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Sulfur-containing trinuclear arene ruthenium clusters

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Abstract

The single-crystal X-ray structure analyses of $[HRu_3(C_6H_6)(C_6Me_6)_2(\mu_3\text{-}SC_6H_4Me)(\mu_2\text{-}O)][BF_4]_2$ ([**1**][BF_4]$_2$), $[HRu_3(C_6H_6)(C_6Me_6)_2(\mu_3\text{-}SC_6H_4Me)(\mu_2\text{-}S)][PF_6]_2$ ([**2**][PF_6]$_2$) and $[H_2Ru_3(1,2,4,5\text{-}Me_4C_6H_2)_3(\mu_2\text{-}S)(Cl)]PF_6$ ([**3**][PF_6]) are presented. The structures show the sulfur ligands to act as bridges between ruthenium atoms. In [**1**][BF_4]$_2$ and [**2**][PF_6]$_2$ the metallic core adopts a nido framework. However, in [**3**][PF_6] the absence of a μ_3-SR ligand combined with the presence of one terminal chloro unit gives rise to a closo metallic arrangement.

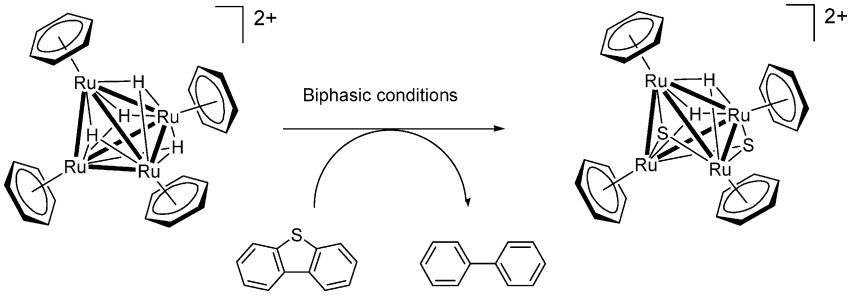
Keywords: Arene ligands; Clusters; Trinuclear complexes; Hydrido; Sulfido; Ruthenium

1. Introduction

The versatility of arene ruthenium units for cluster build-up reactions is well documented [1–14]. Arene ruthenium clusters have an interesting catalytic potential for hydrogenation reactions and for other processes, in particular hydrodesulfurisation reactions that have been extensively studied in recent years, because of the necessity of removing sulfur from petroleum feedstocks [15]. We have shown recently that the tetranuclear cluster dication $[H_4Ru_4(C_6H_6)_4]^{2+}$ reacts with two equivalents of benzothiophene derivatives to give the organometallic cluster $[H_2S_2Ru_4(C_6H_6)_4]^{2+}$ [16].

The double desulfurisation reaction was achieved under mild biphasic conditions; however, the mechanism remains unclear. Therefore, in an attempt to rationalize this initial result, we studied the reactivity of arene ruthenium complexes with thiophenol derivatives.

Herein, we report the single-crystal structure analyses of three cationic trinuclear arene ruthenium clusters, $[HRu_3(C_6H_6)(C_6Me_6)_2(\mu_3\text{-}SC_6H_4Me)(\mu_2\text{-}O)]^{2+}$ (**1**), $[HRu_3(C_6H_6)(C_6Me_6)_2(\mu_3\text{-}SC_6H_4Me)(\mu_2\text{-}S)]^{2+}$ (**2**) and $[H_2Ru_3(1,2,4,5\text{-}Me_4C_6H_2)_3(\mu_2\text{-}S)(Cl)]^{+}$ (**3**), crystallised as the tetrafluoroborate or hexafluorophosphate salts. The molecular structures show the sulfur ligands to act as bridges between ruthenium atoms. In **1** and **2** the metallic core adopts a nido framework, while in **3** the absence of a μ_3-SR ligand combined with the presence of one terminal chloro unit gives rise to a closo metal skeleton.



