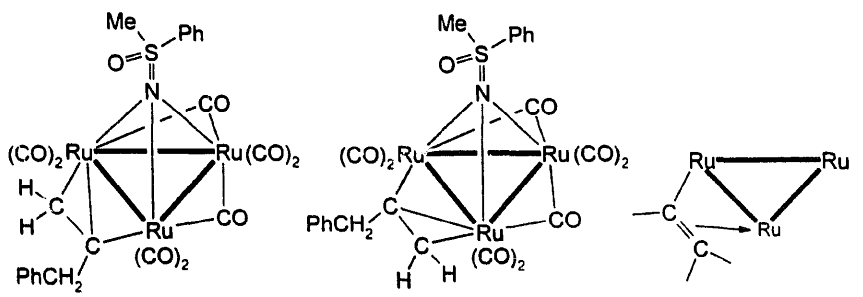
2. Results and discussion

2.1. Reaction of (μ_2-H)$Ru_3(CO)_9$[μ_3-NS(O)MePh] (1) with $PhCH_2C\equiv CH$

The thermal reaction between the electron-deficient cluster (μ_2-H)$Ru_3(CO)_9$[μ_3-NS(O)MePh] (1) [15] and

$$HRu_3(CO)_9[NS(O)MePh] + PhCH_2\text{-}C\equiv CH \longrightarrow Ru_3(CO)_8[PhCH_2C{=}CH_2][NS(O)MePh] + CO$$

(1) (2)



(2a) (2b)

Scheme 2.

Table 1
IR[a] and NMR[b] data of the complexes **2–5**

Complexes		δ
2a	2065(w), 2052(w), 2036(s), 2010(s), 1998(m), 1984(m), 1941(m), 1823(m)	3.25 (CH_3) s; 3.50 (C=CH*H*) s; 4.42 (C=C*H*H) s; 7–8 (Ph) m; 4.486 (PhCH*H*) d; $^2J_{H-H}$ = 13.2 Hz; 3.28 (PhC*H*H) d, $^2J_{H-H}$ = 13.2 Hz
2b	2066(w), 2053(w), 2038(s), 2012(s), 2000(m), 1985(m), 1946(m), 1826(m)	3.06 (CH_3) s; 3.99 (C=CH*H*) s; 4.20 (C=C*H*H) s; 7–8 (*Ph*) m; 4.51 (PhCH*H*) d; $^2J_{H-H}$ = 13.2 Hz; 3.49 (PhC*H*H) d, $^2J_{H-H}$ = 13.2 Hz
3[c]	2060(w), 2031(s), 2009(s), 1994(m), 1979(m), 1965(w), 1945(m), 1823(w)	2.59, 3.09, 3.26 (CH_3) s; 5.165, 4.95 (C=C*H*Pr^n) t, $^3J_{H-H}$ = 6 Hz; 5.05 (C=C*H*Pr^n) t; $^3J_{H-H}$ = 4 Hz; 0.7–3.1(*Pr^n*C=H*Pr^n*) m; 7.70 (Ph) m
4[c]	2061(w), 2049(vw),2030(s), 2012(s), 1995(m), 1968(w), 1947(m), 1875(vw), 1851(vw), 1826(w)	2.68, 3.10, 3.33 (CH_3) s; 5.55, 5.28 (C=C*H*Bu^n) t, $^3J_{H-H}$ = 6.3 Hz; 0.89, 0.91, 1.03 (–C=CH$(CH_2)_3CH_3$) t; $^3J_{H-H}$ = 7.3 Hz; 1.3–2.4 (C=CH$(CH_2)_3CH_3$) m; 7.50 (*Ph*) m
5[d]	2049(w), 2032(s), 2016(s), 1983(m), 1958(w)	−8.37 (Ru–*H*–Ru) s; 3.18 (CH_3) s; 6.62 (PhC=C*H*Ph) s; 6.7–7.8 (*Ph*) m

[a] In cyclohexane (**2–4**) or dichloromethane (**5**) solution.
[b] In a $CDCl_3$ solution.
[c] Three isomers in solution.

the terminal alkyne $PhCH_2C{\equiv}CH$ in refluxing tetrahydrofuran affords within four hours the vinyl complex $Ru_3(\mu_2\text{-}CO)_2(CO)_6[\mu_3\text{-}NS(O)MePh](\mu_2\text{-}\eta^1,\eta^2\text{-}PhCH_2C{=}CH_2)$ (**2**). Two isomers of **2** were separated from the reaction mixture by chromatographic methods (Scheme 2).

Both isomers were characterized by their analytical and spectroscopic data. While **2a** gave suitable crystals for the X-ray structure determination, **2b** did not crystallize, but there is spectroscopic evidence for **2b** being an isomer of **2a**. On the basis of the NMR and IR data, we believe that the $\mu_2\text{-}\eta^1,\eta^2$-vinyl ligand in **2b** is coordi-

