Elimination of sulfur from aromatic heterocycles by a water-soluble arene ruthenium cluster: synthesis and molecular structure of [H₂S₂Ru₄(C₆H₆)₄]Cl₂

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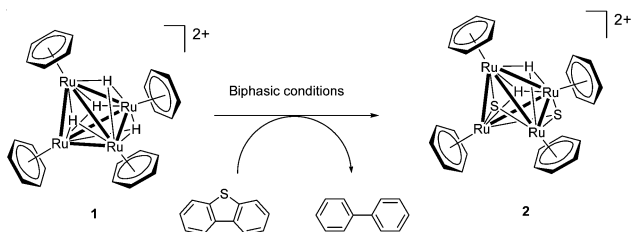**C–S bond cleavage in thiophene, benzothiophene and dibenzothiophene is achieved under biphasic conditions by the water-soluble cluster cation [H₄Ru₄(C₆H₆)₄]²⁺ which is converted into the disulfido cluster [H₂S₂Ru₄(C₆H₆)₄]²⁺.**

During the last 15 years, the hydrodesulfurization (HDS) process has been extensively investigated because of the need to remove sulfur from organosulfur compounds contained in petroleum feedstock or in natural gas.[1] Due to the aromaticity of thiophene and its derivatives, this process is more difficult than in acyclic or aliphatic sulfur compounds. Thus, many studies have been reported to understand the different steps of the cleavage of the carbon–sulfur bonds by molecular organometallic compounds in homogenous phase.[2] However, the mechanisms are still unclear. On the other hand, despite the catalytic potential of metal clusters, there are only a few reports of their use in the HDS process.[3] All these studies have been realized in homogenous phase, although biphasic conditions are interesting for industrial applications.[4] We report in this paper the first example of C–S bond cleavage under biphasic conditions by organometallic clusters and the single-crystal X-ray structure analysis of the resulting organometallic cluster, functionalised with two sulfur atoms.

The tetranuclear cluster dication [H₄Ru₄(C₆H₆)₄]²⁺ **1** which we reported some years ago was found to be soluble in water and stable towards hydrolysis[5] and can be used in the catalytic hydrogenation of benzene under biphasic conditions.[6] We now found **1** to react with two equivalents of thiophene, benzothiophene or dibenzothiophene under biphasic conditions (water/toluene, 110 °C, 4 days) to give the organometallic cluster dication [H₂S₂Ru₄(C₆H₆)₄]²⁺ **2** and the corresponding desulfurized organic compound (buta-1,3-diene, styrene and biphenyl, respectively) as depicted in Scheme 1.[7]

The ¹H NMR spectrum of **2** shows only one hydride resonance at −15.31 ppm and two singlets at 5.95 and 6.40 ppm, corresponding to two pairs of non-equivalent benzene ligands. Accordingly, the ¹³C NMR spectrum shows also two benzene signals (87.05 and 87.55 ppm).

Suitable crystals of [**2**]Cl₂ were obtained from an aqueous solution. The single-crystal X-ray structure analysis reveals for the dication **2** an open metal framework (Fig. 1) as opposed to a closed tetrahedreal skeleton in **1**.‡
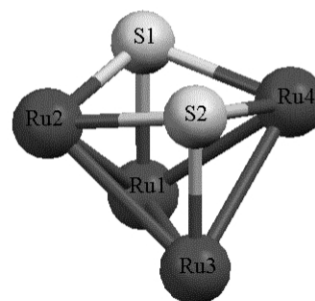
The molecular structure of **2** is very interesting: The open Ru₄ framework shows one elongated Ru–Ru bond [Ru(1)–Ru(3) 2.9953(13) Å] and four normal Ru–Ru distances [average 2.91 Å]. Each ruthenium atom is coordinated in a η⁶-fashion to a benzene ligand. Two sulfur atoms and two hydrogen atoms have been localized as μ₃-capping ligands over the triangular Ru₃ faces of **2**. With an electron count of 64, the metal framework of **2** forms a Ru₄ butterfly structure, the Ru₄S₂ skeleton may be considered as a capped trigonal bipyramidal arrangement in accordance with Wade's rules (Fig. 2). By contrast, the known 62e cluster Ru₄(CO)₉(PMePh₂)₂S₂ has a square planar Ru₄ metal framework, the Ru₄S₂ skeleton being octahedral.[8] However, a few examples of similar structures as in **2** are known, mostly in carbonyl clusters such as the 64e cluster Os₄S₂(CO)₁₂.[9]
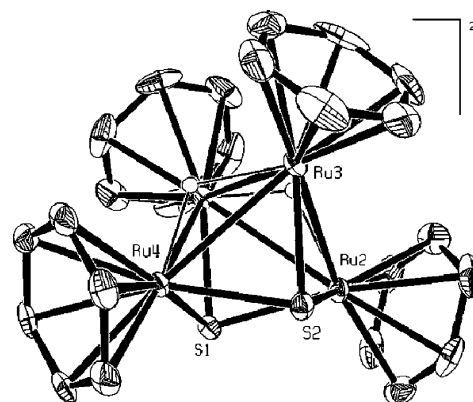
Fig. 1 Ortep drawing of [H₂S₂Ru₄(C₆H₆)₄]²⁺ **2**, displacement ellipsoids are drawn at the 35% probability level, hydrogen atoms, water molecules, and anions are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–Ru(2) 2.9086(9), Ru(1)–Ru(3) 2.9953(13), Ru(1)–Ru(4) 2.8950(9), Ru(2)–Ru(3) 2.9135(12), Ru(3)–Ru(4) 2.9080(12), Ru(1)–S(1) 2.2763(14), Ru(2)–S(1) 2.3394(15), Ru(4)–S(1) 2.3414(14), Ru(2)–S(2) 2.3444(13), Ru(3)–S(2) 2.2686(14), Ru(4)–S(2) 2.3404(14); Ru(2)–S(1)–Ru(4) 96.33(6), Ru(2)–S(2)–Ru(4) 96.22(5), Ru(2)–Ru(1)–Ru(3) 59.12(2), Ru(3)–Ru(1)–Ru(4) 59.14(2), Ru(1)–Ru(2)–Ru(3) 49.69(4), Ru(1)–Ru(3)–Ru(2) 58.96(3), Ru(1)–Ru(3)–Ru(4) 58.71(3), Ru(1)–Ru(4)–Ru(3) 62.15(2).

