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Ring-opening reactions of thiomorpholine and thiazolidine by $[Ru_3(CO)_{12}]$: crystal structures of $[Ru_3(\mu\text{-H})(\mu\text{-}\eta^2\text{-}SCH_2CH_2NH_2)(CO)_9]$ and $[Ru_2(\mu\text{-}\eta^3\text{-}SCH_2CH_2NHCH_2)(CO)_6]$

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Abstract

The reaction of thiomorpholine (C_4H_9NS) with $[Ru_3(CO)_{12}]$ at 68°C afforded $[Ru_3(\mu\text{-H})(\mu\text{-}\eta^2\text{-}SCH_2CH_2NH_2)(CO)_9]$ **5** in 25% yield. An X-ray structure determination of **5** showed that it consists of a closed triruthenium cluster with a $\mu\text{-}\eta^2\text{-}SCH_2CH_2NH_2$ ligand formed by the ring-opening cleavage of thiomorpholine with elimination of a C_2 fragment. In contrast the analogous reaction of thiazolidine (C_3H_7NS) with $[Ru_3(CO)_{12}]$ yielded the dinuclear compound $[Ru_2(\mu\text{-}\eta^3\text{-}SCH_2CH_2NHCH_2)(CO)_6]$ **6** (28%), which was found to contain a $\mu\text{-}\eta^3\text{-}SCH_2CH_2NHCH_2$ ligand formed by the ring-opening cleavage of the C–S bond of the thiazolide ligand.

Keywords: Ruthenium; Ring-opening; Thiomorpholine; Thiazolidine; Crystal structure

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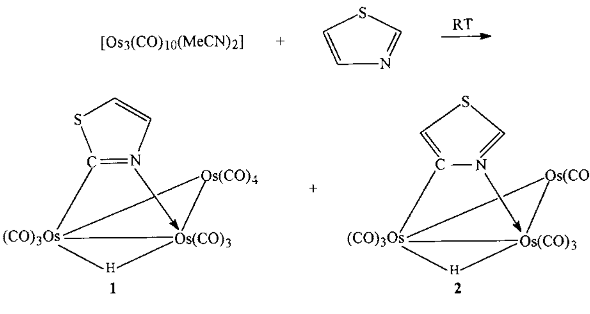
1. Introduction

For many years the reactions of organic heterocycles with N and S donors such as pyridine-2-thione [1], heterocyclic thioamides [2], pyrimidine 2-thione [3], 4-methylthiazole [4] and thiazole [5,6] with trimetallic clusters have received considerable attention because such ligands frequently stabilize the metal cluster framework with respect to degradational fragmentation when subjected to vigorous reaction conditions. Such reactions also attract interest because of their relevance to important catalytic processes. Recently we have reported the reactions between thiazole and $[Os_3(CO)_{10}(MeCN)_2]$ or $[Ru_3(CO)_{12}]$ and observed a remarkable influence on the type of product obtained depending on the metal carbonyl cluster and the reaction conditions [4–6]. For example, two isomeric compounds $[Os_3(\mu\text{-H})(\mu\text{-2,3-}\eta^2\text{-}\overline{C{=}NCH{=}CHS})(CO)_{10}]$ **1** and $[Os_3(\mu\text{-H})(\mu\text{-3,4-}\eta^2\text{-}\overline{C{=}CHSCH{=}N})(CO)_{10}]$ **2** (Scheme 1) were obtained from the reaction of $[Os_3(CO)_{10}(MeCN)_2)]$ with excess thiazole at ambient temperature. The reaction of equimolar amounts of



Scheme 1.

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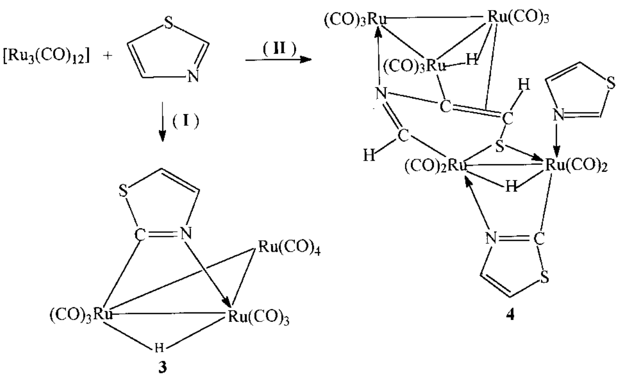