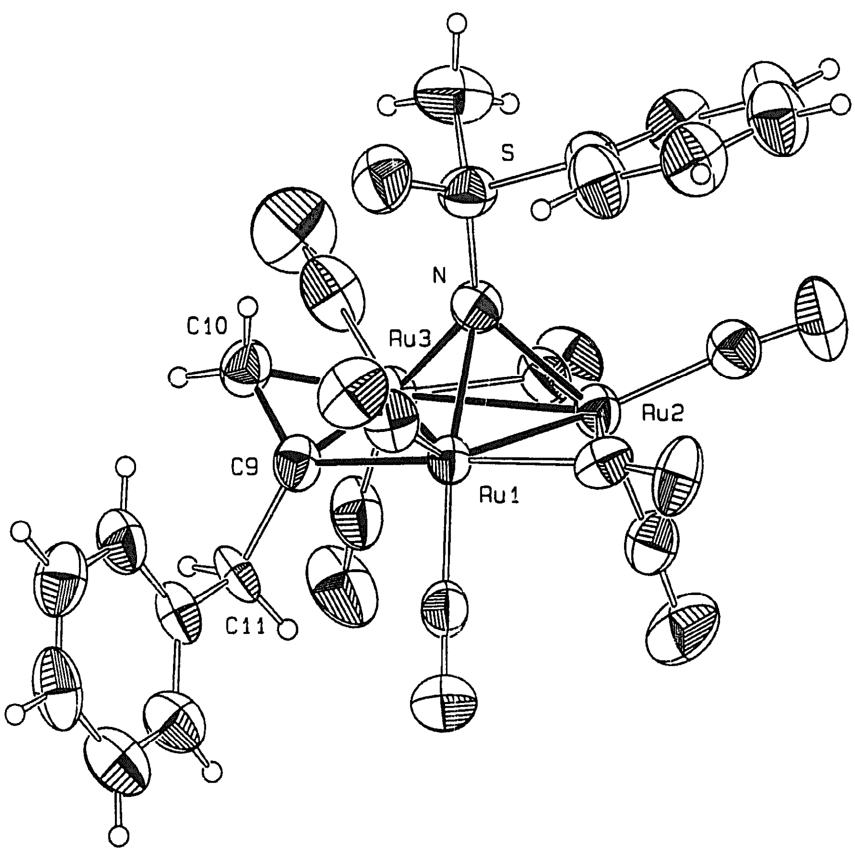


Fig. 1. ORTEP plot of **2a**. Thermal ellipsoids are drawn at 40% of probability.

nated in an inverted fashion with respect to **2a**. The IR spectra of the two isomers **2a** and **2b** in cyclohexane are very similar in the carbonyl region, both presenting six bands in the region of terminal CO vibrations and one absorption at 1823 cm^{-1} for **2a** and 1826 cm^{-1} for **2b**, which is attributed to bridging carbonyl ligands (Table 1). The ^1H NMR spectra of **2a** and **2b** also show a very similar pattern of signals, but differ in the chemical shifts (Table 1). In both cases, the hydride signal of the starting compound **1** at δ − 15.84 ppm has disappeared, indicating the insertion of the carbon–carbon triple bond into the M–H bond. A multiplet between δ 7.0 and 8.0 ppm can be assigned to the phenyl protons. The two hydrogen atoms of the benzyl group are non-equivalent and resonate as two doublets (**2a**: δ 4.42 and 3.50 ppm; **2b**: δ 4.51 and 3.49 ppm, $^2J_{HH}$ 13.2 Hz]. The vinyl protons appear as two singlets (**2a**: δ 4.49 ppm and δ 4.28 ppm; **2b**: δ 4.20 and δ 3.99 ppm). The methyl group of the nitrogen cap is observed at higher field (**2a**: δ 3.25 ppm, **2b**: δ 3.06 ppm) than in **1** (δ 3.36 ppm).

The ^{13}C {^1H} spectrum of **2a** at low temperature (−80°C) in CD_2Cl_2 shows the two bridging carbonyls ligands at δ 238 and 227 ppm, and the six terminal carbonyl signals at δ 190, 192, 196, 199, 199.6, 205 ppm. The two carbon atoms of the vinyl group are found at δ 60.7 and 59 ppm, indicating these two carbon atoms are more sp^3 than sp^2 hybridized, due to the back-bonding from the ruthenium d orbitals.

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

C(9)–C(10)	1.39(2)
C(9)–C(11)	1.57(2)
C(9)–Ru(1)	2.120(12)
C(9)–Ru(3)	2.231(12)
C(10)–Ru(3)	2.272(13)
N–S	1.559(10)
N–Ru(2)	2.158(10)
N–Ru(3)	2.170(9)
N–Ru(1)	2.166(10)
S–O(9)	1.481(10)
Ru(1)–Ru(2)	2.698(1)
Ru(2)–Ru(3)	2.703(1)
Ru(1)–Ru(3)	2.797(1)
C(10)–C(9)–C(11)	117.5(11)

Estimated standard deviations in parentheses.

2.2. *Molecular structure of $Ru_3(\mu_2\text{-}CO)_2(CO)_6[\mu_3\text{-}NS(O)MePh](\mu_2\text{-}\eta^1,\eta^2\text{-}PhCH_2C{=}CH_2)$ (2a)*

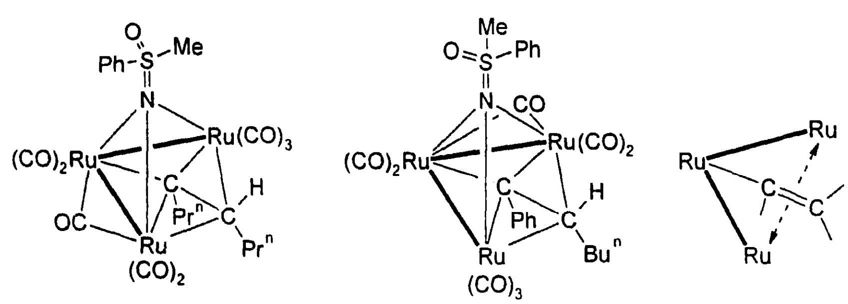
The molecular structure of **2a** was confirmed by single-crystal X-ray analysis. Suitable crystals of **2a** were obtained by crystallization at 20°C from a mixture of cyclohexane and pentane. Fig. 1 shows the molecular

$HRu_3(CO)_9[NS(O)MePh]$ + RC≡CR' ⟶

(**1**)

$Ru_3(CO)_8[RC{=}CHR'][NS(O)MePh]$ + CO

(**3**: R = R' = Pr^n; **4**: R = Ph; R' = Bu^n)



(**3**) (**4**)

Scheme 3.

structure of **2a**; selected bond lengths and angles are presented in Table 2.

