

Preparation and X-Ray Crystal Structures of Trinuclear Ruthenium(II) Clusters containing Capped Sulfide Ligands, $[\text{Ru}_3(\text{C}_5\text{Me}_5)_3(\mu_3\text{-S})(\mu_3\text{-Cl})]$ and $[\text{Ru}_3(\text{C}_5\text{Me}_5)_3(\mu_3\text{-S})(\mu_3\text{-SP}^i)]$

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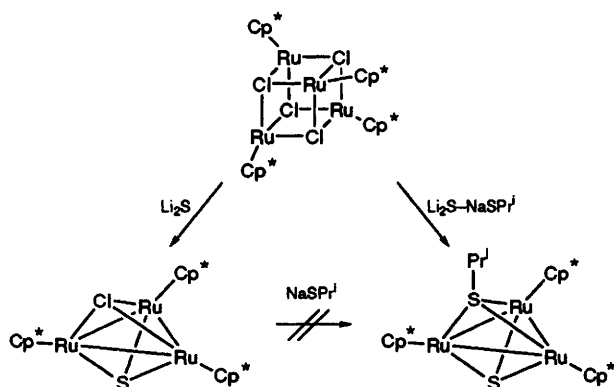
Triruthenium sulfide clusters $[\text{Ru}_3(\text{C}_5\text{Me}_5)_3(\mu_3\text{-S})(\mu_3\text{-Cl})]$ and $[\text{Ru}_3(\text{C}_5\text{Me}_5)_3(\mu_3\text{-S})(\mu_3\text{-SP}^i)]$ were obtained from the reaction of $[\text{Ru}_4(\text{C}_5\text{Me}_5)_4(\mu_3\text{-Cl})_4]$ with Li_2S alone or a Li_2S - NaSP^i mixture, respectively; their structures have been determined by X-ray crystallography.

Intensive studies on ruthenium complexes containing the $\text{Ru}(\text{C}_5\text{Me}_5)$ unit, $[\text{Ru}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_2(\mu_2\text{-Cl})_2]$,¹ $[\text{Ru}_4(\text{C}_5\text{Me}_5)_4(\mu_3\text{-Cl})_4]$ 1,² and $[\text{Ru}_2(\text{C}_5\text{Me}_5)_2(\mu_2\text{-OMe})_2]$,³ have recently shown that these complexes serve as excellent precursors to prepare numerous multinuclear ruthenium complexes which can exhibit interesting reactivities and electronic properties distinctive of their unique core structures. Our current interest in novel reactions and catalysis promoted at noble-metal sites embedded in metal-sulfur clusters has prompted us to investigate the reactions of these $\text{Ru}(\text{C}_5\text{Me}_5)$ complexes with various sulfur compounds, which has already led to the

syntheses of a series of thiolate-bridged diruthenium complexes⁴ as well as WRu_2 ,⁵ PtRu_2 , and Pd_2Ru_2 mixed-metal sulfido clusters. Furthermore, it has also been demonstrated that some thiolate-bridged diruthenium complexes obtained here can undergo unique organic transformations on their diruthenium sites.⁷ In this communication we wish to describe the syntheses from 1 of new types of clusters containing a triangular Ru_3 core capped by a $\mu_3\text{-S}$ ligand. Formation of trinuclear Ru-S clusters from $\text{Ru}(\text{C}_5\text{Me}_5)$ precursors is, until now, unknown, although the preparation of several di-^{4,8} and tetra-nuclear^{8b,9} Ru-S complexes has been reported previously.