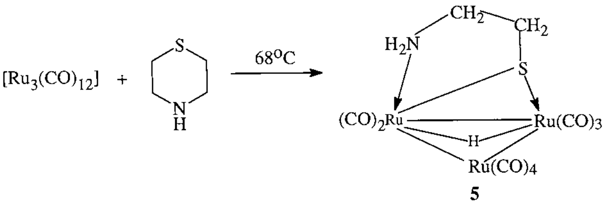
Scheme 2.

thiazole at 68°C gave $[Ru_3(\mu\text{-}H)(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}NCH{=}CHS})(CO)_{10}]$ **3** (Scheme 2) whereas use of excess thiazole leads to the pentanuclear compound $[Ru_3(\mu\text{-}H)(\mu_5\text{-}\eta^5\text{-}HC{=}N\overline{C{=}CHS})(CO)_9Ru_2(\mu\text{-}H)(\eta^1\text{-}H\overline{C{=}NCH{=}CHS})(\mu\text{-}2,3\text{-}\eta^2\text{-}\overline{C{=}NCH{=}CHS})(CO)_4]$ **4** (Scheme 2) containing three thiazole derived ligands in different coordination modes [6].

Recently, the utilization of transition metal cluster compounds in ring-opening reactions of sulphur heterocycles has drawn considerable attention [7–15]. This trend is partly due to interest in a molecular level understanding of metal catalyzed hydrodesulphurization of S-heterocycles. Metal carbonyl complexes have been shown to facilitate the ring-opening reactions of nitrogen or sulphur containing heterocycles such as thietane [7,8], dimethylthietane [9–11], azetidine [12], thiophene [13,14] and tetrahydrothiophene [15]. It has been demonstrated that bridging coordination of sulphur or nitrogen atoms promotes cleavage of the carbon–sulphur or carbon–nitrogen bonds by nucleophilic addition and spontaneous insertion of the metal atoms into such bonds [9]. As an extension of our earlier work on the reactivity of organic heterocycles containing N and S atoms towards metal carbonyl clusters, we have investigated the reactions of thiomorpholine and thazolidine with $[Ru_3(CO)_{12}]$ and the results are described herein.

2. Results and discussion

The reaction of $[Ru_3(CO)_{12}]$ with thiomorpholine (C_4H_9NS) at 68°C gives $[Ru_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}SCH_2CH_2NH_2)(CO)_9]$ **5** (Scheme 3) in 25% yield, which has been characterized by elemental analysis, infrared, ^{1}H-NMR, mass spectroscopic data and by single crystal X-ray diffraction studies. The molecular structure of **5** is shown in Fig. 1 and selected bond distances and bond angles are presented in Table 1. The molecule is based upon a triangular arrangement of three ruthenium atoms with nine terminal carbonyl ligands. One of the ruthenium atoms [Ru(2)] is associated with four carbonyl ligands, while the other two [Ru(3) and Ru(1)] are linked to three and two terminal carbonyl ligands, respectively. An intriguing structural feature of **5** is the presence of a bridging and chelating $SCH_2CH_2NH_2$ ligand, which has been formed during the reaction by the simultaneous cleavage of the C–S and C–N bonds of thiomorpholine accompanied by the loss of a C_2 fragment whose fate was not determined.



Scheme 3.

The Ru(1) and Ru(3) atoms are bridged both by a hydride and the $\mu\text{-}\eta^2\text{-}SCH_2CH_2NH_2$ ligands. The hydride ligand bridges the same metal–metal edge as the sulphur atom but lies on the other side of the cluster. Although the Ru(1)–H(13) and Ru(3)–H(13) distances (1.63 and 1.77 Å, respectively) are only approximate, these suggest a nearly ‘symmetrical disposition’ of the hydride ligand. Within the Ru_3 system, the doubly bridged Ru(1)–Ru(3) bond [2.8460(10) Å] and the unbridged Ru(2)–Ru(3) bond [2.8348(10) Å] are both significantly longer than the Ru(1)–Ru(2) bond [2.7996(9) Å]. In comparison, the average metal–metal bond length in the parent cluster $[Ru_3(CO)_{12}]$ is 2.854

