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Triruthenium clusters derived from the reactions of [$Ru_3(CO)_{12}$] with benzothiazole, pyrimidine-2-thione and benzimidazole-2-thione; X-ray structures of [$Ru_3(\mu\text{-}H)(\mu\text{-}2,3\text{-}\eta^2\text{-}NSC_7H_4)(CO)_{10}$] and [$Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}SN_2C_4H_3)(CO)_9$]

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Abstract

The reaction of [$Ru_3(CO)_{12}$] with benzothiazole (C_7H_5NS) in THF at 68°C yields [$Ru_3(\mu\text{-}H)(\mu\text{-}2,3\text{-}\eta^2\text{-}NSC_7H_4)(CO)_{10}$] **3** and [$Ru_3(\mu\text{-}H)(\mu_3\text{-}1,2,3\text{-}\eta^3\text{-}NSC_7H_4)(CO)_9$] **4**. An X-ray diffraction analysis of **3** shows that the benzothiazolide ligand is coordinated through the imino-nitrogen and C-2 carbon atoms. The organic ligand in **4** is coordinated through the sulfur, the imino nitrogen and the C-2 carbon atoms as suggested by IR, ^{1}H-NMR and MS data. Compound **3** converts to **4** on thermolysis in cyclohexane. The reactions of pyrimidine-2-thione ($C_4H_4N_2S$) and benzimidazole-2-thione ($C_7H_6N_2S$) with [$Ru_3(CO)_{12}$] give the new compounds [$Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}SN_2C_4H_3)(CO)_9$] (**5**) and [$Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}N_2SC_7H_5)(CO)_9$] (**6**), respectively. An X-ray structure analysis of **5** shows that the pyrimidine-2-thiolato ligand bridges two ruthenium atoms through the sulfur atom and bonds to a third ruthenium through one of the ring N atoms. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Benzothiazole; Pyrimidine-2-thione; Benzimidazole-2-thione; Crystal structure

1. Introduction

In recent years we [1–3] and others [4–7] have reported the reactions of N- and S-containing heterocycles with trimetallic clusters of osmium and ruthenium. These reactions are usually associated with activation of C–H, N–H, S–H and C–N bonds of the heterocyclic ligand and markedly influenced by the structure of the heterocycle as well as the reaction conditions and starting clusters. We have further reported [8] that the reaction of thiomorpholine (C_4H_9NS) with [$Ru_3(CO)_{12}$] at 68°C gives the cluster [$Ru_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}SCH_2CH_2NH_2)(CO)_9$] (**1**) by a ring-opening reaction of thiomorpholine (C_4H_9NS) followed by elimination of a C_2 fragment whereas thiazolidine (C_3H_7NS) under identical conditions gave the dinuclear compound [$Ru_2(\mu\text{-}\eta^3\text{-}SCH_2CH_2NHCH_2)(CO)_6$] (**2**) formed also by ring-opening cleavage of the C–S bond of the ligand (Scheme 1).

Continuing our studies of the reactions between [$Ru_3(CO)_{12}$] and N- and S-heterocycles such as 4-methylthiazole [1], thiazole [2,3], thiomorpholine [8] and thiazolidine [8], we now report on the reactions of [$Ru_3(CO)_{12}$] with benzothiazole, pyrimidine-2-thione and benzimidazole-2-thione.

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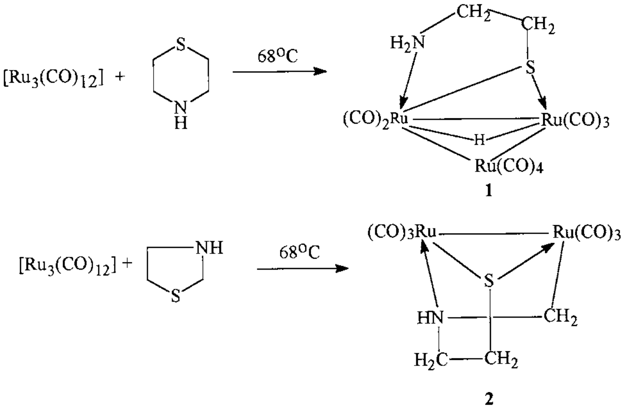
2. Results and discussion

The reaction of $[Ru_3(CO)_{12}]$ with two equivalents of benzothiazole at 68°C gives two new clusters $[Ru_3(\mu\text{-}H)(\mu\text{-}2,3\text{-}\eta^2\text{-}NSC_7H_4)(CO)_{10}]$ (**3**) and $[Ru_3(\mu\text{-}H)(\mu_3\text{-}1,2,3\text{-}\eta^3\text{-}NSC_7H_4)(CO)_9]$ (**4**) (Scheme 2) in 45 and 25% yields, respectively. The complexes have been characterized by elemental analysis, IR, ^{1}H-NMR and MS data together with a single-crystal X-ray study for **3**.

