

# Suppression of Cluster Unsaturation by Formation of Extensive but Long-Range Metal-Metal Bonding: Crystal Structures of $[\text{Ru}_3\text{H}(\text{pyS})(\text{CO})_9]$ and $[\{\text{Ru}_3\text{H}(\text{pyS})(\text{CO})_7\}_3]$ , Where pyS Is the Pyridine-2-thiolato Ligand

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The cluster  $[\text{Ru}_3(\text{CO})_{12}]$  reacts with 1 mol equiv of pyridine-2-thiol (pySH) in refluxing cyclohexane to give the yellow cluster  $[\text{Ru}_3(\mu\text{-H})(\mu_3\text{-pyS})(\text{CO})_9]$  (**1**). Crystals of **1** are monoclinic, of space group  $P2_1/c$ , with  $a = 9.171$  (2) Å,  $b = 14.986$  (5) Å,  $c = 15.094$  (5) Å,  $\beta = 107.14$  (2)°, and  $Z = 4$ . The pyS ligand of **1** bridges two Ru atoms through the S atom and bonds to the third Ru atom through the pyridine ring. The cluster doubly decarbonylates and trimerizes in refluxing cyclohexane to give the dark red crystalline product  $[\{\text{Ru}_3(\mu_3\text{-H})(\mu_4\text{-pyS})(\text{CO})_7\}_3]$  (**2**). Crystals of **2** are trigonal, of space group  $P3c1$ , with  $a = 22.401$  (4) Å,  $c = 17.271$  (3) Å, and  $Z = 6$ . There are three independent  $\text{Ru}_9$  molecules in the unit cell, two of which are structurally equivalent. Each molecule contains three symmetry-related  $\text{Ru}_3$  clusters linked by an  $\text{Ru}_3\text{S}_3$  ring in a chair conformation and has an overall screw arrangement. Each  $\mu_4\text{-pyS}$  ligand is bonded as in **1** within its  $\text{Ru}_3$  unit but is further bonded through the S atom to one Ru atom of an adjacent  $\text{Ru}_3$  unit. One independent molecule has a right-handed screw, while the other is left-handed. The formation of three Ru-S bonds per molecule in the formation of **2** is insufficient to give saturation; this is achieved by the formation of six long-range contacts (3.2–3.3 Å) between the  $\text{Ru}_3$  units. Attempts to add CO to cleave these long-range Ru-Ru bonds while maintaining the integrity of the  $\text{Ru}_9$  molecule led to complete carbonylation back to cluster **1**.

## Introduction

The pyridine-2-thiolato ligand (pyS) is known to bond to one metal atom through the S atom (1-electron donor) or through both S and N atoms (3-electron donor),<sup>2,3</sup> to two metal atoms through the S atom alone (3-electron donor)<sup>4</sup> or through both heteroatoms in different ways (3- or 5-electron donor),<sup>4,5</sup> or to three metal atoms through both heteroatoms (5-electron donor).<sup>6-8</sup> Even in this  $\mu_3$  mode, there is still a lone pair of electrons at the S atom, giving the potential to behave as a 7-electron donor by bridging four metal atoms, and the first example of this is reported in this paper. Our previous attempts to achieve this situation of maximum electron donation led to an alternative C-S bond

cleavage as, for example, in the formation of the  $\mu_2$ -pyridyl compound  $[\text{Ru}_3\text{Re}(\mu_4\text{-S})(\mu\text{-C}_5\text{H}_4\text{N})(\text{CO})_{14}]$ , in which the original pyS ligand donates 9 electrons as the separated  $\mu_4\text{-S}$  and  $\mu_2$ -pyridyl ligands.<sup>7,8</sup> Here we will describe a novel cluster condensation process whereby a  $\mu_3\text{-pyS}$  ligand makes a new M-S bond and in doing so links trinuclear clusters through  $\mu_4$ -bridges. As the cluster  $[\text{Ru}_3(\mu\text{-H})(\mu\text{-pyS})(\text{CO})_9]$  (**1**) doubly decarbonylates and trimerizes to  $[\{\text{Ru}_3(\mu_3\text{-H})(\mu\text{-pyS})(\text{CO})_7\}_3]$  (**2**), the loss of CO is partially compensated for by the formation of these extra Ru-S bonds that link the  $\text{Ru}_3$  units, but this effect is supplemented by the formation of six long-range Ru-Ru contacts between the clusters.