Treatment of 1 with Li_2S ($\text{Ru}:\text{S} = 2:1$) in THF at 50 °C resulted in the formation of $[\text{Ru}_3(\text{C}_5\text{Me}_5)_3(\mu_3\text{-S})(\mu_3\text{-Cl})]$ 2, which was isolated in 50% yield as brown crystals upon cooling the filtered reaction mixture at -20 °C. On the other hand, when a mixture containing 1, Li_2S , and NaSP^i ($\text{Ru}:\text{S}:\text{SP}^i = 3:1:1$) in THF was stirred at 50 °C $[\text{Ru}_3(\text{C}_5\text{Me}_5)_3(\mu_3\text{-S})(\mu_3\text{-SP}^i)]$ 3 was obtained from the resulting reaction mixture in ca. 60% yield as brown crystals.† Attempts to prepare 3 from 2 failed; reaction of 2 with NaSP^i in THF at 50 °C resulted only in the recovery of 2 (Scheme 1).

The structures of both 2 and 3 have been unequivocally determined by X-ray crystallography,‡ although the *R* values for the former are not satisfactory due to the poor quality of the diffraction data. ORTEP drawings of 2 and 3 are depicted in Figs. 1 and 2, respectively, with important bond lengths and angles. The structures of the $\text{Ru}_3(\text{C}_5\text{Me}_5)_3(\mu_3\text{-S})$ core in the two clusters are quite similar to each other except for the



Scheme 1 $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$

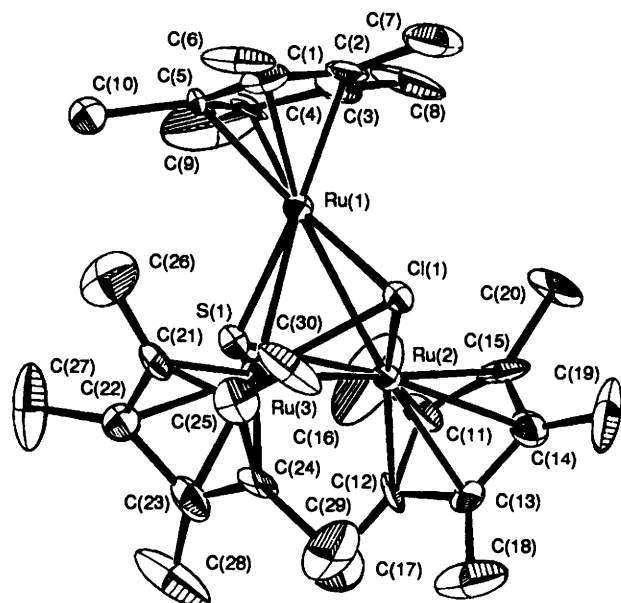


Fig. 1 Molecular structure of 2. Selected bond distances (Å) and angles (°): $\text{Ru}(1)\text{-Ru}(2)$ 2.877(2), $\text{Ru}(1)\text{-Ru}(3)$ 2.901(2), $\text{Ru}(2)\text{-Ru}(3)$ 2.874(2), $\text{Ru}(1)\text{-S}(1)$ 2.300(5), $\text{Ru}(2)\text{-S}(1)$ 2.287(5), $\text{Ru}(3)\text{-S}(1)$ 2.288(5), $\text{Ru}(1)\text{-Cl}(1)$ 2.359(5), $\text{Ru}(2)\text{-Cl}(1)$ 2.358(5), $\text{Ru}(3)\text{-Cl}(1)$ 2.370(4); Ru-Ru-Ru 59.66(5)-60.59(5), $\text{Ru-S}(1)\text{-Ru}$ 77.7(2)-78.4(2), $\text{Ru-Cl}(1)\text{-Ru}$ 74.9(1)-75.7(1).