The solid-state structure of **3** is shown in Fig. 1 and selected bond distances and angles are given in Table 1. The molecule is based upon a triangle of ruthenium atoms, one of which Ru(1) is associated with four terminal carbonyl ligands, while the other two Ru(2) and Ru(3) are each linked to three terminal carbonyl ligands and mutually bridged both by a hydride ligand and the $\mu\text{-}2,3\text{-}\eta^2\text{-}NSC_7H_4$ ligand. The bridged Ru(2)–(Ru(3) bond (2.9239(10) Å) is significantly longer than the other two Ru–Ru bonds (2.8469(9), 2.8515(9) Å), and also longer than the average Ru–Ru distance in $[Ru_3(CO)_{12}]$ (2.854(7) Å) [9]. The organic ligand forms the bridge through the N(1) and C(11) atoms of the thiazolide moiety. The Ru(2)–N(1) (2.123(4) Å) and Ru(3)–C(11) (2.068(6) Å) bonds in **3** are slightly asymmetric and shorter than the related bonds in the related phenanthridine complex $[Ru_3(\mu\text{-}H)(\mu\text{-}NC_{13}H_8)(CO)_{10}]$, in which the Ru–N and Ru–C bonds are both 2.133(1) Å [10]. The Ru(3)–C(11)–N(1)–Ru(2) bridge is nearly perpendicular to the metal cluster with N(1)–Ru(2)–Ru(1) and C(11)–Ru(3)–Ru(1) angles being 90.53(12) and 87.3(2)°. Similar arrangement of the organic ligand was also observed in the phenanthridine [10] and benzimidazole [11] analogs. As expected, the presence of the bridging hydride in **3** results in opening of the Ru(2)–Ru(3)–C(8) and Ru(3)–Ru(2)–C(6) angles (112.1(2) and 114.4(2)°, respectively). The internal geometry parameters of the coordinated benzothiazolide ligand are normal as are the dimensions of all CO ligands.

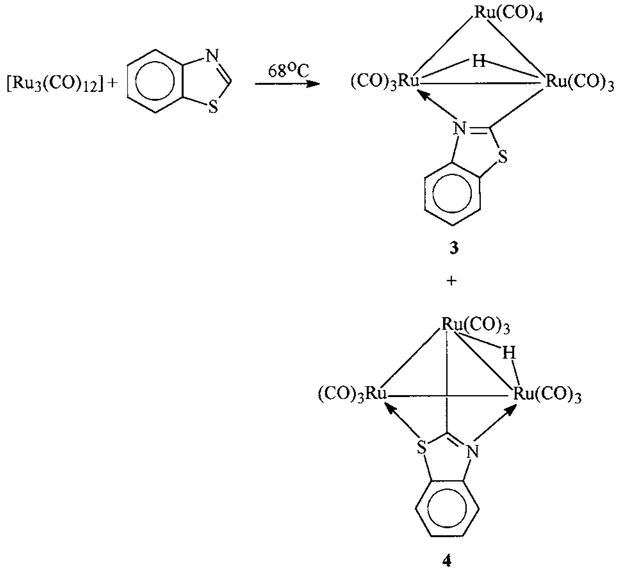
The CO stretches in the IR spectrum of **3** are similar to those observed for the complexes $[Ru_3(\mu\text{-}H)(\mu\text{-}NC_{13}H_8)(CO)_{10}]$ [10] and $[Ru_3(\mu\text{-}H)(\mu\text{-}1,2\text{-}\eta^2\text{-}N_2C_7H_5)(CO)_{10}]$ [11] and suggest that the distribution of the CO ligands are comparable in these complexes. The ^{1}H-NMR spectrum of **3** consists of a pair of doublets at δ 7.75 and 7.30, a pair of apparent triplets formed by two overlapping doublet of doublets at 7.54 and 7.48 and a singlet at − 14.26 each integrating for one hydrogen. The mass spectrum confirms the stoichiometry with a molecular ion peak at m/z 721 and ions formed by stepwise loss of ten CO ligands. Thus the spectroscopic properties of **3** in solution are in accord with the solid-state structure.



Scheme 1.

No single-crystals suitable for X-ray diffraction studies could be obtained for **4**, so its identity is based on elemental analysis, IR, ^{1}H-NMR and MS data. The CO stretches in the IR spectrum of **4** (2090–1968 cm^{-1}) are consistent with all the carbonyl groups being terminally placed. The ^{1}H-NMR spectrum in $CDCl_3$ shows two doublets at δ 7.80 and 7.61, two apparent triplets at 7.46 and 7.30 and a singlet at − 12.78. The doublets at δ 7.80 and 7.61 and triplets at 7.46 and 7.30 each integrate for one hydrogen and have been attributed, respectively, to the C(4), C(7), C(5) and C(6) protons of the ligand. These assignments are based on a comparison of the chemical shift and coupling constants with those of the free ligand. The mass spectrum shows the molecular ion peak at m/z 692 with sequential loss of nine CO groups. Thermolysis of **3** in refluxing cyclohexane for 1 h gives **4** in 30% yield.

The reaction of $[Ru_3(CO)_{12}]$ with excess pyrimidine-2-thione at 68°C gives the compound $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}SN_2C_4H_3)(CO)_9]$ (**5**) (Scheme 3) in 35% yield, which has also been structurally characterized.