## Experimental Section

$[\text{Ru}_3(\text{CO})_{12}]$  and pyridine-2-thiol were purchased from Strem Chemicals Inc. and Aldrich Chemical Co. Ltd., respectively, and used as supplied.

**Treatment of  $[\text{Ru}_3(\text{CO})_{12}]$  with Thiols. (a) Pyridine-2-thiol (pySH).** A suspension of  $[\text{Ru}_3(\text{CO})_{12}]$  (0.500 g, 0.78 mmol) and pySH (0.086 g, 0.78 mmol) in cyclohexane (50 cm<sup>3</sup>) was heated under nitrogen under reflux for 30 min to give a clear orange solution. The solvent was removed under reduced pressure and the deep yellow residue separated by TLC [ $\text{SiO}_2$ ; eluant petroleum ether (bp <40 °C)] to give a yellow band yielding  $[\text{Ru}_3\text{H}(\text{pyS})(\text{CO})_9]$  (**1**) as a bright yellow solid (0.211 g, 40%). Anal. Calcd for  $\text{C}_{14}\text{H}_5\text{NO}_9\text{Ru}_3\text{S}$ : C, 25.23; H, 0.76; N, 2.10. Found: C, 25.30; H, 0.90; N, 1.97. IR  $\nu(\text{CO})$  (cyclohexane): 2082 m, 2052 vs, 2031 vs, 2003 s, 1993 s, 1972 w, 1966 w cm<sup>-1</sup>. <sup>1</sup>H NMR ( $\text{CD}_3\text{COCD}_3$ , 200 MHz):  $\delta$  8.93 (m, H<sup>6</sup>), 7.77 (m, H<sup>4</sup>), 7.70 (m, H<sup>3</sup>), 7.40 (m, H<sup>5</sup>), -13.20 (s, RuH) ( $J_{34} = 7.9$ ,  $J_{45} = 7.3$ ,  $J_{56} = 5.6$ ,  $J_{35} = 1.9$ ,  $J_{46} = 1.5$  Hz). Unreacted  $[\text{Ru}_3(\text{CO})_{12}]$  (0.050 g) was recovered, and traces of  $[\text{Ru}(\text{pyS})_2(\text{CO})_2]$ <sup>9</sup> were detected spectroscopically. Use of a 6-fold excess of pySH at higher temperatures (refluxing *m*-xylene) gave high yields (89%) of the mononuclear compound.

**(b) 6-Methylpyridine-2-thiol.** A similar treatment gave  $[\text{Ru}_3\text{H}(\text{MepyS})(\text{CO})_9]$  as a deep yellow solid (0.053 g, 17%). Anal. Calcd for  $\text{C}_{15}\text{H}_7\text{NO}_9\text{Ru}_3\text{S}$ : C, 26.47; H, 1.03; N, 2.05; S, 4.71. Found: C, 26.61; H, 1.33; N, 2.04; S, 4.26. IR  $\nu(\text{CO})$  (cyclohexane): 2082 m, 2052 vs, 2027 vs, 2003 s, 1993 s, 1968 w, 1959 w cm<sup>-1</sup>. <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 200