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2. Experimental section

2.1. General remarks

The starting compounds $[H_2Ru_2(C_6Me_6)_2(\mu_2\text{-}SC_6H_4Me)][BF_4]$, $[Ru(C_6H_6)(H_2O)_3][BF_4]_2$ and $[H_4Ru_4(1,2,4,5\text{-}Me_4C_6H_2)_4][Cl]_2$ were prepared according to published methods [17–19].

2.2. Crystallisations

Preparation of $[HRu_3(C_6H_6)(C_6Me_6)_2(\mu_3\text{-}SC_6H_4Me)(\mu_2\text{-}O)][BF_4]_2$ ([**1**][BF_4]$_2$) and of $[HRu_3(C_6H_6)(C_6Me_6)_2(\mu_3\text{-}SC_6H_4Me)(\mu_2\text{-}S)][PF_6]_2$ ([**2**][PF_6]$_2$): in a pressure Schlenk tube $[H_2Ru_2(C_6Me_6)_2(\mu_2\text{-}SC_6H_4Me)][BF_4]$ (80 mg, 0.27 mmol) is dissolved in degassed acetone (20 ml) and a filtered aqueous solution (20 ml) of $[Ru(C_6H_6)(H_2O)_3][BF_4]_2$ (0.11 mmol) is added ($[Ru(C_6H_6)(H_2O)_3][BF_4]_2$ being prepared quantitatively *in situ* by reacting $[(C_6H_6)_2Ru_2Cl_4]$ with four equivalents of $AgBF_4$). The mixture is stirred and heated to 50 °C for 3 days. Then the solution is filtered and the solvent removed under reduced pressure. The residue is purified by preparative thin-layer chromatography on silica (eluent acetone/dichloromethane 2:5). The lowest yellow–orange band containing a mixture of products is recovered and extracted with acetone.

Crystals of [**1**][BF_4]$_2$ are obtained by slow diffusion of ether into an acetone solution containing the extracted mixture of compounds.

Crystals of [**2**][PF_6]$_2$ are obtained after addition of KPF_6 and slow evaporation of an acetone solution of the extracted mixture.

Preparation of $[H_2Ru_3(1,2,4,5\text{-}Me_4C_6H_2)_3(\mu_2\text{-}S)(Cl)][PF_6]$ ([**3**][PF_6]): $[H_4Ru_4(1,2,4,5\text{-}Me_4C_6H_2)_4][Cl]_2$ (100 mg, 0.1 mmol) and *p*-bromothiophenol (100 mg, 0.5 mmol) are dissolved in degassed technical grade ethanol (60 ml) and heated under reflux for 12 h. After cooling to room temperature the red solution is filtered through celite and the solvent is removed under reduced pressure. The red oil obtained is purified by column chromatography (silica gel, ethanol/dichloromethane 1:1, r_f close to 0.7). The red fraction containing the chloride salt of **3** is recovered.

Crystals of [**3**][PF_6] are obtained by diffusion of benzene into a saturated solution of NH_4PF_6 and $CHCl_3$.

2.3. X-ray crystallographic study

Crystals of [**1**][BF_4]$_2\cdot H_2O$, [**2**][PF_6]$_2\cdot$acetone and [**3**][PF_6] were mounted on a Stoe Image Plate Diffraction system equipped with a ϕ circle goniometer, using Mo Kα graphite monochromated radiation ($\lambda = 0.71073$ Å) with ϕ range 0–200°, increment of 0.7, 1.2 and 0.7°, respectively, 2θ range from 2.0 to 26°, $D_{max} - D_{min} = 12.45$–$0.81$ Å. The structures were solved by direct methods using the program SHELXS-97 [20]. The refinement and all further calculations were carried out using SHELXL-97 [21]. In the three structures, the hydrido ligands were not located from Fourier difference maps and they were generated at their positions, whereas the remaining H-atoms were included in

Table 1
Crystallographic and selected experimental data for [**1**][BF_4]$_2$, [**2**][PF_6]$_2$ and [**3**][PF_6]