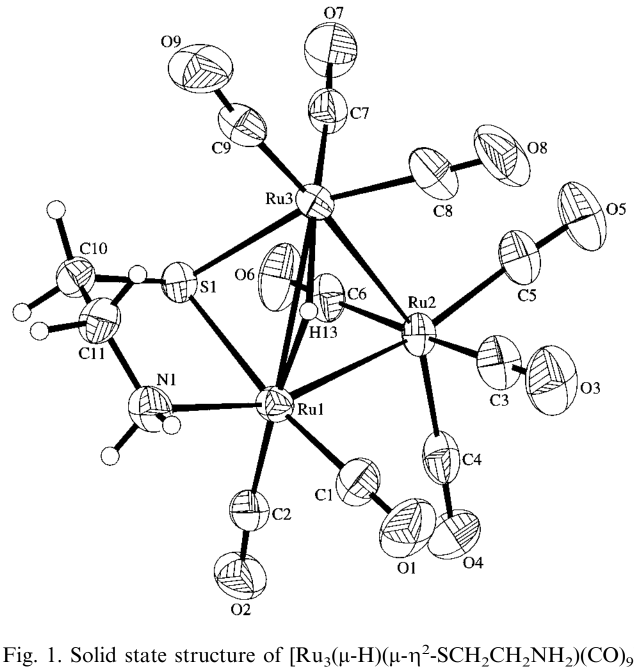


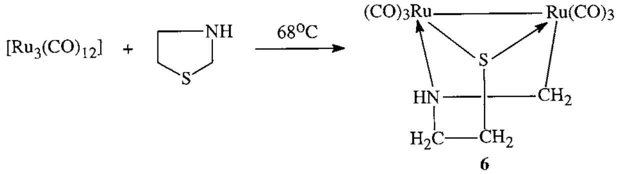
Fig. 1. Solid state structure of $[Ru_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}SCH_2CH_2NH_2)(CO)_9]$ **5** showing the atom labelling scheme. Thermal ellipsoids are drawn at the 35% probability level.

Table 1
Selected bond lengths (Å) and angles (°) for $[Ru_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}SCH_2CH_2NH_2)(CO)_9]$ **5**

Ru(1)–Ru(2)	2.7996(9)	Ru(1)–Ru(3)	2.8460(10)
Ru(2)–Ru(3)	2.8348(10)	Ru(1)–N(1)	2.212(5)
Ru(1)–S(1)	2.393(2)	Ru(3)–S(1)	2.405(2)
C(2)–Ru(1)–C(1)	88.2(4)	C(2)–Ru(1)–N(1)	100.0(3)
C(1)–Ru(1)–N(1)	97.7(3)	C(2)–Ru(1)–S(1)	101.5(3)
C(1)–Ru(1)–S(1)	170.2(3)	N(1)–Ru(1)–S(1)	82.0(2)
C(2)–Ru(1)–Ru(2)	94.2(2)	C(1)–Ru(1)–Ru(2)	94.4(2)
N(1)–Ru(1)–Ru(2)	161.6(2)	S(1)–Ru(1)–Ru(2)	83.71(5)
C(2)–Ru(1)–Ru(3)	143.7(3)	C(1)–Ru(1)–Ru(3)	117.0(3)
N(1)–Ru(1)–Ru(3)	101.7(2)	S(1)–Ru(1)–Ru(3)	53.80(5)
Ru(2)–Ru(1)–Ru(3)	60.28(2)	C(4)–Ru(2)–C(3)	91.8(4)
C(4)–Ru(2)–C(5)	102.6(4)	C(3)–Ru(2)–C(5)	90.6(4)
C(4)–Ru(2)–C(6)	93.3(4)	C(3)–Ru(2)–C(6)	173.6(4)
C(5)–Ru(2)–C(6)	92.2(3)	C(4)–Ru(2)–Ru(1)	92.4(3)
C(3)–Ru(2)–Ru(1)	82.7(3)	C(5)–Ru(2)–Ru(1)	163.8(3)
C(6)–Ru(2)–Ru(1)	93.1(2)	C(4)–Ru(2)–Ru(3)	152.8(3)
C(3)–Ru(2)–Ru(3)	88.8(3)	C(5)–Ru(2)–Ru(3)	104.6(3)
C(6)–Ru(2)–Ru(3)	84.9(2)	Ru(1)–Ru(2)–Ru(3)	60.67(2)
C(9)–Ru(3)–C(8)	94.8(4)	C(9)–Ru(3)–C(7)	97.9(4)
C(8)–Ru(3)–C(7)	95.8(4)	C(9)–Ru(3)–S(1)	95.2(3)
C(8)–Ru(3)–S(1)	164.6(3)	C(7)–Ru(3)–S(1)	94.4(3)
C(9)–Ru(3)–Ru(2)	174.4(3)	C(8)–Ru(3)–Ru(2)	86.3(3)
C(7)–Ru(3)–Ru(2)	87.5(3)	S(1)–Ru(3)–Ru(2)	82.74(5)
C(9)–Ru(3)–Ru(1)	115.5(2)	C(8)–Ru(3)–Ru(1)	111.5(3)
C(7)–Ru(3)–Ru(1)	133.6(3)	S(1)–Ru(3)–Ru(1)	53.43(5)
Ru(2)–Ru(3)–Ru(1)	59.05(2)	C(10)–S(1)–Ru(1)	100.9(3)
C(10)–S(1)–Ru(3)	110.2(3)	Ru(1)–S(1)–Ru(3)	72.76(6)