The three ruthenium atoms form a closed isoceles triangle [Ru(1)–Ru(2) 2.698(1); Ru(1)–Ru(3) 2.797(1); Ru(2)–Ru(3) 2.703(1) Å]. Each ruthenium atom is bonded to two terminal CO groups and to the nitrogen cap, as in **1** [15]. Two of the three ruthenium–ruthenium bonds, Ru(1)–Ru(2) and Ru(2)–Ru(3), are bridged by CO groups which are in the same plane as the metal framework, while the Ru(1)–Ru(3) edge is bonded by the vinyl ligand. The vinyl group is almost perpendicular to the metal plane [C(9)–C(10) ⊥ Ru(1)–Ru(3): 98.5°]. The carbon atom C(9) occupies an equatorial site and is σ-bonded to Ru(1). Due to the coordination to the Ru(1)–Ru(3) bond, the C(9)–C(10) double bond is longer (1.39(2) Å) than a free carbon–carbon double bond (average 1.316Å) [16]. The nitrogen cap is further away from the metal plane in **2a** than in complex **1**, the average Ru–N distances in **2a** being 2.16 Å, whereas in **1** they are 2.11 Å. At present we have no other explanation for this elongation.

The structure of **2a** compares well with previously reported vinyl complexes, for example $Ru_3(CO)_8[\mu_3-\eta^2-N(Me)_2NH](\mu-\eta^2-PhC{=}CH_2)$ [14]. However, while all these clusters present the expected electron count of 48 e, the complexes **2a** and **2b** contain only 46 e and are electron-deficient.

2.3. Reaction of $(\mu_2-H)Ru_3(CO)_9[\mu_3-NS(O)MePh]$ (1) with $RC{\equiv}CR'$ (3: $R = R' = Pr^n$; 4: $R = Ph$; $R' = Bu^n$)

With internal alkynes, $(\mu_2-H)Ru_3(CO)_9[\mu_3-NS(O)MePh]$ (**1**) reacts differently in refluxing THF: with an excess of $Pr^nC{\equiv}CPr^n$ or $PhC{\equiv}CBu^n$, the vinyl complexes $Ru_3(\mu_2-CO)(CO)_7[\mu_3-NS(O)MePh](\mu_3-\eta^1,\eta^2-Pr^nC{=}CHPr^n)$ (**3**) and $Ru_3(\mu_2-CO)(CO)_7[\mu_3-NS(O)MePh](\mu_3-\eta^1,\eta^2-PhC{=}CHBu^n)$ (**4**) are obtained in good yields (Scheme 3).

The IR spectra of **3** and **4** (Table 1) show the same carbonyl pattern with seven bands in the region of terminal carbonyl groups and one absorption at 1823 cm^{-1} (**3**) and 1826 cm^{-1} (**4**) which is assigned to a bridging carbonyl ligand. The ^1H NMR spectra of **3** and **4** in $CDCl_3$ are very complicated, indicating the presence of several isomers in solution (Table 1): while the crystals of **3** and **4** contain only one isomer (see Section 2.4 below), the solution in $CDCl_3$ contains, in both cases, three isomers which can be recognized by the different singlets for the methyl substituents at the sulfur atom and by three triplets for the vinyl proton. Two of these three triplets are well resolved and with a 1:1 ratio, having a coupling constant of 6.0 Hz (**3**), or 6.3 Hz (**4**), whereas the third triplet is not well resolved. A multiplet centered around δ 7.70 ppm (**3**) or δ 7.50 ppm (**4**) is caused by the various phenyl protons. In the case of **4**, the three isomers give rise to three triplets at δ 1.03, 0.95, 0.89 ppm which are assigned to the methyl groups of the butyl chains.

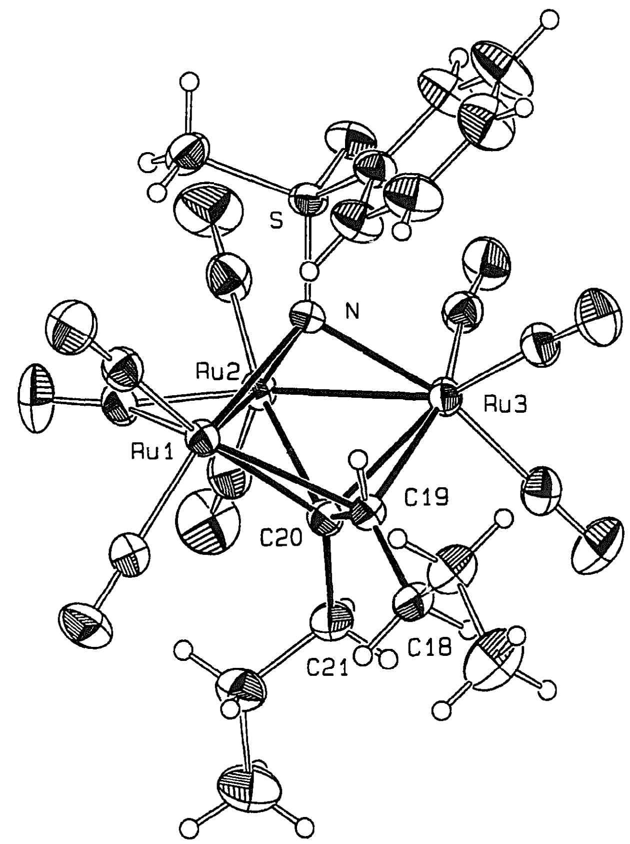


Fig. 2. ORTEP plot of **3**. Thermal ellipsoids are drawn at 40% of probability.

2.4. Molecular structure of $Ru_3(\mu_2-CO)(CO)_7[\mu_3-NS(O)MePh](\mu_3-\eta^1,\eta^2-RC{=}CHR')$ (3: $R = R' = Pr^n$; 4: $R = Ph$; $R' = Bu^n$)

Suitable crystals of **3** and **4** were obtained at −18°C from hexane or a mixture of CH_2Cl_2 and hexane, respectively. The molecular structure of **3** is depicted in Fig. 2, and that of **4** in Fig. 3. Selected bond lengths and angles of both compounds are presented in Tables 3 and 4. Both **3** and **4** have the same overall structure, showing the same carbonyl and vinyl coordination. The three ruthenium atoms form an open triangle with three different ruthenium–ruthenium distances [**3**: Ru(1)–Ru(2) 2.690(1), Ru(1) ··· Ru(3) 3.542(2), Ru(2)–Ru(3) 2.776(1) Å; **4**: Ru(1)–Ru(2) 2.6786(13), Ru(1) ··· Ru(3) 3.5394(7), Ru(2)–Ru(3) 2.7649(13) Å]. 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 groups. A carbonyl group bridges the Ru(1)–Ru(2) edge and lies in the same plane as the metal framework: probably due to this linkage, this bond is shorter than the other ruthenium–ruthenium bonds.

