

New Pentanuclear Carbonyl Ruthenium Clusters containing a Sulfido Ligand. Synthesis and Structure of $[\text{N}(\text{PPh}_3)_2]_2[\text{Ru}_5(\text{CO})_{14}\text{S}]^\dagger$

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The new series of pentanuclear sulfido clusters $[\text{Ru}_5(\text{CO})_{14}\text{S}]^{2-}$ **1**, $[\text{Ru}_5\text{H}(\text{CO})_{14}\text{S}]^-$ **2** and $[\text{Ru}_5\text{H}_2(\text{CO})_{14}\text{S}]$ **3** have been prepared; the monoanion **2**, accessible from $[\text{Ru}_3(\text{CO})_{12}]$ and $\text{SC}(\text{NMe}_2)_2$, gives **1** upon deprotonation and **3** upon protonation.

While a large number of neutral carbonylruthenium clusters containing sulfido ligands^{1,2} is known, only three anionic ones have been reported so far: $[\text{Ru}_3\text{H}(\text{CO})_9\text{S}]^-$ (ref. 3) and $[\text{Ru}_3(\text{CO})_9\text{S}]^{2-}$ (ref. 4) belong to a series of pseudo-tetrahedral clusters and are obtained by deprotonation of the neutral complex $[\text{Ru}_3\text{H}_2(\text{CO})_9\text{S}]$.⁵ Only recently we found the hexanuclear raft cluster anion $[\text{Ru}_6\text{H}(\text{CO})_{15}\text{S}_3]^-$ in the reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with an excess of $\text{SC}(\text{NMe}_2)_2$ under methane pressure.⁶

In the presence of an excess of $[\text{Ru}_3(\text{CO})_{12}]$ in the reaction with $\text{SC}(\text{NMe}_2)_2$ under methane pressure at 150 °C the new anionic cluster $[\text{Ru}_5\text{H}(\text{CO})_{14}\text{S}]^-$ **2**† (Scheme 1) is formed exclusively instead of $[\text{Ru}_6\text{H}(\text{CO})_{15}\text{S}_3]^-$; it is precipitated as the formamidinium salt from a concentrated dichloromethane solution of the reaction mixture. In an attempt to crystallize **2**

† Non-SI unit employed: bar = 10^5 Pa.

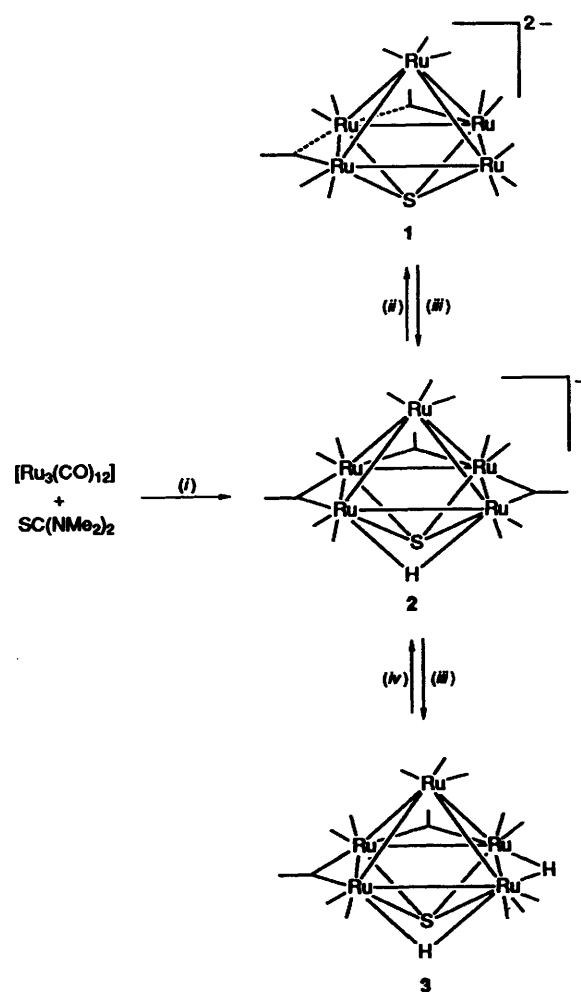
‡ All steps were performed under nitrogen in dried, N_2 -saturated solvents.