Å [16]. The organic ligand bridges Ru(1) and Ru(3) atoms through the sulphur atom S(1) while the nitrogen atom N(1) is coordinated to one of the sulphur bridged ruthenium atoms Ru(1). An interesting feature of the structure of **5** is the formation of a five-membered cyclic ring which includes the atoms Ru(1), N(1), C(11), C(10) and S(1). The two Ru–S distances [2.393(2) and 2.405(2) Å] in **5** are comparable with the values [2.384(2), 2.390(2) Å] in $[Ru_3(\mu\text{-}SCH_2CH_2S)(CO)_7]$ [17]. The Ru–S–Ru angle [72.76(6)°] is comparable with the Os–S–Os angle [72.6(2)°] in $[Os_3(\mu\text{-}H)(\mu\text{-}\eta^3\text{-}SCH_2CH_2CH{=}CH_2)CO)_9]$ [15] in which the organic ligand is bonded in a similar bridging and chelating fashion. The Ru–N distance [2.212(5) Å] is significantly longer than that [2.133(1) Å] in $[Ru3(\mu\text{-}H)(\mu\text{-}C_{13}H_8N)(CO)_{10}]$ [18]. The bond lengths and angles associated with the organic ligand are as expected. The NH_2 protons could not be experimentally located, but the presence of a broad resonance at d 2.84 in the ^{1}H-NMR spectrum indicated their presence.

There are seven ν(CO) bands in the infrared spectrum of **5** characteristic of terminal carbonyl ligands while the ^{1}H-NMR spectrum contains five multiplets at δ 3.20, 2.84, 2.45, 1.95 and 1.85 and a singlet resonance for the hydride at δ −14.69 in a relative intensity of 1:2:1:1:1:1, respectively. The mass spectrum confirms the stoichiometry, with molecular ion peak at m/z 635 and ions formed by stepwise loss of up to nine CO groups. Thus, the spectroscopic data of **5** are in accord with the solid state structure.



6

Scheme 4.

The reaction of $[Ru_3(CO)_{12}]$ with thiazolidine (C_3H_7NS) at 68°C gave the dinuclear compound $[Ru_2(\mu\text{-}\eta^3\text{-}SCH_2CH_2NHCH_2)(CO)_6]$ **6** (Scheme 4) in 35% yield. This compound has been characterized by elemental analysis, infrared, ^{1}H-NMR and mass spectroscopic data and by X-ray crystallography.

The solid state structure of **6** is shown in Fig. 2 and selected bond distances and angles are listed in Table 2. The molecule is based on a $(CO)_3Ru–Ru(CO)_3$ unit, with a Ru–Ru distance of 2.6990(8) Å. The most striking feature of the structure of **6** is presence of a $\mu\text{-}\eta^3\text{-}SCH_2CH_2NHCH_2$ ligand which is simultaneously bridging and chelating and provides additional stabilization to the $Ru_2(CO)_6$ moiety. Another important aspect is the breakdown of the trinuclear Ru_3 framework of $[Ru_3(CO)_{12}]$ during the reaction and production of the dinuclear species found in **6**. The presence of the above organic ligand in the molecule was surprising and it must have been formed during the reaction by ring-opening cleavage of the C–S bond of the thiazolidine ligand. The C8–N1–C9 part of the $SCH_2CH_2NHCH_2$ ligand was disordered between two orientations, with each of the N1 and C9 sites being occupied by a half nitrogen and a half carbon (see

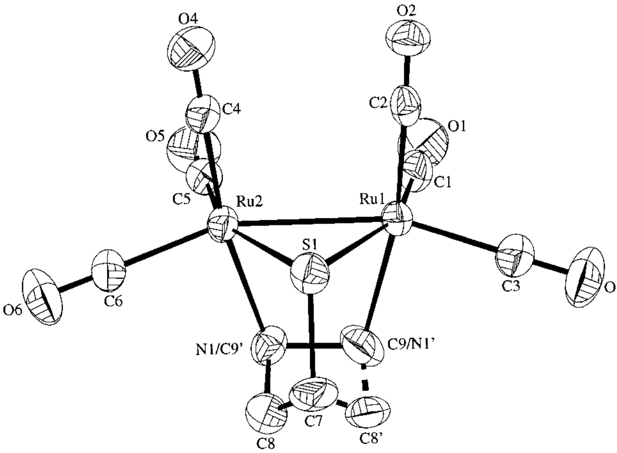


Fig. 2. Solid state structure of $[Ru_2(\mu\text{-}\eta^3\text{-}SCH_2CH_2NHCH_2)(CO)_6]$ **6** showing the atom labelling scheme. The two orientations of the disordered ligand are indicated by the S1–C7–C8–N1–C9 and S1–C7–C8′–N1′–C9′ lines. Thermal ellipsoids are drawn at the 35% probability level.

