

Preliminary communication

# Synthesis and X-ray structure of a ruthenium cluster with a chiral oxazoline ligand

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## Abstract

The cluster  $\text{Ru}_3(\text{CO})_{12}$  reacts with (4*S*,5*S*)-(-)-2-methyl-5-phenyl-2-oxazoline-4-methanol (HL) to give  $\text{H}_2\text{Ru}_6(\text{CO})_{14}(\text{L})_2$ ; the metal framework consists of two triangles with weak interactions between two edges.

**Keywords:** Ruthenium; Ruthenium cluster; X-ray structure analysis

## 1. Introduction

Ruthenium clusters have been used as precatalysts in a variety of reactions [1]. Such clusters with chiral ligands may have potential as asymmetric catalysts. Here we report the synthesis and structure of a hexaruthenium cluster,  $\text{H}_2\text{Ru}_6(\text{CO})_{14}(\text{L})_2$  (**1**), with the chiral oxazoline anion (L) [HL = (4*S*,5*S*)-(-)-2-methyl-5-phenyl-2-oxazoline-4-methanol] (Fig. 1). Chiral rhodium and copper oxazoline complexes have been successfully used in asymmetric catalysis [2]. To the best of our knowledge **1** is the first example of a ruthenium cluster with a chiral oxazoline ligand; it also possesses a previously unreported metal framework.

## 2. Results and discussion

The cluster **1** was obtained from the reaction of  $\text{Ru}_3(\text{CO})_{12}$  with HL in cyclohexane at 80°C in 10% yield [3]. It was separated from  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$  and  $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ , the other major products, by column chromatography with hexane/dichloromethane (70:30) as eluant. The formulation as **1** was consistent with spectroscopic data and was confirmed by an X-ray

structural study of the acetone solvate, obtained from acetone/hexane [4]. The molecular structure is shown in Fig. 2. The metal core can be described as two triangles  $\text{Ru}1/2/3$  and  $\text{Ru}4/5/6$ , the average Ru–Ru distance within the triangles being 2.757 Å. The average of three Ru–Ru contacts between the triangles (dashed lines in Figs. 1 and 2) is 3.061 Å. Comparably long Ru–Ru distances in hexaruthenium clusters have previously been reported [5]. The average metal–metal distances in the inner triangles of  $\text{H}_2\text{Ru}_6(\text{CO})_{16}(\text{OC}_6\text{H}_4)$  (**2**) and  $\text{H}_2\text{Ru}_6(\text{CO})_{15}(\text{OC}_6\text{H}_4)(\text{P}(\text{OMe})_3)$  (**3**) are 3.018(2) and 3.042(1) Å respectively (Fig. 1). In a cyclic anionic hexaruthenium cluster  $[\text{HRu}_6(\text{O}=\text{CN}-\text{Me}_2)(\text{CO})_{18}]^-$  an Ru–Ru distance of 3.227(2) Å for the inner triangle has been taken to be indicative of the absence of transannular interactions [6]. In **2** and **3**, however, the long Ru–Ru distances were interpreted as weak bonding interactions. The lengthening of the bonds has been attributed to the occupation of a low-lying antibonding molecular orbital and the presence of a triply bridging hydride.

Based on the assumption that L donates seven valence electrons, two from nitrogen and five from triply bridging oxygen, the total number of valence electrons in all three hexaruthenium clusters **1**, **2** and **3**, is 92. The total number of valence electrons for each triangular unit in **1** is 46, two electrons fewer than required by the EAN rule [7]. Taking into consideration the comparatively long Ru–Ru distances in **1**, **2** and **3**, their valence

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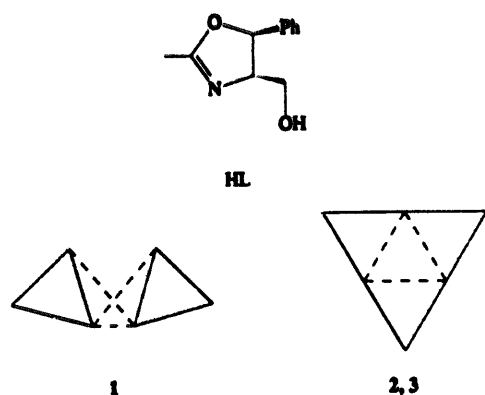


Fig. 1. Formula diagrams of HL and the metal frameworks in 1, 2 and 3.

electron counts and the location of the hydrogen atoms (see below), an appropriate description for the metal framework in 1 would involve weak interactions between the two edges of the two triangular units.

Each ligand L acts as a tetradentate ligand, with the ring nitrogen atom and the alcoholate function coordinating to one and three ruthenium atoms respectively. The Ru–O distances show a notable asymmetry; the average Ru–O distance involving endogenous ruthenium (e.g. O15–Ru4,5) is about 0.1 Å shorter than that involving exogenous ruthenium (e.g. O15–Ru2). The two metal hydrides are symmetrically disposed, capping the faces Ru1/4/5 and Ru1/4/2. Their presence (and equivalence) is also evident from the <sup>1</sup>H NMR spectrum, which shows only one sharp signal in the metal hydride region (at  $\delta = 11.6$  ppm) and does not change within the temperature range of +20 to  $-70^\circ\text{C}$ .