Scheme 2.

The X-ray structure of **5** is shown in Fig. 2 and selected bond distances and angles are given in Table 2. The molecule possesses a noncrystallographic mirror plane of symmetry passing through the plane of the organic ring and also containing the Ru(2), H(31), C(6) and O(6) atoms. The ruthenium atoms form an isosceles triangle with metal–metal distances (Ru(1)–Ru(2) = 2.7741(8), Ru(2)–Ru(3) = 2.7732(8), Ru(1)–Ru(3) = 2.8384(8) Å) very similar to those reported for the related compounds $[Ru_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-pyS})(CO)_9]$ (unbridged bonds, 2.790(1) and 2.774(1) Å, bridged bond, 2.841(2) Å) [4] and $[Ru_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-}C_7H_4NS)(CO)_9]$ (unbridged bonds, 2.798(6) and 2.786(5) Å, bridged bond, 2.836(5) Å) [7]. It is also noted that the unbridged Ru–Ru distances in all these complexes are significantly shorter than the average Ru–Ru distance of 2.854(7) Å in $[Ru_3(CO)_{12}]$ [9]. The pyrimidine-2-thiolato ligand in **5** bridges Ru(1) and Ru(3) atoms via the exocyclic S-atom and bonds to the Ru(2) atom by the N(1) atom (Ru(2)–N(1) = 2.172(5) Å). The Ru(1)–Ru(3) edge is also bridged by a hydride ligand and consistent with a resonance at δ −13.16 in the ^{1}H-NMR spectrum. The Ru–S distances (2.407(2) and 2.409(2) Å) are similar to those found in other μ-S triosmium and triruthenium clusters [12–16]. Within the thioamide ligand, the exocyclic C(10)–S(1) bond 1.779(6) Å is close that expected for a C–S single bond [17] and also comparable with that in the dmpymt analog $[Ru_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-dmpymt})(CO)_9]$ (**7**) [18]. Both the C(10)–N(1) and C(10)–N(2) bonds (1.332(8) and 1.323(8) Å, respectively) indicate appreciable double bond character [17]. The dimensions of the coordinated pyrimidine-2-thione ligand and of the CO groups are normal. The observed molecular structure of **5** is fully consistent with its spectroscopic data.

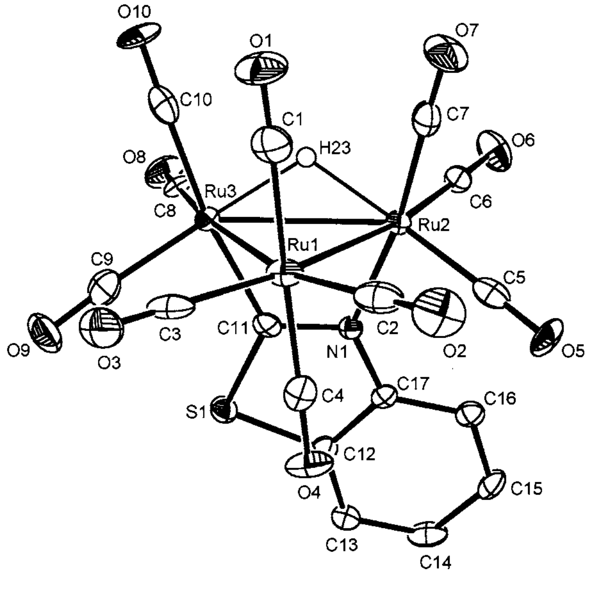
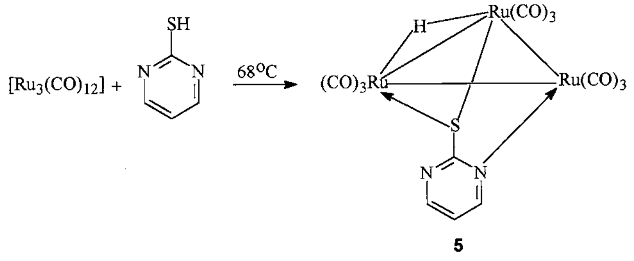


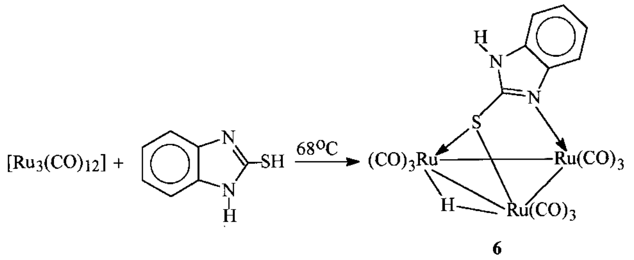
Fig. 1. Molecular structure of $[Ru_3(\mu\text{-H})(\mu\text{-2,3-}\eta^2\text{-NSC}_7H_4)(CO)_{10}]$ (**3**) showing the atom labeling scheme. The ring hydrogens are omitted for clarity. The thermal ellipsoids are drawn at 45% probability level.