	[**1**][BF_4]$_2\cdot$0.5 H_2O	[**2**][PF_6]$_2\cdot$acetone	[**3**][PF_6]
Chemical formula	$C_{74}H_{102}F_{16}B_4O_3S_2Ru_6$	$C_{40}H_{56}F_{12}OP_2S_2Ru_3$	$C_{30}H_{44}ClF_6PSRu_3$
Formula weight	2057.34	1210.12	920.34
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	*P* $2_1/c$	*P-1*	$P2_1/n$
Crystal colour and shape	Orange block	Orange block	Red plate
Crystal size	$0.18\times0.09\times0.08$	$0.29\times0.25\times0.12$	$0.52\times0.43\times0.19$
a (Å)	35.293(4)	10.9418(10)	9.4900(8)
b (Å)	10.5397(6)	12.3926(11)	18.2420(10)
c (Å)	21.3698(17)	18.8377(16)	19.2584(19)
α (°)		80.993(11)	
β (°)	90.914(11)	79.661(11)	78.234(11)
γ (°)		73.977(11)	
V (Å^3)	7948.0(11)	2399.7(4)	3263.9(5)
Z	4	2	4
T (K)	153(2)	153(2)	153(2)
D_c (g cm^{-3})	1.719	1.675	1.873
μ (mm^{-1})	1.246	1.163	1.620
Scan range (°)	$3.96 < 2\theta < 51.98$	$3.88 < 2\theta < 51.80$	$4.32 < 2\theta < 51.94$
Unique reflections	12,655	8705	6325
Reflections used	4185	5830	3365
R_{int}	0.1427	0.0593	0.1729
Final *R* indices [$I > 2\sigma(I)$]	0.0832, wR_2 0.1788	0.0389, wR_2 0.0823	0.0482, wR_2 0.0870
R indices (all data)	0.1954, wR_2 0.2046	0.0654, wR_2 0.0874	0.1117, wR_2 0.0991
Goodness-of-fit	0.808	0.869	0.788
Max, min $\Delta\rho/e$ (Å^{-3})	1.481, −1.619	0.793, −0.831	0.858, −0.950