$[\text{HC}(\text{NMe}_2)_2][\text{Ru}_5\text{H}(\text{CO})_{14}\text{S}]$. The compound $[\text{Ru}_3(\text{CO})_{12}]$ (640 mg, 1 mmol) and $\text{SC}(\text{NMe}_2)_2$ (100 mg, 0.77 mmol) were dissolved in tetrahydrofuran (thf) (15 cm^3) in a stainless-steel autoclave (working volume 100 cm^3). The mixture was pressurized with 65 bar CH_4 and stirred at 150 °C. After 2 h the autoclave was cooled, the pressure released, and the red-brown solution evaporated to dryness. The residue was dissolved in CH_2Cl_2 (5 cm^3); from this solution the salt $[\text{HC}(\text{NMe}_2)_2][\text{Ru}_5\text{H}(\text{CO})_{14}\text{S}]$ precipitated as a brown microcrystalline solid crystalline. It was washed with CH_2Cl_2 and dried. Yield: 312 mg (52%). IR(thf): 2015vs, 1978(sh)w, 1964m, 1849w, 1832m and 1816w cm^{-1} (CO). ^1H NMR $[\text{OC}(\text{CD}_3)_2]$, 200 MHz: δ 8.02 (s, 1 H, CH), 3.51 (br s, 6 H, 2 CH_3), 3.37 (br s, 6 H, 2 CH_3) and -13.28 (s, 1 H, Ru_2H).

$[\text{N}(\text{PPh}_3)_2]_2[\text{Ru}_5(\text{CO})_{14}\text{S}]$. Salt **2** (100 mg, 0.1 mmol) dissolved in MeOH (20 cm^3) was added to a concentrated solution of $[\text{N}(\text{PPh}_3)_2]\text{Cl}$ (86 mg, 0.15 mmol) in MeOH. Dark red crystals of $[\text{N}(\text{PPh}_3)_2]_2[\text{Ru}_5(\text{CO})_{14}\text{S}]$ formed upon slow evaporation at room temperature. Yield: 146 mg (97%). IR(thf): 2029vw, 1973vs, 1960(sh)s, 1917w, 1900(sh)w, 1778vw and 1756(sh)vw cm^{-1} (CO). ^1H NMR $[\text{OC}(\text{CD}_3)_2]$, 200 MHz: δ 7.59 (m, C_6H_5).

$[\text{Ru}_5\text{H}_2(\text{CO})_{14}\text{S}]$. To a solution of salt **2** (50 mg, 0.048 mmol) in CH_2Cl_2 (50 cm^3), was added a 50% diethyl ether solution (10 μl) of HBF_4 (0.05 mmol). Complex **3** precipitated spontaneously. The red-brown precipitate was washed with CH_2Cl_2 and dried. Yield: 87 mg (97%). IR(thf): 2070s, 2054vs, 2045vs, 2021m, 2004w, 1995m, 1874w and 1847w cm^{-1} . ^1H NMR ($[\text{H}_2\text{H}_6]$ toluene, 400 MHz): δ -14.98 (s, Ru_2H).

Satisfactory C, H, N, analyses were obtained for all compounds.



Scheme 1 Synthesis of clusters 1-3. (i) 65 bar CH_4 , 150 °C; (ii) $[\text{N}(\text{PPh}_3)_2]\text{Cl}$; (iii) $+\text{HBF}_4$; (iv) $-\text{H}^+$

as the $[\text{N}(\text{PPh}_3)_2]^+$ salt, deprotonation was observed: from the methanolic solution of $[\text{HC}(\text{NMe}_2)_2][\text{Ru}_5\text{H}(\text{CO})_{14}\text{S}]$ and $[\text{N}(\text{PPh}_3)_2]\text{Cl}$ the salt $[\text{N}(\text{PPh}_3)_2]_2[\text{Ru}_5(\text{CO})_{14}\text{S}]$ (anion **1**)‡ crystallizes (Scheme 1). By contrast, protonation of **1** with