Table 2
Selected bond lengths (Å) and angles (°) for [Ru_2(μ-η^3-$SCH_2CH_2NHCH_2$)$(CO)_6$] **6**

Ru(1)–Ru(2)	2.6990(8)	Ru(1)–C(9)	2.184(8)
Ru(1)–S(1)	2.387(2)	Ru(2)–N(1)	2.169(6)
Ru(2)–S(1)	2.382(2)		
C(1)–Ru(1)–C(2)	91.8(3)	C(1)–Ru(1)–C(3)	98.3(3)
C(2)–Ru(1)–C(3)	96.5(3)	C(1)–Ru(1)–C(9)	91.5(3)
C(2)–Ru(1)–C(9)	169.5(3)	C(3)–Ru(1)–C(9)	92.9(3)
C(1)–Ru(1)–S(1)	154.0(2)	C(2)–Ru(1)–S(1)	92.2(2)
C(3)–Ru(1)–S(1)	106.7(3)	C(9)–Ru(1)–S(1)	80.5(2)
C(1)–Ru(1)–Ru(2)	98.6(2)	C(2)–Ru(1)–Ru(2)	96.1(2)
C(3)–Ru(1)–Ru(2)	158.5(2)	C(9)–Ru(1)–Ru(2)	73.6(2)
S(1)–Ru(1)–Ru(2)	55.44(5)	C(5)–Ru(2)–C(4)	92.2(3)
C(5)–Ru(2)–C(6)	99.5(3)	C(4)–Ru(2)–C(6)	95.7(3)
C(5)–Ru(2)–N(1)	91.0(3)	C(4)–Ru(2)–N(1)	169.8(3)
C(6)–Ru(2)–N(1)	93.3(3)	C(5)–Ru(2)–S(1)	154.3(2)
C(4)–Ru(2)–S(1)	91.7(2)	C(6)–Ru(2)–S(1)	105.4(3)
N(1)–Ru(2)–S(1)	81.3(2)	C(5)–Ru(2)–Ru(1)	98.7(2)
C(4)–Ru(2)–Ru(1)	97.2(2)	C(6)–Ru(2)–Ru(1)	157.3(2)
N(1)–Ru(2)–Ru(1)	72.7(2)	S(1)–Ru(2)–Ru(1)	55.61(5)
Ru(2)–S(1)–Ru(1)	68.94(5)		

Section 3). The NH proton could not be located from difference maps, but a broad resonance at δ 3.26 in the ^{1}H-NMR spectrum indicated its presence. The sulphur atom forms an almost symmetrical bridge with the two ruthenium atoms with Ru–S distances of 2.382(2) and 2.387(2) Å and a Ru–S–Ru angle of 68.94(5)°. The Ru–Ru distance in **6** is smaller than that in **5**, but similar to the value [2.6982(9) Å] reported for the S-bridged Ru–Ru edge in the cluster [Ru_3(μ-SCH_2CH_2S)$(CO)_7$] [17]. The Ru–S distances in **6** are comparable with the values in **5** and also with those [2.384(2), 2.390(2) Å] in [Ru_3(μ-SCH_2CH_2S)$(CO)_7$] [17]. Assuming that ring opening (C–S bond cleavage) thiazolidine ligand (μ-η^3-$SCH_2CH_2NHCH_2$) serves as a six-electron donor, the molecule contains a total of 36 valence electrons and each metal atom obeys the 18-electron rule. The angles C(4)–Ru(2)–C(5) [92.2(3)°] and C(1)–Ru(1)–C(2) [91.8(3)°] are right angles. The angles S(1)–Ru(2)–Ru(1) [55.6(5)°] and S(1)–Ru(1)–Ru(2) [55.44(5)°] are almost equal. The average Ru–C(CO) and C–O distances, and Ru–C–O angles in both the compounds (1.90, 1.14 Å, 176° in **5** and 1.91, 1.13 Å, 178° in **6**) are as expected. The Ru–N and Ru–C distances [2.169(6), 2.184(8) Å] in **6** are somewhat longer than the corresponding values [2.133(1), 2.133(1) Å] in [Ru_3(μ-H)(μ-$C_{13}H_8N$)$(CO)_{10}$] [18].