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**Table I.** Crystallographic Data for [Ru<sub>3</sub>H(pyS)(CO)<sub>9</sub>] (1) and {[Ru<sub>3</sub>H(pyS)(CO)<sub>7</sub>] (2)

formula	C <sub>14</sub> H <sub>5</sub> NO <sub>9</sub> Ru <sub>3</sub> S	C <sub>36</sub> H <sub>15</sub> N <sub>3</sub> O <sub>21</sub> Ru <sub>3</sub> S <sub>3</sub>
fw	666.47	1831.35
space group	P2 <sub>1</sub> /c (No. 14)	P3c1 (No. 158)
a/Å	9.171 (2)	22.401 (4)
b/Å	14.986 (5)	
c/Å	15.094 (5)	17.271 (3)
β/deg	107.14 (2)	
V/Å <sup>3</sup>	1982 (1)	7503 (4)
Z	4	6
ρ <sub>calcd</sub> /g cm <sup>-3</sup>	2.23	2.43
μ(Mo Kα)/cm <sup>-1</sup>	23.6	27.9
λ/Å	0.710 73	0.710 73
T/°C	22 ± 1	25 ± 1
R <sup>a</sup>	0.0475	0.0348
R <sub>w</sub> <sup>b</sup>	0.0520	0.0377

$$^a R = \sum |F_o| - |F_c| / \sum |F_o|. \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}.$$

MHz): δ 7.29–7.43 (m, H<sup>3</sup>, H<sup>4</sup>), 7.07 (dd, H<sup>5</sup>), 2.84 (s, Me), –13.23 (s, RuH) (*J*<sub>45</sub> = 7.3, *J*<sub>35</sub> = 1.6 Hz).

(c) **Quinoline-2-thiol.** A similar treatment gave only a very low yield of the corresponding compound, [Ru<sub>3</sub>H(quinS)(CO)<sub>9</sub>] (0.007 g, 3%), which was characterized spectroscopically but not analytically. IR ν(CO) (cyclohexane): 2082 m, 2052 vs, 2029 vs, 2004 s, 1995 s, 1970 w, 1964 w cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): δ 8.59 (d, H<sup>5</sup>), 8.04 (d, H<sup>3</sup>), 7.90 (ddd, H<sup>6</sup>), 7.78 (dd, H<sup>8</sup>), 7.57 (ddd, H<sup>7</sup>), 7.55 (d, H<sup>4</sup>), –13.20 (s, RuH) (*J*<sub>34</sub> = 8.4, *J*<sub>56</sub> = 8.8, *J*<sub>67</sub> = 6.8, *J*<sub>78</sub> = 8.8, *J*<sub>68</sub> = 1.6 Hz).

**Decarbonylation of [Ru<sub>3</sub>H(pyS)(CO)<sub>9</sub>] (1).** A solution of the non-carbonyl cluster (0.063 g, 0.09 mmol) in cyclohexane (50 cm<sup>3</sup>) was heated under reflux under nitrogen for 3 h to give a deep red-black solution. No IR absorptions for the starting material remained, and the black residue, after removal of the solvent, was separated by TLC [SiO<sub>2</sub>; petroleum ether (bp <40 °C)/dichloromethane (1:1 v/v)] to give one band which yielded deep red crystals of {[Ru<sub>3</sub>H(pyS)(CO)<sub>7</sub>] (2) (0.042 g, 65%) from a dichloromethane and methanol mixture. Anal. Calcd for C<sub>12</sub>H<sub>5</sub>NO<sub>7</sub>Ru<sub>3</sub>S: C, 23.60; H, 0.82; N, 2.29; S, 5.25. Found: C, 23.46; H, 0.83; N, 2.24; S, 5.11. IR ν(CO) (CH<sub>2</sub>Cl<sub>2</sub>): 2075 m, 2055 vs, 2009 s, 2005 sh, 1998 sh, 1939 w cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz): δ 8.61 (ddd, H<sup>6</sup>), 8.00 (ddd, H<sup>3</sup>), 7.72 (ddd, H<sup>4</sup>), 7.25 (ddd, H<sup>5</sup>), –14.62 (s, RuH) (*J*<sub>34</sub> = 7.9, *J*<sub>45</sub> = 7.7, *J*<sub>56</sub> = 5.6, *J*<sub>35</sub> = 1.6, *J*<sub>46</sub> = 1.7 Hz).