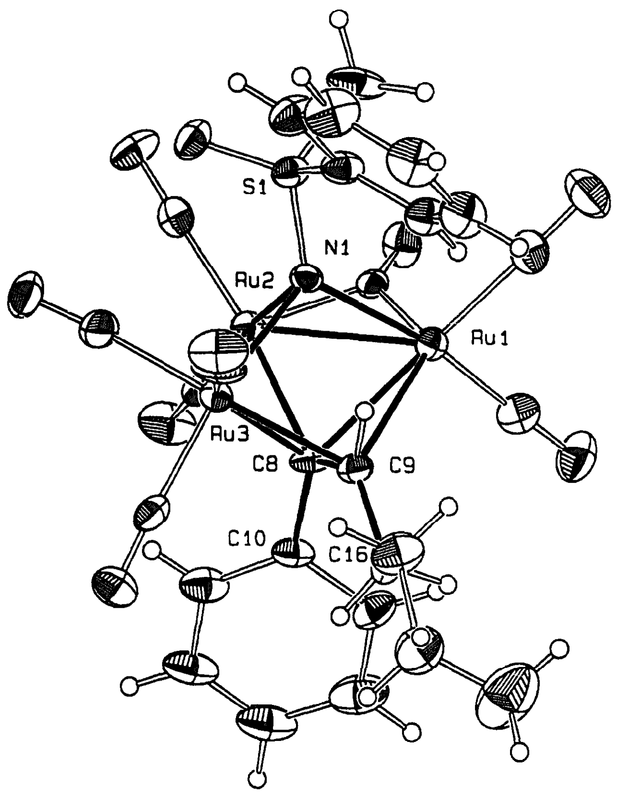


Fig. 3. ORTEP plot of **4**. Thermal ellipsoids are drawn at 40% of probability.

We also observe that in **3** and **4** the nitrogen cap is further away from the Ru_3 triangle than in **1**, all the Ru–N bond lengths being different [**3**: Ru(1)–N 2.23(3), Ru(2)–N 2.14(3), Ru(3)–N 2.19(3) Å; **4**: Ru(1)–N 2.224(9), Ru(2)–N 2.128(9), Ru(3)–N 2.156(8) Å], in contrast to **2**. The vinyl ligand, being a three-electron donor, is coordinated in a similar fashion as a μ_3-η^1,η^2-alkynyl group which is a five-electron donor.

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

C(19)–C(20)	1.425(6)
C(18)–C(19)	1.510(5)
C(20)–C(21)	1.529(5)
C(20)–Ru(3)	2.235(4)
C(20)–Ru(2)	2.241(4)
C(20)–Ru(1)	2.329(4)
C(19)–Ru(3)	2.243(4)
C(19)–Ru(1)	2.427(4)
C(19)–H(19)	0.96(5)
N–S	1.554(3)
N–Ru(2)	2.144(3)
N–Ru(3)	2.193(3)
N–Ru(1)	2.233(3)
S–O(9)	1.448(3)
Ru(1)–Ru(2)	2.690(1)
Ru(2)–Ru(3)	2.776(1)
Ru(1)···Ru(3)	3.542(2)
C(18)–C(19)–C(20)	125.7(3)
C(19)–C(20)–C(21)	116.7(3)

Estimated standard deviations in parentheses.

Table 4
Selected bond lengths [Å] and bond angles [°] for **4**

C(8)–C(9)	1.42(2)
C(8)–C(10)	1.51(2)
C(9)–C(16)	1.54(2)
C(8)–Ru(3)	2.235(12)
C(8)–Ru(2)	2.274(10)
C(8)–Ru(1)	2.292(12)
C(9)–C(16)	1.54(2)
C(9)–Ru(3)	2.195(11)
C(9)–Ru(1)	2.499(11)
C(9)–H(9)	0.93(1)
N(1)–S(1)	1.560(9)
N(1)–Ru(2)	2.130(9)
N(1)–Ru(3)	2.156(8)
N(1)–Ru(1)	2.224(9)
S(1)–O(1)	1.450(9)
Ru(1)–Ru(2)	2.6786(13)
Ru(2)–Ru(3)	2.7649(13)
Ru(1)···Ru(3)	3.5394(7)
C(9)–C(8)–C(10)	117.7(9)
C(8)–C(9)–C(16)	126.1(10)

Estimated standard deviations in parentheses.

This type of vinyl coordination has only been observed so far in $Ru_3(CO)_8(\mu_3$-η^1,η^2-PhC=CH_2)[μ_3-η^1,η^2-N(Me)$_2$NH] [14]. The C=C double bond [**3**: C(19)–C(20); **4**: C(8)–C(9)] adopts a perpendicular coordination with respect to the open edge [Ru(1)···Ru(3) ⊥ C(8)–C(9): 84°; Ru(1)···Ru(3) ⊥ C(19)–C(20): 89°] and is situated above the metal plane. The nitrogen atom, the three ruthenium atoms, and the carbon atoms C(20) in **3** and C(8) in **4**, form a trigonal–bipyramidal CRu_3N core (Figs. 2 and 3). The carbon–carbon double bond of the vinyl is longer in clusters **3** and **4** [**3**: C(19)–C(20) 1.425(6) Å; **4**: C(8)–C(9) 1.425(2) Å] than in **2** [C(9)–C(10) 1.39(2) Å], probably due to the coordination to the three metal centers.