The infrared spectrum of **6** exhibits peaks at 2078s, 2043vs, 2004s, 1989s, 1972w cm^{-1} indicating that all the carbonyl ligands are terminal. In the ^{1}H-NMR spectrum, the methylene protons of the μ-$SCH_2CH_2NHCH_2$ ligand appear as six well separated equal intensity signals at δ 3.20 (m), 2.98 (dd, $J = 9.6$, 8.8 Hz), 2.86 (t, $J = 10.2$ Hz), 2.59 (overlapping dd) and 2.05 (δ, $J = 9.6$ Hz) while the NH proton appears as a broad singlet at δ 3.26. The mass spectrum contains the molecular ion peak at m/z 461 which is fragmented by the usual loss of six CO groups. These data are consistent with the X-ray structure.

In summary, we have shown that in spite of very close structural similarities, the reactivities of thiomorpholine and thiazolidine toward [$Ru_3(CO)_{12}$] are very different. The former undergoes both C–S and C–N bond cleavage, affording [Ru_3(μ-H)(μ-η^2-$SCH_2CH_2NH_2$)$(CO)_9$] **5**, but in the latter case only the C–S bond is cleaved resulting in the formation of [Ru_2(μ-η^3-$SCH_2CH_2NHCH_2$)$(CO)_6$] **6**. Another major difference in the reactions of [$Ru_3(CO)_{12}$] with thiomorpholine and thiazolidine is the preservation of the Ru_3 core in the compound obtained from thiomorpholine. We are currently probing the generality of this reaction in order to extend this methodology to ring-opening reactions of other heterocycles.

Table 3
Crystal data and details of data collection and structure refinement[a] for [Ru_3(μ-H)(μ-η^2-$SCH_2CH_2NH_2$)$(CO)_9$] **5** and [Ru_2(μ-η^3-$SCH_2CH_2NHCH_2$)$(CO)_6$] **6**

	5	**6**
Chemical formula	$C_{11}H_7NO_9Ru_3S$	$C_9H_7NO_6Ru_2S$
Formula weight	632.45	459.36
a (Å)	13.891(2)	9.431(2)
b (Å)	11.375(2)	14.0653(9)
c (Å)	11.476(3)	10.8771(10)
β (°)	90.464(11)	101.057(9)
U (Å^3)	1813.3(6)	1416.0(3)
Space group	$P2_1/c$	$P2_1/n$
D_c (g cm^{-3})	2.317	2.155
μ(Mo–K_α) (cm^{-1})	26.24	22.98
F(000)	1200	880
Crystal size (mm)	0.08 × 0.08 × 0.06	0.20 × 0.15 × 0.08
θ range for data collection (°)	2.31–25.10	2.40–24.91
Index ranges	$-15 \le h \le 14$ $-10 \le k \le 12$ $-13 \le l \le 13$	$-8 \le h \le 10$ $-15 \le k \le 16$ $-12 \le l \le 11$
Reflections collected	7321	5780
Independent reflections	2757 ($R_{int} = 0.0745$)	2125 ($R_{int} = 0.0771$)
Absorption correction factors	0.899–1.022	0.859–1.019
Data/parameters	2757/226	2125/181
Goodness-of-fit on F^2	0.821	0.997
Final R^b indices (all data)	$R_1 = 0.0539$, $wR_2 = 0.0779$	$R_1 = 0.0506$, $wR_2 = 0.0938$
R indices [$F_o^2 > 2\sigma(F_o^2)$]	$R_1 = 0.0324$, $wR_2 = 0.0752$	$R_1 = 0.0390$, $wR_2 = 0.0917$
Largest diff. peak and hole (e Å^{-3})	0.665 and −0.563	0.981 and −0.739

[a] Details in common: X-radiation, Mo–K_α, $\lambda = 0.71069$ Å, $T =$ 293 K, monoclinic, $Z = 4$, refinement method: full-matrix least-squares on F^2 using all unique data.

[b] $R_1 = \Sigma[(F_o) - (F_c)]/\Sigma(F_o)$; $wR_2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$; $w = [\sigma^2(F_o)^2 + (aP)^2]$, where $P = [(F_o)^2 + 2(F_c)^2]/3$, and $a = 0.0236$ (**5**) and 0.0348 (**6**).