Scheme 1 Formation of [H₂S₂Ru₄(C₆H₆)₄]²⁺ by the desulfurization of dibenzothiophene.

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Fig. 2 Geometry of the Ru₄S₂ skeleton in [H₂S₂Ru₄(C₆H₆)₄]²⁺ **2**.

This is the first example of an organometallic compound extracting two sulfur equivalents, because normally only one equivalent of an organosulfur compound reacts with one equivalent of an organometallic complex.[3] For example, in a similar approach with the unsaturated trinuclear ruthenium trihydrido cluster $[(C_5Me_5)_3Ru_3(\mu_3\text{-H})_2(\mu_2\text{-H})_3]$, Suzuki *et al.* have observed the insertion of one sulfur atom during the process.[3a] In this case, the desulfurization reaction has induced the substitution of two hydrides (μ_3-H) by one sulfur atom to finally give $[(C_5Me_5)_3Ru_3(\mu_3\text{-S})(\mu_2\text{-H})_3]$. A second uptake of sulfur is not possible, since there is no μ_3-H ligand left for a second substitution.

In the case of electron-deficient cluster $[H_4Ru_4(C_6H_6)_4]^{2+}$ **1** (58e), the desulfurization of sulfur-containing aromatics leads to the replacement of two μ_3-H ligands (1e) by two μ_3-S ligands (4e), which increases the electron count of the cluster by 6 to 64e. As a consequence of this, one Ru–Ru bond of the Ru_4 tetrahedron is opened (Ru(2)–Ru(4): 3.487 Å) and a second one is widened (Ru(1)–Ru(3): 2.995 Å). Thus, the driving force of the reaction seems to be due to two additional effects: i) the electron deficiency of the starting cluster **1**, and ii) the structural modification of the tetrahedral Ru-framework of **1** which leads to the open cluster **2**. Despite several attempts, we have not succeeded in isolating or determining the presence of intermediates during the desulfurization process as they have been characterized in the case of carbonyl metal clusters.[3b–f]

In conclusion, we have found a new approach to enhance the desulfurization process by an unsaturated organometallic ruthenium cluster. This process can be achieved, for the first time, under mild biphasic conditions. The fundamental concept of this new approach is the use of the structural transformation of an electron deficient tetrahedral cluster to an electron saturated arachno cluster as driving force of the reaction. This effect has led to a double desulfurization reaction with only one equivalent of starting cluster.

Notes and references

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7 *General Procedure*: [H$_4$Ru$_4$(C$_6$H$_6$)$_4$]Cl$_2$ (0.1 mmol, 79 mg) was dissolved in 10 ml of water. 0.5 mmol of aromatic sulfur heterocycles (thiophene, 42 mg; benzothiophene, 67 mg and dibenzothiophene, 92 mg, respectively) were dissolved in 10 ml of toluene. The biphasic mixture was heated at 110 °C for 4 days. After cooling to room temperature, the two layers were separated, the aqueous phase was filtered over celite and then removed under reduced pressure to give the pure salt [H$_2$S$_2$Ru$_4$(C$_6$H$_6$)$_4$]Cl$_2$ as brown power. The organic products were analysed by mass spectroscopy and they were recovered by removing the solvent (toluene) under reduced pressure. [H$_2$S$_2$Ru$_4$(C$_6$H$_6$)$_4$]Cl$_2$: Yield: 80%. ^{1}H NMR (CD$_3$OD, 200 MHz): -15.31 (2H, s, hydrides), 5.95 (12H, s, C*H* of benzene ligands), 6.40 (12H, s, C*H* of benzene ligands). ^{13}C NMR (CD$_3$OD, 50 MHz): 87.05 (s, C*H* of benzene ligands), 87.55 (s, C*H* of benzene ligands). MS (ESI): 784 (M + H).

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