The σ–π coordination of the vinyl ligand in **3** and **4** is not easy to describe in terms of localized bonds. Whereas the distances Ru(2)–C(20) **3** and Ru(2)–C(8) **4** of 2.241(4) and 2.274(10) Å, respectively, correspond to a σ-single bond, the π-bonding of the C(20)–C(19) backbone in **3** and the C(8)–C(9) backbone in **4** is divided between the two ruthenium atoms Ru(3) and Ru(1). In both cases the C=C unit is, however, closer to Ru(3) than to Ru(1) [**3**: Ru(1)–C(19) 2.427(4), Ru(3)–C(19) 2.243(4) Å; **4**: Ru(1)–C(9) 2.499(11), Ru(3)–C(9) 2.195(11) Å]. Unlike in $Ru_3(CO)_8(\mu_3$-η^1,η^2-PhC=CH_2)[μ_3-η^1,η^2-N(Me)$_2$NH] [14] which represents a 48e cluster, clusters **3** and **4** present an electron count of only 46 e. For an open M_3 triangle, the noble gas rule would require 50 e, hence, **3** and **4** are even more electron-deficient than the closed clusters **1** and **2**.

2.5. Reaction of (μ_2-H)$Ru_3(CO)_9$[μ_3-NS(O)MePh] (1) with PhC≡CPh

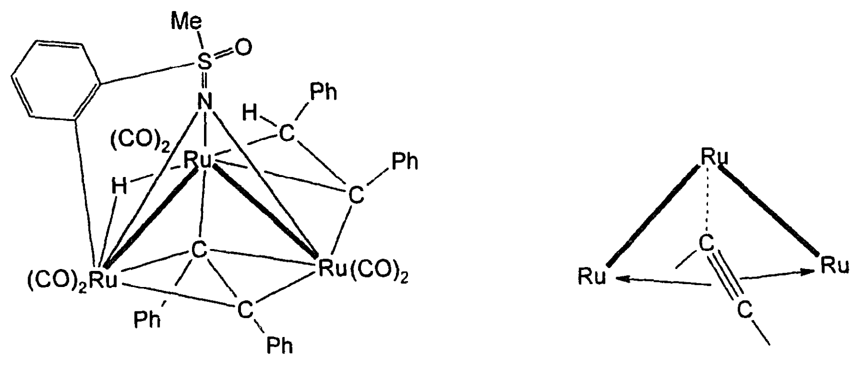
With diphenylacetylene, the electron-deficient cluster (μ_2-H)$Ru_3(CO)_9$[μ_3-NS(O)–MePh] (**1**) reacts at 100°C

$HRu_3(CO)_9[NS(O)MePh] + 2\ PhC{\equiv}CPh \longrightarrow$

(1)

$HRu_3(CO)_6[PhC{=}CHPh][PhC{\equiv}CPh][NS(O)Me(C_6H_4)] + 3\ CO$

(5)



(5)

Scheme 4.

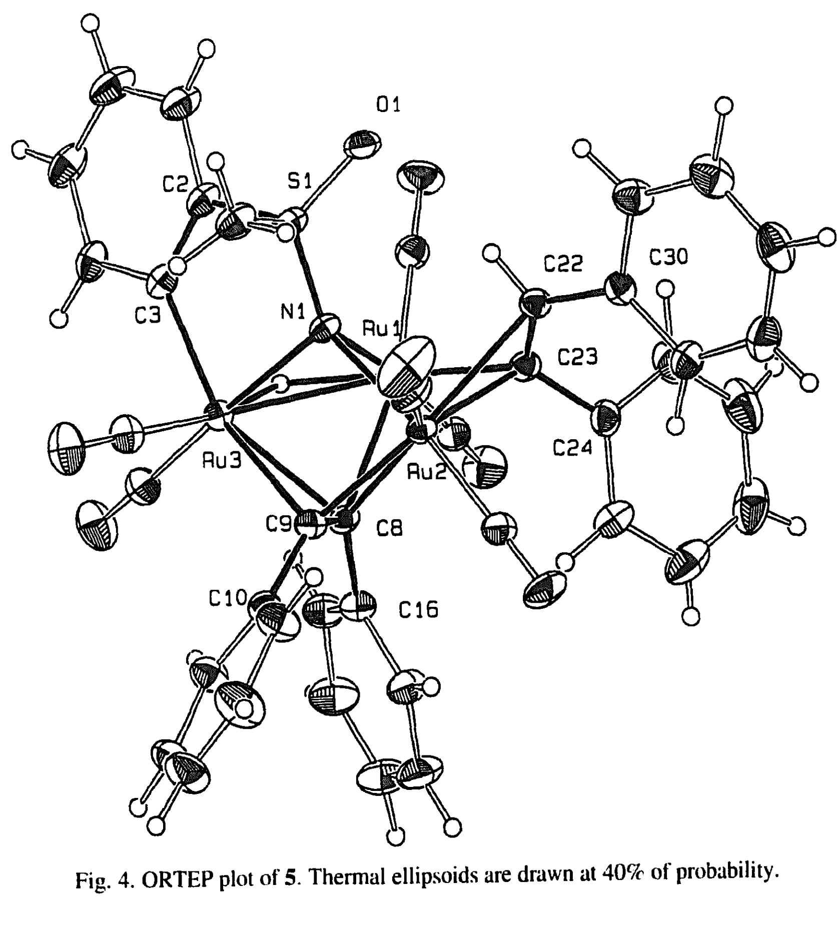


Fig. 4. ORTEP plot of **5**. Thermal ellipsoids are drawn at 40% of probability.

in THF to afford the vinyl–alkyne complex (μ_2-H)$Ru_3(CO)_6$(μ_2-η^1,η^2-PhC=CHPh)(μ_3-η^1,η^2-PhC≡CPh)[μ_3,η^1,η^2-NS(O)Me(C_6H_4)] (**5**). In this case, two equivalents of the alkyne are consumed to replace three carbonyl ligands: one alkyne inserts into the ruthenium-hydrogen bridge, whereas the other one opens up a ruthenium–ruthenium bond and coordinates as an almost perpendicular 4 e donor across the open site. In addition, the phenyl substituent at the sulfur atom undergoes, an *ortho*-metallation and transfers a hydrogen atom to the ruthenium framework (Scheme 4).