3. Experimental

All reactions were carried out under an atmosphere of prepurified nitrogen using standard Schlenk techniques unless otherwise indicated. All solvents were dried and deoxygenated immediately before use. Sodium benzophenone ketyl was used as the drying agent for all the solvents, except dichloromethane, which was distilled over P_2O_5. Infrared spectra were recorded on a Schimadzu FT IR 8101 spectrophotometer. ^{1}H-NMR spectra were recorded on a Varian Unity Plus 400 MHz spectrometer. Thiomorpholine and thiazolidine were purchased from Aldrich while $[Ru_3(CO)_{12}]$ was obtained from Strem Chemicals.

3.1. Reaction of $[Ru_3(CO)_{12}]$ with thiomorpholine

A THF solution (70 ml) of $[Ru_3(CO)_{12}]$ (0.200 g, 0.31 mmol) and thiomorpholine (173 ml, 1.72 mmol) was heated to reflux for 4 h with monitoring by analytical TLC. The colour of the solution changed from orange to red. The solvent was removed under reduced pressure. The residue was chromatographed by TLC on silica gel. Elution with hexane/acetone (7:3, v/v) gave two bands. The major band yielded $[Ru_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}SCH_2CH_2NH_2)(CO)_9]$ **5** as pale yellow crystals (0.050 g, 25%). Anal. Calc. for $C_{11}H_7NO_9Ru_3S$: C, 20.89; H, 1.12; N, 2.22. Found: C, 21.12; H, 1.25; N, 2.29%. IR (νCO, hexane): 2094m, 2051s, 2019vs, 2006s, 1993w, 1948w, 1998w cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 3.20 (m, 1H), 2.84 (m, 2H), 2.45 (m, 1H), 1.95 (m, 1H), 1.85 (m, 1H), -14.69 (s, 1H). MS (m/z) 635(M$^+$), 607 (M$^+$–CO), 579 (M$^+$–2CO), 551 (M$^+$–3CO), 523 (M$^+$–4CO), 495 (M$^+$–5CO), 467 (M$^+$–6CO), 439 (M$^+$–7CO), 411 (M$^+$–8CO), 383 (M$^+$–9CO). The minor band gave a small quantity (ca. 0.004 g) of an uncharacterized compound.

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for $[Ru_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}SCH_2CH_2NH_2)(CO)_9]$ **5**

	x	*y*	*z*	U_{eq}[a]
Ru(1)	1844.5(5)	1505.1(5)	2323.2(6)	40(1)
Ru(2)	1866.1(5)	−919.5(5)	1905.1(5)	43(1)
Ru(3)	3634.2(5)	298.3(5)	2177.7(6)	40(1)
S(1)	2938(2)	1568(2)	723(2)	42(1)
O(1)	785(6)	1326(6)	4602(7)	104(3)
O(2)	−58(5)	1806(5)	1143(6)	81(2)
O(3)	1688(6)	−1104(6)	4551(6)	102(3)
O(4)	−306(5)	−976(6)	1642(7)	98(3)
O(5)	2393(6)	−3537(5)	1837(5)	89(2)
O(6)	2182(5)	−680(5)	−748(6)	81(2)
O(7)	4558(5)	−1355(5)	414(6)	86(2)
O(8)	4001(6)	−1205(7)	4294(7)	112(3)
O(9)	5478(5)	1701(6)	2531(7)	98(2)
N(1)	2321(5)	3350(5)	2527(6)	58(2)
C(1)	1173(7)	1377(7)	3727(9)	64(3)
C(2)	678(7)	1739(7)	1578(8)	56(2)
C(3)	1772(7)	−996(8)	3566(8)	65(3)
C(4)	516(8)	−979(7)	1727(8)	63(3)
C(5)	2225(7)	−2559(8)	1845(7)	59(3)
C(6)	2083(6)	−715(6)	218(8)	49(2)
C(7)	4164(7)	−764(7)	1079(8)	55(2)
C(8)	3849(8)	−669(8)	3496(9)	72(3)
C(9)	4734(7)	1224(7)	2425(8)	59(3)
C(10)	3422(6)	3060(6)	875(7)	51(2)
C(11)	3261(6)	3555(7)	2097(8)	58(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for $[Ru_2(\mu\text{-}\eta^3\text{-}SCH_2CH_2NHCH_2)(CO)_6]$ **6**