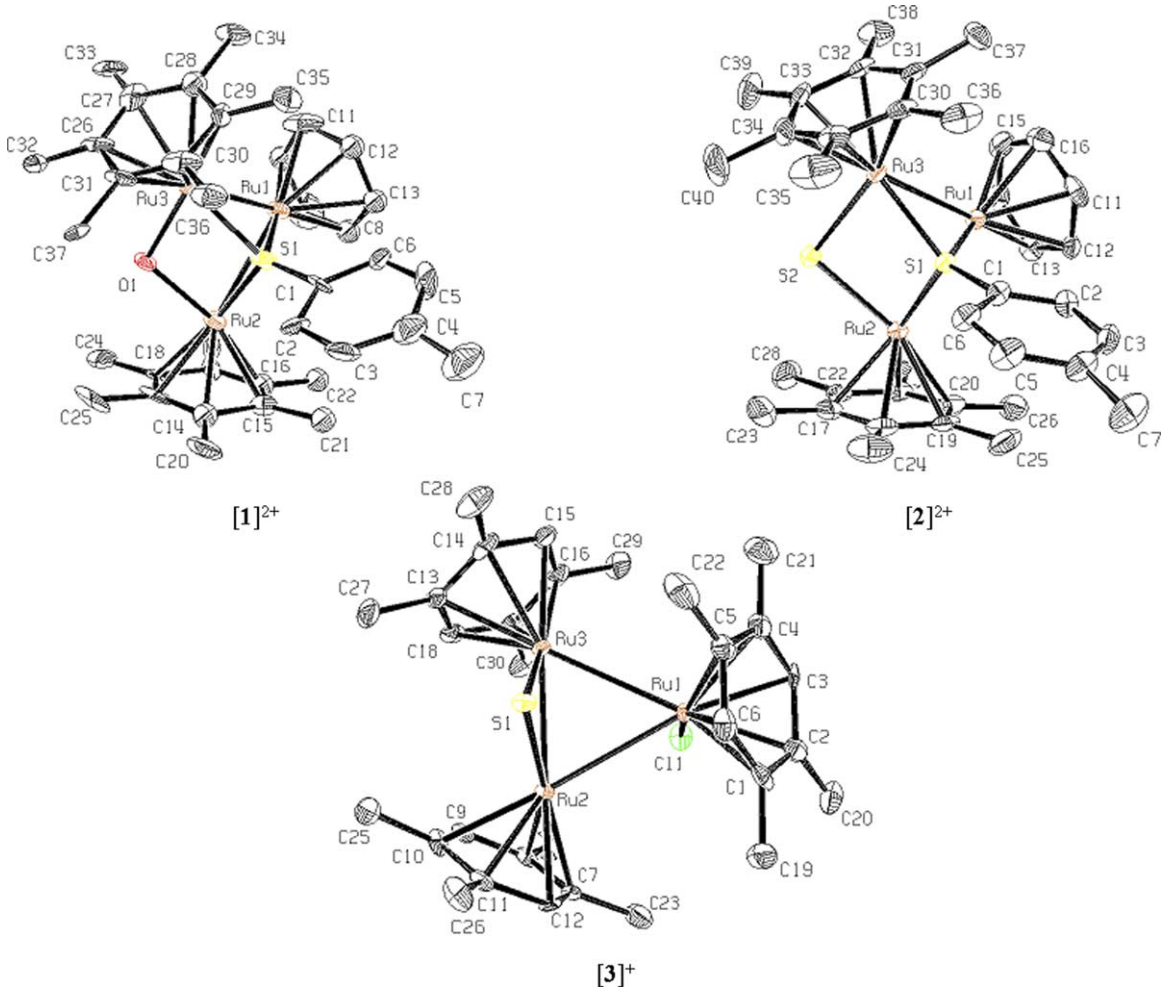


Fig. 1. Molecular structures of cations **1**, **2** and **3**. Displacement ellipsoids are drawn at the 35% probability level, anions, solvents and hydrogen atoms are omitted for clarity.

calculated positions and treated as riding atoms using the SHELXL default parameters. In all cases the non-H atoms were refined anisotropically, using weighted full-matrix least-square on F^2. In complex **1**, the residual electron densities greater then 1e $Å^{-3}$ are all observed around the ruthenium atoms at less than 1 Å. Crystallographic details are summarised in Table 1. Fig. 1 was drawn with ORTEP [22] and Figs. 2 and 3 with MERCURY [23].

CCDC-259888 [**1**][BF_4]$_2$·H_2O, 259889 [**2**][PF_6]$_2$·acetone and 259887 [**3**][PF_6] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44 1223 336 033; deposit@ccdc.cam.ac.uk]

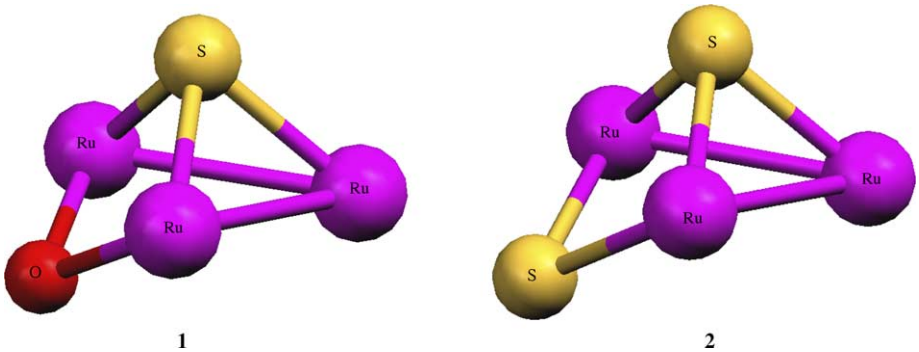


Fig. 2. Geometry of the nido metallic core of **1** and **2**.