The IR spectrum of **5** (Table 1) shows only absorptions of terminal carbonyl ligands in the ν_{CO} region. The ^{1}H NMR spectrum exhibits a single hydride resonance at δ −8.37 ppm. The methyl group of the nitrogen cap is observed at δ 3.18 ppm, and the vinyl proton appears as a singlet at δ 6.60 ppm. A multiplet centered around δ 7.5 ppm is assigned to the different phenyl groups. The structure of **5** was confirmed by a single crystal X-ray structure analysis.

2.6. *Molecular structure of (μ_2-H)$Ru_3(CO)_6$(μ_2-η^1,η^2-PhC=CHPh)(μ_3-η^1,η^2-PhC≡CPh)[μ_3,η^1,η^2-NS(O)Me(C_6H_4)] (5)*

Suitable crystals of **5** were grown at room temperature crystallization from a mixture of CH_2Cl_2 and hexane. The molecular structure of **5** is depicted in Fig. 4. Selected bond lengths and angles are presented in Table 5. The molecular structure of **5** is quite complex, because it contains not only a μ_2-η^1,η^2-vinyl ligand, but also an alkyne ligand coordinated in a rare fashion over an open ruthenium–ruthenium site; furthermore the phenyl group of the sulfoximido cap has undergone an *ortho*-metallation. The three ruthenium atoms form an open triangle [Ru(1)–Ru(2) 2.7336(9), Ru(1)–Ru(3) 2.7376(8), Ru(2) ··· Ru(3) 3.3957(10) Å], each ruthenium atom being bonded to two terminal CO groups. The hydride ligand is coordinated quasi-symmetrically between Ru(1) and Ru(3) [Ru(1)–H(1Ru1) 1.79(5), Ru(3)–H(1Ru1) 1.77(5) Å] forming a dihedral angle of 4.198° with the Ru_3 core. The other metal–metal bond Ru(1)–Ru(2) is bridged by the vinyl ligand in the classical μ_2-η^1,η^2-fashion. The ligand is coordinated almost perpendicularly with respect to the Ru(1)–Ru(2) edge [Ru(1)–Ru(2) ⊥ C(22)–C(23): 100°] and adopts a *cis* configuration in order to avoid steric hindrance, in line with other vinyl complexes [5–8,17–30], e.g. $Ru_3(CO)_8$[μ-η^2-N(C_6H_5)(C_5H_4N)](μ_2-η^2-PhC=CHPh) [8]. The diphenylacetylene ligand adopts the μ_3-η^1,η^2-coordination, almost perpendicular with regard to the Ru(2) ··· Ru(3) edge [C(8)–C(9) ⊥ Ru(2)–Ru(3) 80°]. The perpendicular coordination of an alkyne to a metal cluster [31–33] was first observed for the unsaturated complex $Fe_3(CO)_9$(μ_3-η^2-RC≡CR) [34]. In trinuclear ruthenium cluster chemistry, there is only one alkyne complex known to have a perpendicular alkyne coordination: Ru_3(μ_3-η^2-PhC≡CPh)$(CO)_7$ (dppm) [35,36]. In the vinyl–alkyne complex $CpWRu_2(CO)_5$(μ_2-NPh)[μ_3-η^2-$C_2(CF_3)_2$][μ_2-η^2-C(CF_3)CH(CF_3)], the bis(trifluoromethyl) acetylene ligand is coordinated in a parallel fashion with respect to the metal–metal bond, and the Ru_2W core forms a closed metal triangle [37]. In the case of **5**, the alkyne axis is not exactly perpendicular with respect to the Ru(2) ··· Ru(3) vector (80°), unlike the known complex [35,36], and there is no metal–metal bond between the two ruthenium atoms Ru(2) and Ru(3). The carbon atom C(8) is closer to Ru(1) and Ru(3) than to Ru(2) [Ru(1)–C(8) 2.309(4), Ru(2)–C(8) 2.385(4), Ru(3)–C(8) 2.296(4) Å], whereas the carbon atom C(9) is closer to Ru(2) than to Ru(3) [Ru(2)–C(9) 2.084(4), Ru(3)–C(9) 2.401(4) Å]. The C(8)–C(9) bond length is shorter (C(8)–C(9) 1.3515(4) Å) than in Ru_3(μ_3-η^2-PhC_2Ph)$(CO)_7$ (dppm) [35,36] (C≡C 1.409(6) Å), probably due to reduced back bonding from the Ru_3 core in **5**.

Table 5
Selected bond lengths [Å] and bond angles [°] for **5**

C(8)–C(9)	1.352(5)
C(8)–C(16)	1.493(5)
C(9)–C(10)	1.482(5)
C(8)–Ru(1)	2.309(4)
C(8)–Ru(2)	2.385(4)
C(8)–Ru(3)	2.296(4)
C(9)–Ru(2)	2.084(4)
C(9)–Ru(3)	2.401(4)
C(22)–C(23)	1.395(5)
C(22)–Ru(2)	2.419(4)
C(23)–Ru(1)	2.111(4)
C(23)–Ru(2)	2.308(4)
C(22)–H(22)	0.94(4)
C(22)–C(30)	1.479(5)
C(23)–C(24)	1.489(5)
Ru(1)–H(1Ru)	1.79(5)
Ru(3)–H(1Ru)	1.77(5)
N(1)–S(1)	1.558(3)
S(1)–C(2)	1.756(4)
C(2)–C(3)	1.396(6)
C(3)–Ru(3)	2.084(4)
N(1)–Ru(1)	2.122(3)
N(1)–Ru(2)	2.132(3)
N(1)–Ru(3)	2.135(3)
S(1)–O(1)	1.450(3)
Ru(1)–Ru(2)	2.7336(9)
Ru(2) ··· Ru(3)	3.396(1)
Ru(1)–Ru(3)	2.7376(8)
C(8)–C(9)–C(10)	129.7(4)
C(9)–C(8)–C(16)	124.2(3)
C(23)–C(22)–C(30)	127.7(4)
C(22)–C(23)–C(24)	122.9(3)
Ru(3)–Ru(1)–Ru(2)–H(1Ru)	4.198

Estimated standard deviations in parentheses.