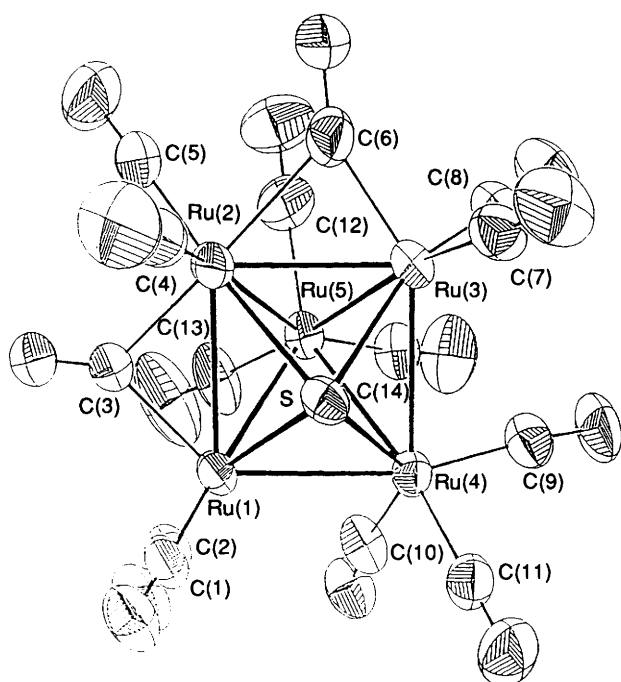


Fig. 1 Molecular structure of $[\text{Ru}_5(\text{CO})_{12}(\mu\text{-CO})_2(\mu_4\text{-S})]^{2-}$ (ORTEP plot,⁹ thermal ellipsoids, 50% probability). Selected bond distances (Å) and angles (°): Ru(1)–Ru(2) 2.7847(6), Ru(1)–Ru(4) 2.8304(5), Ru(1)–Ru(5) 2.8725(6), Ru(1)–S 2.4187(11), Ru(2)–Ru(3) 2.7991(6), Ru(2)–Ru(5) 2.8558(6), Ru(2)–S 2.4673(12), Ru(3)–Ru(4) 2.8176(6), Ru(3)–Ru(5) 2.8317(5), Ru(3)–S 2.4088(11), Ru(4)–Ru(5) 2.8311(6), Ru(4)–S 2.4009(11), Ru(2)–Ru(1)–Ru(4) 90.307(15), Ru(5)–Ru(1)–S 80.35(3), Ru(1)–Ru(2)–Ru(3) 90.353(16), Ru(5)–Ru(2)–S 79.90(3), Ru(2)–Ru(3)–Ru(4) 90.277(15), Ru(5)–Ru(3)–S 81.36(3), Ru(1)–Ru(4)–Ru(3) 89.050(15), Ru(5)–Ru(4)–S 81.50(3), Ru(1)–Ru(5)–Ru(3) 87.942(15), Ru(2)–Ru(5)–Ru(4) 88.864(15), Ru(1)–S–Ru(3) 110.25(4), Ru(2)–S–Ru(4) 109.72(4)

HBF_4 in diethyl ether gives the monoanion **2** and, in the presence of excess of HBF_4 , the neutral complex $[\text{Ru}_5\text{H}_2\text{-}$

* Stoe-Siemens AED2 four-circle diffractometer [$\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073$ Å), graphite monochromator, ω - θ scan technique], solution with SHELXS,⁷ refinement with NRCVAX.⁸

Crystal data. $\text{C}_{86}\text{H}_{60}\text{N}_2\text{O}_{14}\text{P}_4\text{Ru}_5\text{S}$, $M_r = 2006.7$, space group $P\bar{1}$, $a = 12.815(2)$, $b = 14.834(1)$, $c = 22.106(2)$ Å, $\alpha = 87.69(1)$, $\beta = 85.21(1)$, $\gamma = 81.46(1)^\circ$, $U = 4139.4(6)$ Å³, $Z = 2$, $D_c = 1.61$ g cm⁻³, $\mu = 10.4$ cm⁻¹, $\theta_{\text{max}} = 25^\circ$; crystal size $0.34 \times 0.244 \times 0.228$ mm; h –14 to 15, k 0–17, l –26 to 26; 14 586 independent reflections, 10 175 with $I > 2.5\sigma(I)$; three standards measured every hour, 9% intensity variation over 15 d of data collection.