**Carbonylation of [Ru<sub>3</sub>H(pyS)(CO)<sub>7</sub>] (2).** Carbon monoxide was bubbled through a deep red-purple solution of cluster 2 (0.030 g) in refluxing toluene (30 cm<sup>3</sup>) for 8 h, by which time the solution had become greenish yellow. The solvent was removed under reduced pressure, and the residue was separated by TLC [SiO<sub>2</sub>; eluant petroleum ether (bp <40 °C)–dichloromethane (4:1 v/v)] to give only one band that contained any appreciable material. This was characterized as cluster 1 (0.006 g, 20%) by comparison of IR and NMR data with those of an authentic sample.

**X-ray Structure Determinations for [Ru<sub>3</sub>H(pyS)(CO)<sub>9</sub>] (1) and [Ru<sub>3</sub>H(pyS)(CO)<sub>7</sub>] (2).** An orange crystal of 1 and a deep red crystal of 2 were obtained from hexane solutions by slow evaporation and cooling to –20 °C, respectively. The air-stable crystals were mounted on glass fibers on goniometers of a Nicolet R3m/V and an Enraf-Nonius CAD4 diffractometer, respectively. Details of crystal data, collection of intensity data, and structure solution and refinement for each compound are given in Table I and in the supplementary material.

The intensities of two or three check reflections were measured periodically during data collection and the data sets corrected for the observed minor changes in the intensities of these reflections. Lorentz and polarization corrections and an empirical absorption correction based on a series of ψ-scan data were also made in each case.

Structures were solved by direct methods for cluster 1 (SHELXL-PLUS<sup>10</sup>) and by the Patterson heavy-atom method for 2 (SHELXS-86<sup>11</sup>). The Patterson solution revealed the positions of the Ru atoms of 2, and in both cases the non-hydrogen atoms were located by successive difference Fourier syntheses and least-squares refinements. All non-H atoms of 1 and the Ru and S atoms of 2 were refined anisotropically. The H atoms of the pyS ligands were included in the model in calculated positions with a fixed thermal parameter (C–H = 0.96 Å; U = 0.08 Å<sup>2</sup>) for 1 but were not included for 2. The hydride position in 1 was calculated

**Table II.** Fractional Atomic Coordinates for the Cluster [Ru<sub>3</sub>(μ-H)(μ<sub>3</sub>-pyS)(CO)<sub>9</sub>] (1)

	x	y	z	U(eq) <sup>a</sup> /Å <sup>2</sup>
Ru(1)	0.3549 (1)	0.0925 (1)	0.2491 (1)	0.043 (1)
Ru(2)	0.2250 (1)	0.0460 (1)	0.3920 (1)	0.040 (1)
Ru(3)	0.1411 (1)	0.2031 (1)	0.2929 (1)	0.038 (1)
S	0.1515 (3)	–0.0120 (2)	0.2371 (2)	0.047 (1)
N	–0.0374 (8)	0.1291 (6)	0.1931 (5)	0.050 (3)
C(1)	–0.0181 (11)	0.0416 (6)	0.1747 (7)	0.051 (4)
C(2)	0.1250 (14)	–0.0032 (9)	0.1059 (9)	0.071 (5)
C(3)	–0.2554 (16)	0.0387 (10)	0.0568 (10)	0.092 (6)
C(4)	–0.2781 (14)	0.1258 (10)	0.0766 (10)	0.082 (5)
C(5)	–0.1706 (13)	0.1673 (9)	0.1455 (8)	0.067 (4)
C(11)	0.5080 (13)	0.1796 (10)	0.2793 (9)	0.071 (5)
O(11)	0.6043 (11)	0.2320 (9)	0.2950 (9)	0.115 (6)
C(12)	0.4908 (15)	–0.0016 (9)	0.2280 (9)	0.072 (5)
O(12)	0.5687 (14)	–0.0512 (8)	0.2118 (9)	0.121 (6)
C(13)	0.2708 (13)	0.1407 (8)	0.1293 (8)	0.060 (4)
O(13)	0.2133 (12)	0.1680 (7)	0.0566 (6)	0.088 (4)
C(21)	0.3160 (11)	0.1049 (8)	0.5056 (7)	0.051 (4)
O(21)	0.3730 (11)	0.1391 (7)	0.5754 (6)	0.083 (4)
C(22)	0.2810 (12)	–0.0730 (7)	0.4450 (7)	0.053 (4)
O(22)	0.3047 (10)	–0.1406 (5)	0.4779 (7)	0.079 (4)
C(23)	0.0234 (12)	0.0522 (7)	0.4020 (7)	0.050 (4)
O(23)	–0.0976 (9)	0.0547 (6)	0.4045 (6)	0.072 (4)
C(31)	0.3074 (12)	0.2575 (7)	0.3770 (8)	0.054 (4)
O(31)	0.4074 (10)	0.2928 (6)	0.4275 (6)	0.082 (4)
C(32)	0.0026 (11)	0.2468 (7)	0.3588 (7)	0.051 (4)
O(32)	–0.0707 (10)	0.2740 (6)	0.4002 (7)	0.079 (4)
C(33)	0.1174 (12)	0.2981 (7)	0.2043 (8)	0.057 (4)
O(33)	0.1022 (11)	0.3560 (6)	0.1536 (7)	0.089 (4)
H(1)	0.4140	0.0566	0.3719	0.080