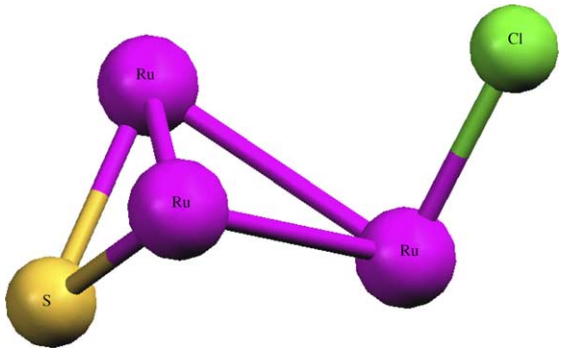


Fig. 3. Geometry of the closo Ru_3SCl skeleton in **3**.

3. Results and discussion

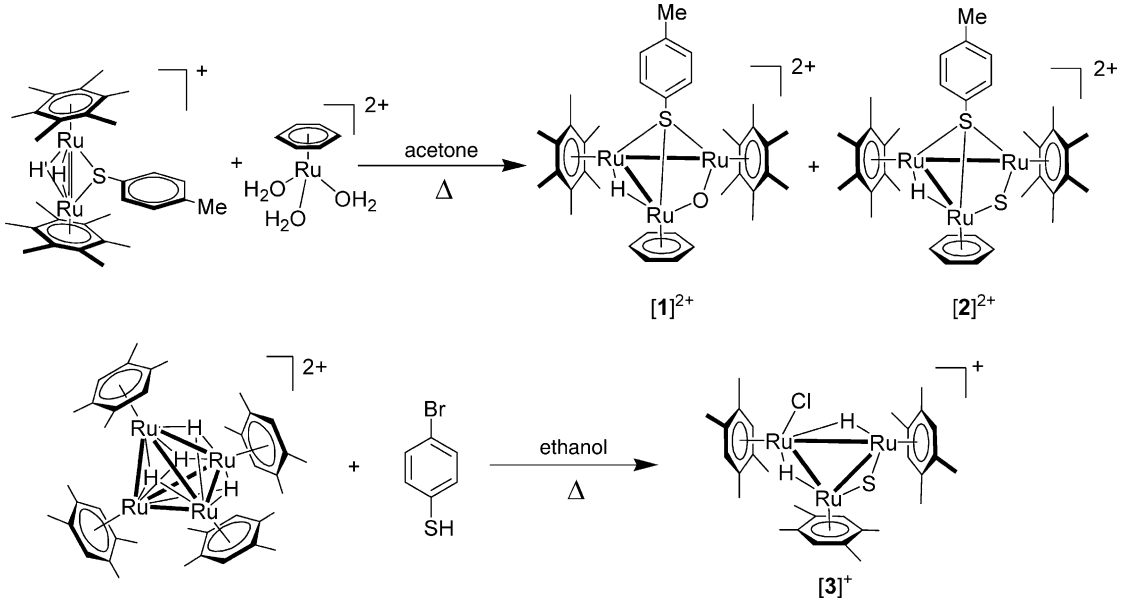
The dinuclear thiolato complex $[H_2Ru_2(C_6Me_6)_2(\mu_2\text{-}SC_6H_4Me)]^+$ was found to react with the mononuclear triaqua complex $[Ru(C_6H_6)(H_2O)_3]^{2+}$, and the tetranuclear hydrido complex $[H_4Ru_4(1,2,4,5\text{-}Me_4C_6H_2)_4]^{2+}$ was found to react with *p*-bromo-thiophenol, to give sulfur-containing trinuclear arene ruthenium clusters, see Scheme 1. In all cases, the reactions yield a complex mixture of nearly insoluble materials. ESI MS reveals the presence of many different species with peaks $m/z > 750$. Purification by chromatography of the soluble products allows us to isolate in low yield three compounds. Fortunately crystals were obtained and their structures determined, see Fig. 1.

The trinuclear arene ruthenium clusters show the metals to be in a pseudo-octahedral geometry, where the arene ligands are facially coordinated. $[\mathbf{1}][BF_4]_2$ crystallises in the centrosymmetric space group $P2_1/c$ with two independent trinuclear complexes per asymmetric unit. Fig. 1 shows only one independent molecule of **1**. The significant bond lengths and angles are given in Table 2.