Table 1
Selected bond lengths (Å) and angles (°) for $C_{17}H_5NO_{10}Ru_3S$ (**3**)

Ru(1)–Ru(2)	2.8469(9)	Ru(1)–Ru(3)	2.8515(9)
Ru(2)–N(1)	2.123(4)	Ru(2)–Ru(3)	2.9239(10)
Ru(3)–C(11)	2.068(6)	S(1)–C(11)	1.737(6)
S(1)–C(12)	1.753(6)	N(1)–C(11)	1.297(7)
N(1)–C(17)	1.388(7)		
C(3)–Ru(1)–C(2)	101.3(3)	C(3)–Ru(1)–C(1)	90.8(3)
C(2)–Ru(1)–C(1)	91.3(3)	C(3)–Ru(1)–C(4)	93.3(3)
C(2)–Ru(1)–C(4)	92.0(3)	C(1)–Ru(1)–C(4)	174.1(3)
C(3)–Ru(1)–Ru(2)	159.1(2)	C(2)–Ru(1)–Ru(2)	99.4(2)
C(1)–Ru(1)–Ru(2)	91.8(2)	C(4)–Ru(1)–Ru(2)	82.9(2)
C(3)–Ru(1)–Ru(3)	97.7(2)	C(2)–Ru(1)–Ru(3)	161.0(2)
C(1)–Ru(1)–Ru(3)	87.0(2)	C(4)–Ru(1)–Ru(3)	88.3(2)
Ru(2)–Ru(1)–Ru(3)	61.74(2)	C(7)–Ru(2)–C(5)	93.2(3)
C(7)–Ru(2)–C(6)	93.2(2)	C(5)–Ru(2)–C(6)	100.3(3)
C(7)–Ru(2)–N(1)	172.2(2)	C(5)–Ru(2)–N(1)	92.7(2)
C(6)–Ru(2)–N(1)	90.7(2)	C(7)–Ru(2)–Ru(1)	84.7(2)
C(5)–Ru(2)–Ru(1)	87.3(2)	C(6)–Ru(2)–Ru(1)	172.3(2)
N(1)–Ru(2)–Ru(1)	90.53(12)	C(7)–Ru(2)–Ru(3)	104.2(2)
C(5)–Ru(2)–Ru(3)	139.7(2)	C(6)–Ru(2)–Ru(3)	114.4(2)
N(1)–Ru(2)–Ru(3)	68.06(13)	Ru(1)–Ru(2)–Ru(3)	59.21(2)
C(9)–Ru(3)–C(8)	96.9(3)	C(9)–Ru(3)–C(10)	97.2(3)
C(8)–Ru(3)–C(10)	92.9(3)	C(9)–Ru(3)–C(11)	90.3(3)
C(8)–Ru(3)–C(11)	87.2(2)	C(10)–Ru(3)–C(11)	172.4(2)
C(9)–Ru(3)–Ru(1)	90.2(2)	C(8)–Ru(3)–Ru(1)	171.0(2)
C(10)–Ru(3)–Ru(1)	91.7(2)	C(11)–Ru(3)–Ru(1)	87.3(2)
C(9)–Ru(3)–Ru(2)	140.5(2)	C(8)–Ru(3)–Ru(2)	112.1(2)
C(10)–Ru(3)–Ru(2)	107.0(2)	C(11)–Ru(3)–Ru(2)	66.0(2)
Ru(1)–Ru(3)–Ru(2)	59.05(2)	C(11)–S(1)–C(12)	91.0(3)
C(11)–N(1)–C(17)	114.3(5)	C(11)–N(1)–Ru(2)	108.3(4)
C(17)–N(1)–Ru(2)	137.3(4	N(1)–C(11)–S(1)	112.3(4)
N(1)–C(11)–Ru(3)	117.3(4)	S(1)–C(11)–Ru(3)	130.3(3)



Scheme 3.



Scheme 4.

Treatment of $[Ru_3(CO)_{12}]$ with benzimidazole-2-thione at 68°C yields $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}N_2SC_7H_5)(CO)_9]$ (**6**) in 25% yield (Scheme 4). The compound has been characterized by elemental analysis, IR, ^{1}H-NMR and MS data.

The ν(CO) stretches of **6** are similar to those reported for **5**, **7** and $[Ru_3(\mu\text{-}H)(\mu_3\text{-}pyS)(CO)_9]$ [4] in both appearance and position of the bands indicating structural similarities. The ^{1}H-NMR spectrum of **6** in $CDCl_3$ shows a singlet at δ −12.92 for the bridging hydride and three sets of signals for the organic ligands, a singlet at 9.48, a doublet at 7.41 and a multiplet at 7.30 in a 1:1:1:3 ratio. The singlet at δ 9.48 is attributed to the N–H proton of the benzimidazolide ligand. The doublet at δ 7.41 and the multiplet at 7.30 are assigned to the ring protons of the ligand. Thus compound **6** is suggested to be structurally similar with **5** and **7** [18]. Complexes **3**–**6** contain intact heterocyclic ligands, no evidence being found for the cleavage of C–S and C–N bonds resulting in the formation of ring-opening products as observed for thiomorpholine and thiazolidine [8].