	x	*y*	*z*	U_{eq}[a]
Ru(1)	843.2(6)	7769.7(4)	5586.8(5)	44(1)
Ru(2)	3426.9(6)	8380.0(4)	5179.5(5)	44(1)
S(1)	1927(2)	7266(2)	3885(2)	57(1)
O(1)	818(7)	8864(4)	7973(6)	86(2)
O(2)	−918(5)	9302(4)	3991(5)	66(2)
O(3)	−1658(8)	6396(5)	5731(9)	127(3)
O(4)	2300(6)	10012(5)	3430(6)	93(2)
O(5)	4195(7)	9681(5)	7407(6)	89(2)
O(6)	6345(7)	8252(5)	4405(7)	112(3)
C(1)	795(8)	8455(6)	7082(8)	58(2)
C(2)	−286(7)	8719(6)	4584(7)	48(2)
C(3)	−740(9)	6899(6)	5650(8)	72(2)
C(4)	2723(8)	9402(6)	4082(7)	56(2)
C(5)	3905(7)	9198(5)	6555(7)	54(2)
C(6)	5282(10)	8298(6)	4692(9)	70(2)
C(7)	2758(9)	6090(6)	4428(8)	81(3)
C(8)[b]	3978(12)	6297(9)	5547(11)	66(5)
N(1)[b]	3829(7)	7148(4)	6396(6)	55(2)
C(9)[b]	2457(8)	6786(6)	6582(9)	98(3)
C(8′)[b]	2471(20)	5912(8)	5733(10)	90(7)
N(1′)[b]	2457(8)	6786(6)	6582(9)	98(3)
C(9′)[b]	3829(7)	7148(4)	6396(6)	55(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

[b] Atoms with partial occupancies 0.5.

3.2. Reaction of $[Ru_3(CO)_{12}]$ with thiazolidine

A mixture of $[Ru_3(CO)_{12}]$ (0.200 g, 0.31 mmol) and thiazolidiene (98 ml, 1.25 mmol) in dry THF (70 ml) was heated to reflux for 2 h. The reaction was monitored by analytical TLC. The colour of the solution changed from orange to brown. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with petroleum ether (40–60°C)/CH_2Cl_2 (9:1, v/v) gave one major and three very minor bands. The major band yielded $[Ru_2(\mu\text{-}\eta^3\text{-}SCH_2CH_2NHCH_2)(CO)_6]$ **6** as pale yellow crystals (0.040 g, 28%). Anal. Calc. for $C_9H_7NO_6Ru_2S$: C, 23.53; H, 1.54; N, 3.05. Found: C, 23.72; H, 1.85; N, 3.15%. IR (νCO, hexane): 2078m, 2043s, 2004s, 1989s, 1972w cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 3.26 (s, br, 1H), 3.20 (m, 1H), 2.98 (dd, 1H, $J = 9.6$, 8.8 Hz), 2.86 (t, 1H, $J = 10.2$ Hz), 2.59 (m, 2H), 2.05 (d, 1H, $J = 9.6$ Hz). MS (*m*/*z*) 461 (M^+): 433 (M^+–CO), 405 (M^+–2CO), 377 (M^+–3CO), 349 (M^+–4CO), 321 (M^+–5CO), 293 (M^+–6CO). Each of the minor bands gave a small quantity (ca. 0.002 g) of an uncharacterized compound.

3.3. X-ray crystallography

Crystallographic measurements for complexes **5** and **6** were made on a Delft Instruments FAST area detector diffractometer in a manner described previously [19]. In both cases the unit-cell parameters were determined using least-squares refinement of the diffractometer angles for 250 reflections, and the data were corrected for absorption using DIFABS [20]. Full crystallographic data and experimental details are presented in Table 3. The structures were solved by direct methods (SHELXS-86) [21] and refined on F^2 by full-matrix least-squares (SHELXL-93) [22] using all unique data with intensities > 0. All non-hydrogen atoms were anisotropic. In **6**, the C8–N1–C9 part of the $SCH_2CH_2NHCH_2$ ligand (Fig. 2) was disordered between two orientations. Best refinement results were obtained by assuming that the N1 and C9 sites were each occupied by a half-nitrogen and a half-carbon; the anisotropic displacement parameters of these two positions were constrained to refine to the same values. The C8 and C8′ sites were also half-occupied, without any constraint on their displacement coefficients. The C7–C8, C7–C8′, N1–C8 and C9–C8′ distances were all constrained to remain at 1.52 Å. The hydrogen atoms in **6** were ignored. The bridging hydride in **5** was located from difference map, but it was not refined. Other hydrogen atoms in this structure were included in calculated positions (riding model) with $U_{eq} > 1.2 \times U_{iso}$ of the parent atoms. Final *R*-values are quoted in Table 3. The residual electron densities in the final difference map did not indicate any feature of stereochemical significance. The atomic coordinates for the two compounds are given in Tables 4 and 5. Anisotropic thermal parameters, hydrogen atom parameters for **5** and full lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. Diagrams were drawn with SNOOPI [23].

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