The other important point of this structure is the *ortho*-metallation of the phenyl group. The complex $H_2Ru_3(CO)_7(PPh_3)_2[\mu_2\text{-}NC(Ph)C_6H_4]$ [38], which contains an *ortho*-metalated 1-azavinylidene ligand, also shows a five membered ring. The main difference between this complex and **5** resides in the fact that to our knowledge, **5** is the first example of a cluster presenting an *ortho*-metallation involving four different atoms in a five-membered ring: 1Ru, 1N, 1S, 2C, whereas the known *ortho*-metallation clusters normally contain four-membered rings [39]. The five-membered ring is not planar, and two of the five bonds, [Ru(3)–C(3) 2.084(4) and Ru(3)–N 2.135(3) Å] are longer than the others (Table 5). Complex **5** is also unique in as much as it presents both, a μ_2-η^1,η^2-vinyl and a μ_3-η^1,η^2-alkyne coordination at the same Ru_3 framework. With an electron-count of 48e, **5** is electron-deficient like **1** and **2**.

3. Experimental

All manipulations were carried out in a nitrogen atmosphere, using standard Schlenk techniques. The organic solvents were refluxed over appropriate desiccants [40], distilled and saturated with nitrogen prior to use. The NMR spectra were recorded using a Varian Gemini 200 BB instrument or a Bruker AMX 400. The IR spectra were recorded using a Perkin–Elmer FTIR 1720X spectrophotometer (4000–400 cm^{-1}). 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 compound (μ_2-H)$Ru_3(CO)_9$[μ_3-NS(O)MePh] (**1**) was synthesized according to the published method [15]. Methyl phenyl sulfoximine (racemate) was obtained from Professor Carsten Bolm, RWTH Aachen. $PhCH_2C{\equiv}CH$, $Pr^nC{\equiv}CPr^n$, $PhC{\equiv}CBu^n$ were purchased from Aldrich, and diphenylacetylene from Fluka, and were used without further purification.

3.1. *Synthesis of $Ru_3(\mu_2\text{-}CO)_2(CO)_6(\mu_2\text{-}\eta^1,\eta^2\text{-}PhCH_2C{=}CH_2)[\mu_3\text{-}NS(O)MePh]$ (2)*

A solution of (μ_2-H)$Ru_3(CO)_9$[μ_3-NS(O)MePh] (**1**) (150 mg, 0.21 mmol) and $PhCH_2C{\equiv}CH$ (79 μl, 0.63 mmol) in THF (25 ml) was heated in a pressure Schlenk tube to 55°C for 4 h. After evaporation of the solvent the residue was dissolved in CH_2Cl_2 and submitted to thin-layer chromatography (silica gel, CH_2Cl_2/cyclohexane 1:1). The two isomers of **2** separated into two main orange bands. The first one contained **2b**, the second one **2a**. Both isomers were extracted with CH_2Cl_2 and crystallized from pentane, **2a** was recrystallized from cyclohexane/pentane. The orange crystals were dried in vacuo (**2a**: 30 mg, 17%; **2b**: 30 mg, 17%). Anal. Found **2a**: C, 35.91; H, 2.25; N, 1.73. $C_{24}H_{17}NO_9SRu_3$, Calc. C, 36.09; H, 2.14; N, 1.75%. Found **2b**: C, 38.53; H, 2.49; N, 1.65. $C_{24}H_{17}NO_9SRu_3 \cdot 0.5\ C_6H_{14}$, Calc. C, 38.52; H, 2.85; N, 1.66%. Mass Spectrum (FAB) m/z: **2b**: 801(M^+) (^{102}Ru).

3.2. *Synthesis of $Ru_3(\mu_2\text{-}CO)(CO)_7(\mu_3\text{-}\eta^1,\eta^2\text{-}Pr^nC{=}CHPr^n)[\mu_3\text{-}NS(O)MePh]$ (3)*

A solution of (μ_2-H)$Ru_3(CO)_9$[μ_3-NS(O)MePh] (**1**) (150 mg, 0.21 mmol) and $Pr^nC{\equiv}CPr^n$ (93 μl, 0.63 mmol) in THF (25 ml) was heated in a pressure Schlenk tube to 55°C for 5 h. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2 and separated by thin-layer chromatography (silica gel, CH_2Cl_2/cyclohexane 1:1). The main orange band was extracted by CH_2Cl_2 and further purified by thin-layer chromatography (silica gel, CH_2Cl_2/hexane/acetone 20:70:5). The main orange band was extracted with CH_2Cl_2, and **3** was recrystallized from hexane at −18°C. The orange–yellow crystals were dried in vaccuo (**3**: 30 mg, 17%). Anal. Found: C, 35.08; H, 2.94; N, 1.82. $C_{23}H_{23}NO_9SRu_3$, Calc. C, 34.85; H, 2.92; N, 1.77%.

3.3. *Synthesis of $Ru_3(\mu_2\text{-}CO)(CO)_7(\mu_3\text{-}\eta^1,\eta^2\text{-}PhC{=}CHBu^n)[\mu_3\text{-}NS(O)MePh]$ (4)*

A solution of (μ_2-H)$Ru_3(CO)_9$[μ_3-NS(O)MePh] (**1**) (150 mg, 0.21 mmol) and $PhC{\equiv}CBu^n$ (111 μl, 0.63 mmol) in THF (25 ml) was heated in a pressure Schlenk tube to 55°C for 5 h. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2 and separated by a thin-layer chromatography (silica gel, CH_2Cl_2/cyclohexane 1:1). The main red–orange band was extracted by CH_2Cl_2 and further purified by thin-layer chromatography (silica gel, CH_2Cl_2/hexane/acetone 20:70:5). The main red–orange band was extracted with CH_2Cl_2, and **4** was recrystallized from CH_2Cl_2/hexane at −18°C. The orange crystals were dried in vaccuo (**4**: 30 mg, 17%). Anal. Found: C, 38.51; H, 2.80, N, 1.70. $C_{27}H_{23}NO_9SRu_3$, Calc. C, 38.57; H, 2.76; N, 1.67%.