3. Experimental

Unless otherwise stated, all experiments were conducted under an atmosphere of prepurified nitrogen with the use of standard Schlenk techniques. Solvents were distilled from appropriate drying agents and stored under nitrogen. $[Ru_3(CO)_{12}]$ was purchased from Strem Chemicals while benzothiazole, pyrimidin-2-thione and benzimidazole-2-thione were from Aldrich and used as received. IR spectra were recorded on a Shimadzu FT-IR 8101 spectrophotometer. ^{1}H-NMR spectra were recorded on a Varian Unity Plus 400 MHz spectrometer. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, New York.

Table 2
Selected bond lengths (Å) and angles (°) for $C_{13}H_4N_2O_9Ru_3S$ (**5**)

Ru(1)–Ru(2)	2.7741(8)	Ru(1)–Ru(3)	2.8384(8)
Ru(2)–N(1)	2.172(5)	Ru(2)–Ru(3)	2.7732(8)
Ru(1)–S(1)	2.409(2)	Ru(3)–S(1)	2.407(2)
S(1)–C(10)	1.779(6)	N(1)–C(10)	1.332(8)
N(1)–C(11)	1.351(8)	N(2)–C(10)	1.323(8)
N(2)–C(13)	1.347(9)		
C(3)–Ru(1)–C(2)	91.5(3)	C(3)–Ru(1)–C(1)	93.0(3)
C(2)–Ru(1)–C(1)	100.0(3)	C(3)–Ru(1)–S(1)	169.2(2)
C(2)–Ru(1)–S(1)	94.0(2)	C(1)–Ru(1)–S(1)	95.2(2)
C(3)–Ru(1)–Ru(2)	90.6(2)	C(2)–Ru(1)–Ru(2)	89.1(2)
C(1)–Ru(1)–Ru(2)	170.2(2)	S(1)–Ru(1)–Ru(2)	80.17(4)
C(3)–Ru(1)–Ru(3)	116.4(2)	C(2)–Ru(1)–Ru(3)	135.9(2)
C(1)–Ru(1)–Ru(3)	111.1(2)	S(1)–Ru(1)–Ru(3)	53.87(4)
Ru(2)–Ru(1)–Ru(3)	59.21(2)	C(6)–Ru(2)–C(5)	89.1(3)
C(6)–Ru(2)–C(4)	91.8(3)	C(5)–Ru(2)–C(4)	99.5(3)
C(6)–Ru(2)–N(1)	175.3(3)	C(5)–Ru(2)–N(1)	94.2(2)
C(4)–Ru(2)–N(1)	90.9(2)	C(6)–Ru(2)–Ru(3)	88.7(2)
C(5)–Ru(2)–Ru(3)	97.2(2)	C(4)–Ru(2)–Ru(3)	163.4(2)
N(1)–Ru(2)–Ru(3)	87.61(14)	C(6)–Ru(2)–Ru(1)	86.9(2)
C(5)–Ru(2)–Ru(1)	158.4(2)	C(4)–Ru(2)–Ru(1)	101.9(2)
N(1)–Ru(2)–Ru(1)	88.81(14)	Ru(3)–Ru(2)–Ru(1)	61.55(2)
C(8)–Ru(3)–C(9)	93.1(3)	C(8)–Ru(3)–C(7)	93.5(3)
C(9)–Ru(3)–C(7)	99.8(3)	C(8)–Ru(3)–S(1)	169.2(2)
C(9)–Ru(3)–S(1)	93.8(2)	C(7)–Ru(3)–S(1)	93.5(2)
C(8)–Ru(3)–Ru(2)	92.0(2)	C(9)–Ru(3)–Ru(2)	85.5(2)
C(7)–Ru(3)–Ru(2)	172.1(2)	S(1)–Ru(3)–Ru(2)	80.21(4)
C(8)–Ru(3)–Ru(1)	115.6(2)	C(9)–Ru(3)–Ru(1)	133.5(2)
C(7)–Ru(3)–Ru(1)	113.2(2)	S(1)–Ru(3)–Ru(1)	53.91(4)
Ru(2)–Ru(3)–Ru(1)	59.24(2	C(10)–S(1)–Ru(3)	105.3(2)
C(10)–S(1)–Ru(1)	107.5(2)	Ru(3)–S(1)–Ru(1)	72.23(5)
C(10)–N(1)–C(11)	117.0(6)	C(10)–N(1)–Ru(2)	122.1(4)
C(11)–N(1)–Ru(2)	121.0(5)	C(10)–N(2)–C(13)	116.1(6)
N(2)–C(10)–N(1)	126.5(6)	N(2)–C(10)–S(1)	114.8(5)
N(1)–C(10)–S(1)	118.6(5)	N(1)–C(11)–C(12)	120.2(7)