<sup>a</sup> Equivalent isotropic U defined as one-third of the trace of the orthogonalized U<sub>ij</sub> tensor.

using HYDEX<sup>12</sup> but was not included in the final models. Anomalous dispersion effects were included in F<sub>c</sub><sup>13</sup> and the values of Δf' and Δf'' were obtained from standard sources.<sup>14</sup> Calculations were performed on MICROVAX II computers using SHELXL-PLUS<sup>10</sup> for 1 and SDP/VAX<sup>15</sup> for 2. Refinement of the "enantiomorph" structure of 2 was carried out as well, but no clear indication as to which form was correct was possible from the refinement results. Fractional atomic coordinates for 1 are given in Table II, and those for 2, in Table III. Selected bond lengths and angles for both compounds are given in Table IV.

## Results and Discussion

The cluster [Ru<sub>3</sub>(CO)<sub>12</sub>] reacts with pyridine-2-thiol (pySH) (1 mol/mol of Ru<sub>3</sub>) in refluxing cyclohexane for 30 min to give a mixture, including some starting material, traces of [Ru(pyS)<sub>2</sub>(CO)<sub>2</sub>]<sub>9</sub> and [Ru<sub>3</sub>(μ-H)(μ<sub>3</sub>-pyS)(CO)<sub>9</sub>] (1) as the major product (40%) in the form of orange crystals. Longer reaction times and an excess of pySH gave high yields of the monomer [Ru(pyS)<sub>2</sub>(CO)<sub>2</sub>]<sub>9</sub>, although this may be more conveniently prepared directly from RuCl<sub>3</sub>·3H<sub>2</sub>O.<sup>9</sup> Cluster 1 was separated, purified, and characterized by IR and <sup>1</sup>H NMR spectroscopy, elemental analysis, and single-crystal X-ray structure determination (Figure 1). The spectroscopic data compare well with those reported for related compounds such as the mercaptobenzothiazole derivative [Ru<sub>3</sub>(μ-H)(μ<sub>3</sub>-C<sub>7</sub>H<sub>4</sub>NS<sub>2</sub>)(CO)<sub>9</sub>] (3), and their crystal structures are closely related.<sup>16</sup> In particular, the Ru–Ru distances are very similar; the S-bridged Ru–Ru distance of 2.841 (2) Å for 1 compares with 2.836 (5) Å for 3, and the other two corresponding Ru–Ru edges of 2.790 (1) and 2.774 (1) Å for 1 compare with 2.798 (6) and 2.786 (5) Å for 3. No structural details are significantly different except for the obvious differences between the ligands themselves. We have made this point because, as will