Although most hydrogen atoms could be located from difference maps, all were placed in calculated positions and refined isotropically. Refinement with weighted anisotropic thermal parameters for the non-hydrogen atoms, full-matrix least-squares method, $R = 0.033$, $R' = 0.041$, $w^{-1} = \sigma^2(F_o) + 0.0002(F_o^2)$; maximum residual electron density in the final difference map 0.56 e Å⁻³ (max) close to a ruthenium atom, minimum -0.55 e Å⁻³. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

$(\text{CO})_{14}\text{S}] 3^\ddagger$ (Scheme 1). Compound **3** is only sparingly soluble in non-polar solvents; in polar solvents like thf, however, it spontaneously dissolves with formation of **2**.

The structural features of this new series of ruthenium clusters have been established by the X-ray diffraction analysis* of a suitable crystal of $[\text{N}(\text{PPh}_3)_2]_2[\text{Ru}_5(\text{CO})_{14}\text{S}]$ (Fig. 1). The metal framework of dianion **1** is a tetragonal pyramid consisting of five ruthenium atoms, the base of which is capped by a μ_4 -bonded sulfide ligand. The bonds Ru(1)–Ru(2) and Ru(2)–Ru(3) are bridged by carbonyl ligands. The metal–metal bonds between these atoms are slightly shorter [mean 2.7919(4) Å] than Ru(1)–Ru(4) and Ru(3)–Ru(4) [mean 2.8240(4) Å]; the bond lengths of these metal atoms to the fifth ruthenium atom are slightly longer [mean 2.8478(3) Å]. Atoms Ru(1), Ru(2) and Ru(3) have two, Ru(4) and Ru(5) three terminal carbonyl ligands, respectively.

The reversible interconversion of compounds **1**–**3** suggests the same pseudo-octahedral Ru_5S arrangement for the three clusters. However, the infrared spectra are indicative of a different carbonyl arrangement in **2**. While **1** and **3** show only two weak $\nu(\text{CO})$ absorptions in the region for bridging carbonyls, the bridging CO ligands in **2** give rise to three bands of medium intensity. Consequently, three of the fourteen carbonyl ligands are assumed to be bridging in **2**, while in **3** only two carbonyls appear to be bridging as in **1**. In the ¹H NMR spectra the hydride ligands of **2** ($\delta -13.28$) and **3** ($\delta -14.98$) are found in a range typical for bridging hydrides. Probably in **2** and **3** they span the edges which are not occupied by bridging carbonyl ligands.

The known cluster $[\text{Ru}_5(\text{CO})_{15}\text{S}]$,¹⁰ exhibiting the same cluster framework as **1**–**3**, exists as two isomers: in $[\text{Ru}_5(\text{CO})_{11}(\mu\text{-CO})_4\text{S}]$ the four edges of the basal square are bridged by carbonyl ligands, whereas $[\text{Ru}_5(\text{CO})_{11}(\mu\text{-CO})_3(\mu_3\text{-CO})\text{S}]$ contains three bridging and a μ_3 -capping carbonyl.

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References

- 1 R. D. Adams and M. Tasi, *J. Cluster Sci.*, 1990, **1**, 249.
- 2 U. Bodensieck, H. Stoeckli-Evans and G. Süss-Fink, *J. Organomet. Chem.*, in the press.
- 3 M. I. Bruce and O. B. Shawkataly, *J. Organomet. Chem.*, 1985, **286**, 427.
- 4 S. S. D. Brown, S. Hudson, I. D. Salter and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1987, 1967.
- 5 E. Sappa, O. Gambino and G. Cetini, *J. Organomet. Chem.*, 1972, **35**, 375.
- 6 U. Bodensieck, H. Stoeckli-Evans and G. Süss-Fink, *Angew. Chem.*, 1991, **103**, 1147; *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1126.
- 7 G. M. Sheldrick, SHELXS 86, Program for Crystal Structure Determination, University of Göttingen, 1986.
- 8 E. J. Gabe, Y. LePage, J.-P. Charland and F. L. Lee, NRCVAX, an Interactive Program System for Structure Analysis, *J. Appl. Crystallogr.*, 1989, **22**, 384.
- 9 C. K. Johnson, ORTEP II, Report 5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.
- 10 R. D. Adams, J. E. Babin and M. Tasi, *Organometallics*, 1988, **7**, 503.

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