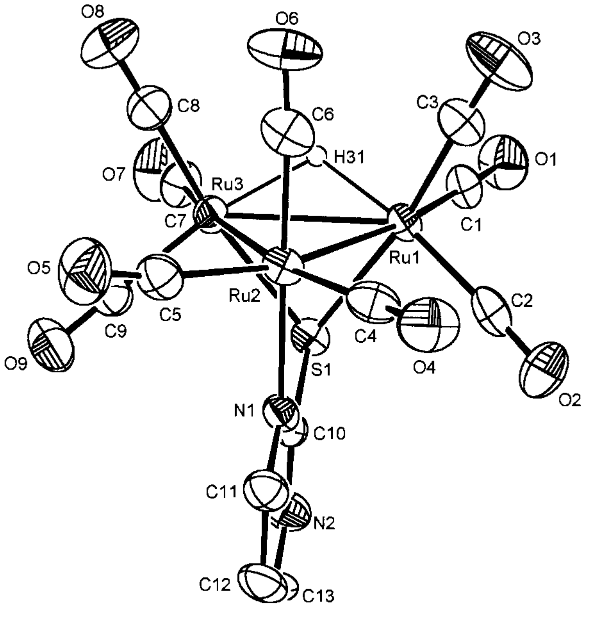


Fig. 2. Molecular structure of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}SN_2C_4H_3)(CO)_9]$ (**5**) showing the atom labeling scheme. The ring hydrogens are omitted for clarity. The thermal ellipsoids are drawn at 45% probability level.

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

A THF solution (100 ml) of $[Ru_3(CO)_{12}]$ (0.400 g, 0.62 mmol) and benzothiazole (140 µl, 1.25 mmol) was heated to reflux for 3 h during which time the color of the solution changed from orange to red. The reaction was monitored by spot TLC. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexanedeveloped two bands. The faster moving band gave $[Ru_3(\mu\text{-}H)(\mu\text{-}2,3\text{-}\eta^2\text{-}NSC_7H_4)(CO)_{10}]$ (**3**) as orange crystals (0.202 g, 45%) from hexane–CH_2Cl_2 at −20°C. Anal. Calc. for $C_{17}H_5NO_{10}Ru_3S$: C, 28.42; H, 0.70; N, 1.95. Found: C, 28.65; H, 0.84; N, 1.98%. IR (ν(CO), hexane): 2103s, 2066vs, 2056vs, 2029vs, 2022vs, 2008s, 1991w, 1978w, 1966w cm^{-1}; ^{1}H-NMR (CDCl$_3$): δ 7.75 (d, 1H, $J = 7.9$ Hz), 7.54 (t, 1H, $J = 6.7$ Hz), 7.48 (t, 1H, $J = 7.6$ Hz), 7.30 (d, 1H, $J = 7.3$ Hz), -14.26 (s, 1H); MS: (m/z) 721 [M$^+$], 693 [M$^+$ − CO], 665 [M$^+$ − 2CO], 637 [M$^+$ − 3CO], 609 [M$^+$ − 4CO], 581 [M$^+$ − 5CO], 553 [M$^+$ − 6CO], 525 [M$^+$ − 7CO], 497 [M$^+$ − 8CO], 469 [M$^+$ − 9CO], 441 [M$^+$ − 10CO].

The slower moving band gave [Ru$_3$(μ-H)(μ-1,2-η^2-NSC$_7$H$_4$)(CO)$_9$] (**4**) as orange microcrystals (0.108 g, 25%) after recrystallization from hexane–CH$_2$Cl$_2$ at −20°C. Anal. Calc. for C$_{16}$H$_5$NO$_9$Ru$_3$S: C, 27.83; H, 0.73; N, 2.03. Found: C, 27.94; H, 0.85; N, 2.09%. IR (ν(CO) hexane): 2090s, 2060vs, 2050vs, 2036w, 2021w, 2012s, 2000w, 1991w, 1970w, 1965w cm^{-1}; ^{1}H-NMR (CDCl$_3$): δ 7.80 (d, 1H, $J = 7.7$ Hz), 7.61 (d, 1H, $J = 8.0$ Hz), 7.46 (t, 1H, $J = 7.7$ Hz), 7.30 (t, 1H, $J = 7.7$ Hz), -12.78 (s, 1H). MS: (m/z) 692 [M$^+$], 664 [M$^+$ − CO], 636 [M$^+$ − 2CO], 608 [M$^+$ − 3CO], 580 [M$^+$ − 4CO], 552 [M$^+$ − 5CO], 524 [M$^+$ − 6CO], 496 [M$^+$ − 7CO], 468 [M$^+$ − 8CO], 440 [M$^+$ − 9CO].

3.2. Thermolysis of **3**

A cyclohexane solution (35 ml) of **3** (0.035 g, 0.05 mmol) was refluxed for 1 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane gave several bands of which the major band afforded **4** (0.010 g, 30%) as an orange microcrystalline product.