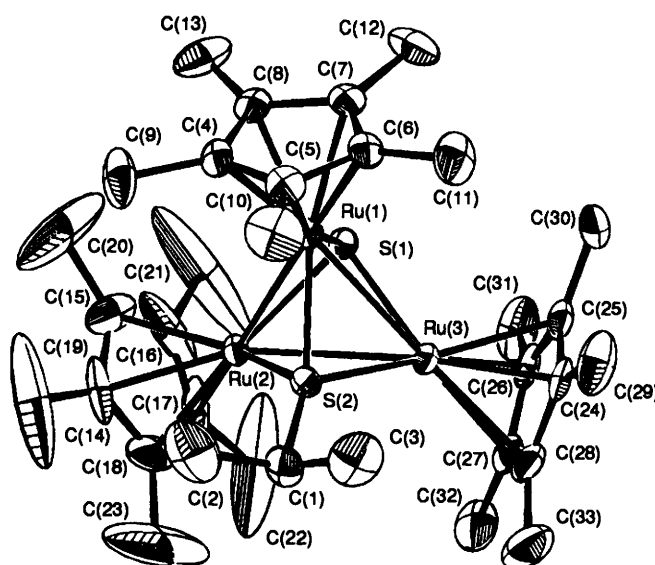


Fig. 2 Molecular structure of 3. Selected bond distances (Å) and angles (°): $\text{Ru}(1)\text{-Ru}(2)$ 2.954(1), $\text{Ru}(1)\text{-Ru}(3)$ 2.960(1), $\text{Ru}(2)\text{-Ru}(3)$ 2.944(1), $\text{Ru}(1)\text{-S}(1)$ 2.281(2), $\text{Ru}(2)\text{-S}(1)$ 2.287(2), $\text{Ru}(3)\text{-S}(1)$ 2.280(2), $\text{Ru}(1)\text{-S}(2)$ 2.249(2), $\text{Ru}(2)\text{-S}(2)$ 2.240(2), $\text{Ru}(3)\text{-S}(2)$ 2.247(2); Ru-Ru-Ru 59.82(2)-60.34(2), $\text{Ru-S}(1)\text{-Ru}$ 80.29(6)-80.92(6), $\text{Ru-S}(2)\text{-Ru}$ 82.00(6)-82.33(6), $\text{Ru-S}(2)\text{-C}(1)$ 130.2(3)-131.2(3).

slightly shorter Ru–Ru distances in **2** than those in **3**. The C₅Me₅ ligands coordinate to the Ru atoms almost perpendicularly to the basal Ru₃ plane, with dihedral angles in the range of 84–88° and 81–85° for **2** and **3** respectively. The sulfide ligand coordinates to the three Ru atoms symmetrically and the Ru–S bond lengths in **2** and **3** are essentially identical. It is noteworthy that these Ru–S bonds [2.280(2)–2.300(5) Å] are slightly shorter than those in the lower-valent ruthenium cluster [Ru₃(CO)₉(μ₃-CO)(μ₃-S)] [2.334(2)–2.354(2) Å].¹⁰ The opposite side of the Ru₃ face is occupied by either a μ₃-Cl or μ₃-SPri ligand in **2** or **3**, respectively. Both the Cl atom and the S atom in the SPri ligand are also bound to the Ru₃ faces symmetrically. The Ru–Cl bonds in **2** [2.358(5)–2.370(4) Å] are significantly shorter than those of μ₃-Cl ligands bound to three Ru atoms without Ru–Ru interactions {e.g. 2.513(3)–2.537(3) Å in **1**;¹¹ 2.559(2) Å (mean) in [Ru₃(C₅Me₅)₃(μ₃-Cl)(μ-Cl)₂(η²-μ-HC≡CSiMe₃)]¹². For the SPri ligand within **3**, the S(2)–C(1) vector is perpendicular to the basal plane and two Me groups are oriented in such a manner that the S(2)–C(1)–C(2) and S(2)–C(1)–C(3) planes bisect the Ru(1)–Ru(2) and Ru(1)–Ru(3) bonds, respectively. The Ru–S(2) distances are comparable to those in [Ru₃(μ₃-η⁷-C₇H₇)(CO)₆(μ₃-SBU^t)] [2.272(1)–2.274(1) Å].¹³ Interestingly, the Ru–S(thiolate) bonds are slightly shorter than the Ru–S(sulfide) lengths in **3**. These Ru–S lengths associated with μ₃-SPri ligand in **3** are even shorter than those in μ-SPri ligands in the triangular Ru₃ cluster [Ru₃(η⁵-C₅H₅)₃(μ-SPri)] [2.286(1)–2.304(1) Å].¹⁴ In contrast, the related oxoalkoxido complex [Ru₃(C₅Me₅)₃(μ₃-O)(μ₃-OPri)] reported recently [Ru–Ru mean distance: 2.888(2) Å] has Ru–O(oxide) bonds [2.03(1)–2.09(1) Å] shorter than the Ru–O(alkoxide) bonds [2.14(1)–2.16(1) Å].¹⁵