3.4. *Synthesis of $Ru_3(\mu_2\text{-}H)(CO)_6(\mu_2\text{-}\eta^1,\eta^2\text{-}PhC{=}CHPh)(\mu_3\text{-}\eta^1,\eta^2\text{-}PhC{\equiv}CPh)[\mu_3\text{-}NS(O)MePh]$ (5)*

A solution of (μ_2-H)$Ru_3(CO)_9$[μ_3-NS(O)MePh](**1**) (150 mg, 0.21 mmol) and $PhC{\equiv}CPh$ (75 mg, 0.28 mmol) in THF (30 ml) was heated in a pressure Schlenk tube to 100°C for 7 h. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2 and separated by a thin-layer chromatography (silica gel,

Table 6
Crystallographic and refinement data for **2a, 3, 4, 5**

Compound	**2a**	**3**	**4**	**5**
Empirical formula	$C_{24}H_{17}NO_9Ru_3S$	$C_{23}H_{23}NO_9Ru_3S \cdot 0.5\ C_6H_{14}$	$C_{27}H_{23}NO_9Ru_3S \cdot 0.5\ CH_2Cl_2$	$C_{41}H_{29}NO_7Ru_3S$
Formula weight (g mol^{-1})	798.66	835.78	883.19	982.92
Temperature (K)	293(2)	293(2)	223(2)	193(2)
Crystal system	orthorhombic	triclinic	monoclinic	triclinic
Space group	*Pbca*	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a, *b*, *c* (Å)	30.573(5), 14.865(2), 12.2252(12)	8.812(3), 9.225(3), 20.904(7)	10.0523(13), 10.9279(14), 28.915(6)	8.998(3), 12.239(3), 17.214(4)
α, β, γ (°)	90, 90, 90	93.39(3), 98.83(3), 110.36(3)	90, 96.43(1), 90	83.92(2), 87.70(2), 81.68(2)
Volume (Å^3)	5556.0(12)	1562.6(9)	3156.4(9)	1864.6(9)
Z	8	2	4	2
D_{calc} (g cm^{-3})	1.910	1.776	1.856	1.751
Absorption coefficient (Mo Kα, mm^{-1})	1.735	1.546	1.619	1.307
F(000)	3104	826	1728	972
Crystal size	0.1 × 0.2 × 0.05	0.1 × 0.2 × 0.2	0.64 × 0.34 × 0.95	0.95 × 0.84 × 0.57
θ scan range (°)	2.54 to 24.00	2.46 to 28.01	2.04 to 24.96	1.69 to 27.51
h, *k*, *l* ranges	−40 to 40, −19 to 19, −15 to 15	−10 to 10, −12 to 12, 0 to 27	−11 to 11, 0 to 12, 0 to 14	−11 to 11, −15 to 15, 0 to 22
Reflections collected	30467	6944	5526	8676
Independent reflections	4342	6944	5526	8491[*R*(int) = 0.0316]
Reflections observed [$I > 2\sigma(I)$]	2850	5320	4269	8043
Data/restraints/parameters	4342/0/343	6944/0/349	5526/0/387	8406/0/594
Goodness of fit on F^2	1.049	1.011	1.095	1.075
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0658$, $wR2 = 0.1466$	$R1 = 0.0331$, $wR2 = 0.0893$	$R1 = 0.0588$, $wR2 = 0.1486$	$R1 = 0.0469$, $wR2 = 0.1264$
R indices (all data)	$R1 = 0.1067$, $wR2 = 0.1697$	$R1 = 0.0502$, $wR2 = 0.0943$	$R1 = 0.1009$, $wR2 = 0.2019$	$R1 = 0.0489$, $wR2 = 0.1291$
Largest differential; peak and hole (e Å^3)	1.997 and −1.147	0.732 and −0.511	1.764 and −1.463	2.120 and −1.970
Empirical absorption correction	–	–	DIFABS	Semi empirical from Ψ scans
Transmission factors: min max	–	–	0.702/1.561	0.1768/0.6497

CH_2Cl_2/cyclohexane 1:1). From the major yellow band, **5** was extracted by CH_2Cl_2 and **5** was recrystallized from CH_2Cl_2/hexane (1:1) at room temperature. The yellow crystals were dried in vaccuo (**5**: 60 mg, 44%). Anal. Found: C, 49.87; H, 2.79; N, 1.49. $C_{41}H_{29}NO_7SRu_3$, Calc. C, 50.10; H, 2.97; N, 1.42%.

3.5. X-ray structure analysis of 2a, 3, 4 and 5

Suitable crystals of **2**, **3**, **4** and **5** were obtained as indicated Sections 3.1, 3.2, 3.3 and 3.4. Intensity data were collected on a STOE IPDS at room temperature for **2a** and **3**, and, on a Stoe–Siemens AED2 4-circle diffractometer at −50°C for **4** and −80°C for **5** (Mo Kα graphite monochromated radiation, $\lambda = 0.71073$ Å; $\omega/2\theta$ scans). Table 6 summarizes the crystallographic and selected experimental data for **2a**, **3**, **4** and **5**. The structures were solved by direct methods using the program SHELXS-86 [41]. The refinement, using weighted full-matrix least-square on F^2, was carried out using the program SHELXL-93 [42]. For **4**, an empirical absorption correction was applied using DIFABS [43] and for **5** based on Ψ scans. The vinyl hydrogen atoms of **3**, **4** and **5** were located from difference maps and refined isotropically. In the case of **3** the temperature factor was fixed at 0.08 Å^2. The methyl, methylene and phenyl hydrogens of **2a**, **3** and **4** were included in calculated positions and refined as riding atoms using the SHELXL 93 default parameters. For **5**, the remainder of the hydrogens were located from difference maps and refined isotropically. The figures were drawn with ZORTEP [44] (thermal ellipsoides, 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, Cambridge CB2 1EZ (UK) on quoting the full journal citation.

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