3.3. Reaction of [Ru$_3$(CO)$_{12}$] with pyrimidine-2-thione

A mixture of [Ru$_3$(CO)$_{12}$] (0.400 g, 0.62 mmol) and pyrimidine-2-thione (1.149 g, 1.33 mmol) in dry THF (80 ml) was heated to reflux for 2 h with monitoring by analytical TLC. The color of the solution changed from orange to red. The solvent was removed in vacuo and the residue chromatographed by TLC on silica gel. Elution with 4:1 hexane–CH$_2$Cl$_2$ gave two bands. The faster moving band yielded [Ru$_3$(μ-H)(μ$_3$-η^2-N$_2$SC$_4$H$_3$)(CO)$_9$] (**5**) as red crystals (0.060 g, 35%) from hexane–CH$_2$Cl$_2$ at −20°C. Anal. Calc. for C$_{13}$H$_4$N$_2$O$_8$S Ru$_3$: C, 23.97; H, 0.62; N, 4.30. Found: C, 24.15; H, 0.74; N, 4.38%. IR (ν(CO) hexane): 2087s, 2058s, 2037vs, 2010s, 1999m, 1976w, 1967w cm^{-1}; ^{1}H-NMR (CDCl$_3$): δ 8.77 (overlapping dd, 1H, $J = 4.0$ Hz), 8.40 (overlapping dd, 1H), 7.10 (t, 1H, $J = 5.2$ Hz), -13.16 (s, 1H). The second band gave a small quantity (ca. 0.002 g) of an uncharacterized compound.

3.4. Reaction of [Ru$_3$(CO)$_{12}$] with benzimidazole-2-thione

A mixture of [Ru$_3$(CO)$_{12}$] (0.400 g, 0.62 mmol) and 2-benzimidazole-2-thione (0.206 g, 1.37 mmol) in THF (80 ml) was refluxed for 2 h with monitoring by spot TLC. The solvent was removed by rotary evaporation and the residue chromatographed by TLC on silica gel. Elution with 9:1 hexane–CH$_2$Cl$_2$ gave two bands. The major band yielded [Ru$_3$(μ-H)(μ$_3$-η^2-N$_2$SC$_7$H$_5$)(CO)$_9$] (**6**) as red microcrystals (0.110 g, 25%) from hexane–CH$_2$Cl$_2$ at −20°C. Anal. Calc. for C$_{16}$H$_6$N$_2$O$_9$Ru$_3$S: C, 27.24; H, 0.86; N, 3.97. Found: C, 27.40; H, 0.94; N, 4.05%. IR(ν(CO) hexane): 2084m, 2054s, 2033s, 2003m, 2068w, 2047w, 2043w cm^{-1}; ^{1}H-NMR (CDCl$_3$): δ 9.48 (s, 1H), 7.41 (d, 1H, $J = 3.2$ Hz), 7.30 (m, 3H), -12.92 (s, 1H). MS: (m/z) 708 [M$^+$], 680 [M$^+$ − CO], 652 [M$^+$ − 2CO], 624 [M$^+$ − 3CO], 596 [M$^+$ − 4CO], 568 [M$^+$ − 5CO], 540 [M$^+$ − 6CO], 512 [M$^+$ − 7CO], 484 [M$^+$ − 8CO], 456 [M$^+$ − 9CO].

3.5. X-ray crystallography

Crystallographic measurements for complexes **3** and **5** were made on a Delft Instruments FAST TV area detector diffractometer in a manner described previously [19]. In both cases the unit cell parameters were determined by least-squares refinement of the diffractometer angles for 250 reflections, and the data were corrected for absorption using DIFABS [20]. The 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 data with intensities > 0. All non-hydrogen atoms were anisotropic. The bridging hydrides were located from difference maps, but not refined. Other hydrogen atoms were included in calculated positions (riding model). The final R-values are quoted in Table 3.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CSD-114653 for compound **3** and 114652 for compound **5**. 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 or http://www.ccdc.cam.ac.uk).

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Table 3
Crystal data and details of data collection and structure refinement [a] for $[Ru_3(\mu\text{-}H)(\mu\text{-}2,3\text{-}\eta^2\text{-}C_7H_4NS)(CO)_{10}]$ (**3**) and $[Ru_3(\mu_3\text{-}\eta^2\text{-}C_4H_3N_2S)(CO)_9]$ (**5**)