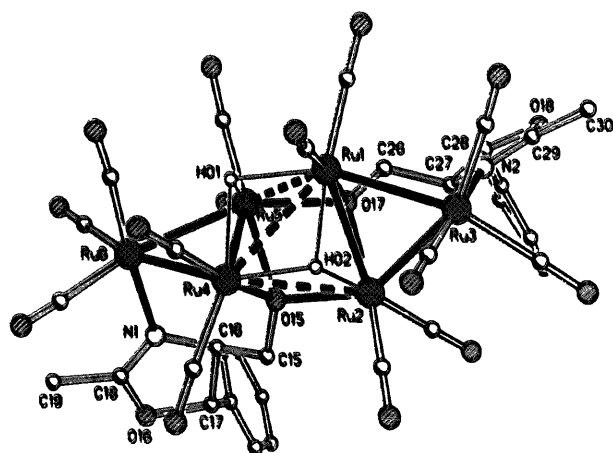


Fig. 2. Structure of 1 as determined by single crystal X-ray diffraction. Radii are arbitrary. Acetone of solvation is not shown. Selected bond lengths (Å): Ru(1)–Ru(3) 2.736(2), Ru(1)–Ru(2) 2.787(2), Ru(1)–Ru(4) 3.023(2), Ru(1)–Ru(5) 3.056(2), Ru(2)–Ru(3) 2.752(2), Ru(2)–Ru(4) 3.093(2), Ru(5)–Ru(6) 2.747(2), Ru(4)–Ru(6) 2.743(2), Ru(4)–Ru(5) 2.775(2), Ru(2)–O(15) 2.261(8), Ru(4)–O(15) 2.117(8), Ru(5)–O(15) 2.180(7), Ru(1)–O(17) 2.124(9), Ru(5)–O(17) 2.250(7), Ru(2)–O(17) 2.190(7), Ru(3)–N(2) 2.220(10), Ru(6)–N(1) 2.193(10).

The catalytic activities of 1 for the hydrogenation of prochiral substrates such as  $\alpha$ -acetamido cinnamic acid and methyl pyruvate have been tested and were disappointing both in terms of conversion (< 20%) and stereoselectivity (e.e. < 5%).

### 3. X-Ray structure determination of 1

Crystal data 1:  $(\text{CH}_3)_2\text{CO}$ ,  $\text{C}_{39}\text{H}_{30}\text{N}_2\text{O}_{19}\text{Ru}_6$ ,  $M = 1437.07$ , orthorhombic,  $P2_12_12_1$ ,  $a = 12.076(3)$ ,  $b = 13.255(4)$ ,  $c = 30.015(9)$  Å,  $V = 4804$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.987$  Mg m<sup>-3</sup>,  $F(000) = 2776$ ,  $\mu(\text{Mo K}\alpha) = 1.9$  mm<sup>-1</sup>,  $T = 20^\circ\text{C}$ . Data collection and reduction: red-brown prism ca.  $0.85 \times 0.3 \times 0.15$  mm<sup>3</sup> Siemens R3 diffractometer,  $2\theta_{\text{max}} 50^\circ$ , 6478 intensities, 6185 unique ( $R_{\text{int}} 0.032$ ) used for all calculations. Cell constants from setting angles of 50 reflections in the range  $2\theta = 20^\circ$ – $23^\circ$ . Absorption correction based on  $\psi$ -scans, transmissions 0.73–0.84. Structure solution and refinement: direct methods, refined on  $F^2$  using the program SHELXL-93 [8]. Hydrogen atoms: hydrides located from difference maps, refined subject to equal Ru–H distances; solvent H not included; others as rigid methyls or using a riding model. Absolute configuration from  $x$  refinement [9];  $x = -0.08(7)$ . Final  $wR(F^2)$  0.147,  $R(F)$  0.051 for 603 parameters and 397 restraints (to light atom displacement parameters). Max.  $\Delta/\sigma$  0.005, max.  $\Delta\rho$  1.3 eÅ<sup>-3</sup>,  $S$  1.07.

Full details of the structure determination have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. Any request for this material should quote a full literature citation and the reference number CSD-404211.

### Acknowledgements

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### References and notes

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- [3] Preparative procedure:  $\text{Ru}_3(\text{CO})_{12}$  (64 mg, 0.1 mmol) is heated with HL (38 mg, 0.2 mmol) at  $80^\circ\text{C}$  for 5 h in cyclohexane (60 ml). The resulting material is column chromatographed with hexane to remove  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ ,  $\text{H}_2\text{Ru}_4(\text{CO})_{13}$  and unreacted  $\text{Ru}_3(\text{CO})_{12}$ . Further chromatography with hexane/dichloromethane (70/30) gives **1** as a red microcrystalline solid.
- [4] Spectroscopic data for **1**: IR (cyclohexane), 2072 m, 2057 s, 1010 m, sh, 2000 vs, 1940 m, 1931  $\text{m cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ), 7.4 (m, 10H), 4.9 (d, 2H), 4.7–4.4 (m, 4H), 3.9 (t, 2H), 2.45 (s, 6H), –11.6 (s, 2H) ppm. Satisfactory analytical data (C, H, N) were obtained.
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