Exploration of the reactivities displayed at the trinuclear sites in **2** and **3** is now in progress.¶ As demonstrated previously for carbonyl clusters of Ru and Os,¹⁶ the presence of the firmly capped sulfide ligand in these clusters may inhibit the fragmentation of the Ru₃ core and possibly provides a robust multimetallic site suitable for the specific substrate activation.

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Footnotes

† Satisfactory analysis was obtained for both compounds. ¹H NMR (C₆D₆): **2** δ 1.83 (s, C₅Me₅), **3** δ 1.92 (s, 45H, C₅Me₅), 1.97 (d, *J* 6.8 Hz, 6H, SCHMe₂), 4.06 (spt, 1H, *J* 6.8 Hz, SCHMe₂). The spectra of the crystalline **3** isolated from filtered reaction mixtures kept at –20 °C in separate runs indicate that the product is always contaminated by a small amount of **2**.

‡ Crystal data for **2**: *M* = 776.4; monoclinic, space group *P*2₁/*n*, *a* = 11.588(2), *b* = 22.517(4), *c* = 12.443(2) Å, β = 101.90(2)°, *V* = 3176(1) Å³, *Z* = 4, *D*_c = 1.623 g cm^{–3}, μ = 15.75 cm^{–1}, *F*(000) = 1560, *R* = 0.077 and *R*_w = 0.11 for 316 variables and 3750 unique reflections [*I* > 3.0σ(*I*)]. For **3**: *M* = 816.1, triclinic, space group *P* $\bar{1}$ (no. 2), *a* = 11.149(3), *b* = 17.195(4), *c* = 9.041(1) Å, α = 90.05(2), β = 102.09(2), γ = 89.33(2)°, *V* = 1754.0(6) Å³, *Z* = 2, *D*_c = 1.545 g cm^{–3}, μ = 14.14 cm^{–1}, *F*(000) = 828, *R* = 0.044 and *R*_w = 0.045 for 343 variables and 4964 unique reflections [*I* > 3.0σ(*I*)]. Intensity data were collected on a Rigaku AFC7R diffractometer with use of graphite-monochromated Mo-Kα radiation and corrected for Lorentz-polarization effect as well as for absorption (ψ scans). Structure

solution and refinements were carried out by using the TEXSAN program package. The heavy atom positions were determined by Patterson methods and remaining non-hydrogen atoms were found by subsequent Fourier syntheses. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques. Hydrogen atoms were placed at calculated positions and included in the final stages of refinements. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ For the X-ray analysis of **2**, although the S and Cl atoms are indistinguishable by the observed electron densities, the distances of the two capped atoms from the Ru atoms differ and the one closer to the Ru atoms was assigned to S, while the other separated further from the basal plane was attributed to Cl. The distances of the former atom from Ru in **2** are in good agreement with the Ru–S(sulfide) bond lengths in **3**, suggesting the correctness of this assignment.

¶ For example, reaction of **2** with CO gives a novel triruthenium cluster with two CO ligands [Ru₃(C₅Me₅)₃(μ₃-S)(μ-Cl)(μ-CO)₂], whose structure has been determined by the X-ray analysis. Details will be reported subsequently.

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