	3	**5**
Empirical formula	$C_{17}H_5NO_{10}Ru_3S$	$C_{13}H_4N_2O_9Ru_3S$
Formula weight	718.49	667.45
a (Å)	8.854(2)	8.9775(7)
b (Å)	9.686(2)	11.7575(6)
c (Å)	24.799(5)	18.0842(10)
β (°)	92.00(3)	93.160(12)
V (Å^3)	2125.5(8)	1905.9(2)
T (K)	150	293
D_{calc} (g cm$^{-3)}$	2.245	2.326
μ (Mo–K$_a$) (cm^{-1})	22.57	25.05
$F(000)$	1368	1264
Crystal size (mm)	$0.10 \times 0.10 \times 0.08$	$0.08 \times 0.08 \times 0.06$
θ Range for data collection (°)	2.26–25.00	2.07–25.09
Index ranges	$-10 \leq h \leq 10$, $-11 \leq k \leq 5$, $-28 \leq l \leq 29$	$-9 \leq h \leq 6$, $-12 \leq k \leq 13$, $-19 \leq l \leq 20$
Reflections collected	7595	7742
Independent reflections	3204 [$R_{int} = 0.0648$]	2852 [$R_{int} = 0.0797$]
Absorption correction factors	0.889–1.012	0.896–1.018
Data/parameters	3204/289	2852/253
Goodness-of-fit on F^2	0.884	0.924
Final R [b] indices (all data)	$R_1 = 0.0438$, $wR_2 = 0.0715$	$R_1 = 0.0457$, $wR_2 = 0.0805$
R indices [$F_o^2 > 2\sigma(F_o^2)$]	$R_1 = 0.0315$, $wR_2 = 0.0694$	$R_1 = 0.0336$, $wR_2 = 0.0785$
Largest difference peak and hole (e Å^{-3})	0.756 and -0.664	0.854 and -0.754

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[a] Details in common: X-radiation, Mo–K$_\alpha$, $\lambda = 0.71069$ Å; monoclinic, space group $P2_1/c$; refinement method: full-matrix least-squares on F^2 using all unique data.

[b] $R_1 = \Sigma[(F_o)-(F_c)]/\Sigma(F_o)$; $wR_2 = [\Sigma\{w(F_o^2-F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$; $w = 1/[\sigma^2(F_o)^2+(aP)^2]$, where $P = [(F_o)^2+2(F_c)^2]/3$, and $a = 0.0168$ (**3**) and 0.0252 (**5**).

References

[1] K.A. Azam, R. Dilshad, S.E. Kabir, L. Nessa, K. Khaton, M.M. Rahman, E. Rosenberg, M.B. Hursthouse, K.M.A. Malik, A.J. Deeming, J. Chem. Soc. Dalton Trans. (1996) 1731.

[2] K.A. Azam, M.B. Hursthouse, S.A. Hussain, S.E. Kabir, M.M. Rahman, K.M.A. Malik, E. Rosenberg, J. Organomet. Chem. 559 (1998) 81.

[3] K.A. Azam, M.B. Hursthouse, S.E. Kabir, K.M.A. Malik, M. Tesmer, H. Vahrenkamp, Inorg. Chem. Commun. 1 (1998) 402.

[4] A.J. Deeming, K.I. Hardcastle, M. Karim, Inorg. Chem. 31 (1992) 4792.

[5] A.M. Brodie, H.D. Holden, J. Lewis, M.J. Taylor, J. Chem. Soc. Dalton Trans. (1986) 633.

[6] Y.K Au, K.K. Cheung, W.T. Wong, J. Chem. Soc. Dalton Trans. (1995) 1047.

[7] S. Jeannin, Y. Jeannin, G. Lavigne, Inorg. Chem. 17 (1978) 2103.

[8] K.M. Hanif, M.B. Hursthouse, S.E. Kabir, K.M.A. Malik, E. Rosenberg, J. Organomet. Chem. 580 (1999) 60.

[9] M.R. Churchill, F.J. Hollander, J.P. Hatchinson, Inorg. Chem. 16 (1977) 2655.

[10] R.H. Fish, T. Kim, J.L. Stewart, J.H. Bashweller, R.K. Rosen, J.W. Dupan, Organometallics 5 (1986) 193.

[11] J.A. Cabeza, L.A. Oro, A.T. Camellini, J. Chem. Soc. Dalton Trans. (1988) 1437.

[12] S.M.T. Abedin, K.A. Azam, M.B. Hursthouse, S.E. Kabir, K.M.A. Malik, R. Miah, H. Vahrenkamp, J. Organomet. Chem. 564 (1998) 133.

[13] R.D. Adams, N.M. Golembeski, J.P. Selegue, J. Am. Chem. Soc. 103 (1981) 546.

[14] R.D. Adams, Z. Dawoodi, D.F. Foust, B.E. Segmuller, Organometallics 2 (1983) 315.

[15] R.D. Adams, D.A. Katahira, L.W. Yang, Organometallics 1 (1982) 235.

[16] H.D. Holden, B.F.G. Johnson, J. Lewis, P.R. Raithbey, G. Uden, Acta Crystallogr. C39 (1983) 1200.

[17] J. Zabicky (Ed.), The Chemistry of Amides, Interscience, London, 1970, p. 388.

[18] Y.K. Au, K.K. Cheung, W.T. Wong, Inorg. Chim. Acta 228 (1995) 267.

[19] J.A. Darr, S.R. Drake, M.B. Hursthouse, K.M.A. Malik, Inorg. Chem. 32 (1993) 5704.

[20] N.P.C. Walker, D. Stuart, Acta Crystallogr. A39 (1983) 158.

[21] G.M. Sheldrick, SHELXS-86, Acta Crystallogr. A46 (1990) 467.

[22] G.M. Sheldrick, SHELXL-93, Program for crystal structure refinement, University of Göttingen, Germany, 1993.