The trinuclear clusters **1** and **2** possess similar geometries, in which two ruthenium atoms are bridged by a *p*-methyl-thiophenolato unit as such as by an oxo or sulfido ligand, respectively (Fig. 2). The two complexes adopt a nido Ru_3 framework. One of the two Ru–Ru single bonds (presumably the longer one [24]), which form two edges of the metal triangle, is bridged by a μ_2-hydrido ligand, which could not be located from the final Fourier difference maps. The non-bonding Ru–Ru distance (3.5997(7) Å) of the μ_2-S bridged cluster cation **2** is slightly longer than that of the μ_2-O cation **1** (3.437(1) Å). However, the distances and angles involving the μ_3-SC_6H_4Me ligand are almost identical. These structures are closely structurally related to the trinuclear arene ruthenium cluster $[H_2Ru_3(C_6H_6)_3(\mu_3\text{-}O)(\mu_2\text{-}Cl)]^+$ [19], in which the μ_3-SC_6H_4Me ligand is replaced by a μ_3-O, and the bridged μ_2-O or μ_2-S by a μ_2-Cl. The open edge Ru–Ru distance (3.331(1) Å) is slightly shorter than the one observed in **1** and **2**.

The synthesis of **3** involves a C–S bond cleavage and the formation of the corresponding desulphurised organic compound, bromobenzene. The X-ray structure analysis of complex **3** reveals that the Ru–Ru distance (2.784(1) Å) of the μ_2-S bridge is within the range (2.28–2.95 Å) of a metal–metal single bond [25]. Consequently, the complex adopts a closo framework, see Fig. 3. The μ_2-S bridged Ru–Ru distance is slightly longer than the one observed in $[Ru_2(p\text{-}MeC_6H_4^iPr)_2(\mu_2\text{-}S_2fc)]^+$ (fc, ferrocenylene) [10] and $[Ru_2(C_6F_5)(Cp^*)_2(\mu_2\text{-}S)(\mu_2\text{-}SC_6F_5)]$ [26]. The Ru-Cl distance is normal at 2.420(2) Å.

In the crystal packing of **3**, an acetone molecule is observed. The solvent forms very weak hydrogen bonds with two neighbouring cluster molecules. Otherwise there is no meaningful interaction between the dinuclear cation and the PF_6 anion, other than normal coulombic attractions.



Scheme 1.

Table 2
Selected bond lengths and angles for cations **1**, **2** and **3**

	1a	**1b**	**2**	**3**
Distances (Å)				
Ru(1)–S(1)	2.263(5)	2.258(5)	2.266(1)	
Ru(2)–S(1)	2.287(4)	2.285(4)	2.306(1)	2.400(2)
Ru(3)–S(1)	2.287(4)	2.302(4)	2.318(1)	2.413(2)
Ru(2)–S(2)	–	–	2.438(1)	–
Ru(3)–S(2)	–	–	2.429(1)	–
Ru(1)–Cl(1)	–	–	–	2.420(2)
Ru(2)–O(1)	2.148(9)	2.107(9)	–	–
Ru(3)–O(1)	2.145(9)	2.141(8)	–	–
Ru(1)–Ru(2)	2.930(2)	2.930(2)	2.9424(6)	3.061(1)
Ru(1)–Ru(3)	2.928(2)	2.926(2)	2.9475(6)	3.045(1)
Ru(2)–Ru(3)	3.437(1)	3.420(1)	3.5997(7)	2.784(1)
Angles (°)				
Ru(1)–S(1)–Ru(2)	80.17(15)	80.31(15)	80.11(4)	
Ru(1)–S(1)–Ru(3)	80.11(15)	79.81(16)	80.03(4)	
Ru(2)–S(1)–Ru(3)	97.43(18)	96.41(18)	102.23(4)	70.69(5)
Ru(2)–O(1)–Ru(3)	106.4(4)	107.3(4)		
Ru(2)–S(2)–Ru(3)			95.38(4)	

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