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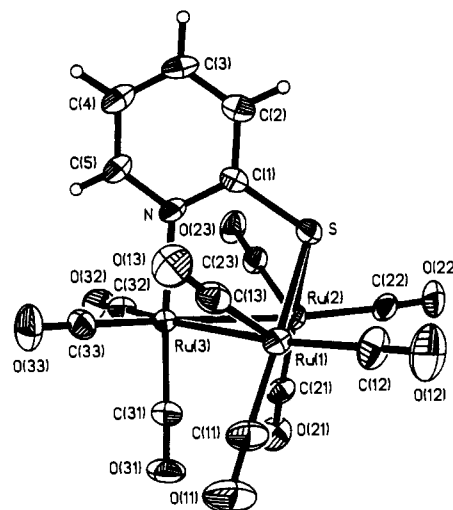
**Table III.** Fractional Atomic Coordinates for the Cluster  $[\text{Ru}_3(\mu_3\text{-H})(\mu_4\text{-pyS})(\text{CO})_7]_3$  (2)

atom	x	y	z	$B^a/\text{\AA}^2$
Ru(1A)	0.01771 (8)	0.12667 (8)	0.093	2.36 (4)
Ru(2A)	-0.07288 (8)	0.02054 (8)	0.2068 (1)	2.50 (4)
Ru(3A)	-0.07749 (9)	0.13880 (8)	0.1770 (1)	3.30 (5)
S(A)	-0.0828 (2)	0.0153 (2)	0.0666 (3)	2.4 (1)
O(11A)	0.1249 (9)	0.2714 (9)	0.126 (1)	5.8 (4)*
O(13A)	-0.0155 (8)	0.1846 (8)	-0.042 (1)	5.1 (4)*
O(21A)	-0.0441 (9)	0.0515 (9)	0.374 (1)	6.1 (5)*
O(23A)	-0.2202 (9)	-0.0366 (9)	0.251 (1)	6.4 (5)*
O(31A)	0.0344 (9)	0.2096 (9)	0.297 (1)	6.4 (5)*
O(32A)	-0.0463 (9)	0.279 (1)	0.113 (1)	7.0 (5)*
O(33A)	-0.187 (1)	0.114 (1)	0.297 (1)	7.7 (6)*
N(A)	-0.1529 (8)	0.0800 (8)	0.087 (1)	3.0 (4)*
C(1A)	-0.151 (1)	0.032 (1)	0.044 (1)	2.7 (4)*
C(2A)	-0.197 (1)	-0.005 (1)	-0.010 (1)	3.6 (5)*
C(3A)	-0.253 (1)	0.006 (1)	-0.026 (2)	5.8 (7)*
C(4A)	-0.253 (1)	0.059 (1)	0.014 (2)	6.2 (7)*
C(5A)	-0.202 (1)	0.094 (1)	0.069 (2)	4.8 (6)*
C(11A)	0.082 (1)	0.215 (1)	0.119 (1)	4.1 (6)*
C(13A)	-0.001 (1)	0.162 (1)	0.012 (1)	4.0 (5)*
C(21A)	-0.055 (1)	0.037 (1)	0.308 (1)	3.5 (5)*
C(23A)	-0.161 (1)	-0.016 (1)	0.228 (1)	3.9 (5)*
C(31A)	-0.010 (1)	0.181 (1)	0.250 (1)	3.4 (5)*
C(32A)	-0.061 (1)	0.226 (1)	0.137 (2)	4.8 (6)*
C(33A)	-0.145 (1)	0.123 (1)	0.247 (2)	5.6 (7)*
Ru(1B)	-0.33470 (9)	0.24855 (8)	0.2112 (1)	3.07 (5)
Ru(2B)	-0.44856 (8)	0.21005 (8)	0.3226 (1)	2.86 (5)
Ru(3B)	-0.4376 (1)	0.11463 (9)	0.2379 (1)	4.09 (5)
S(B)	-0.3293 (3)	0.2441 (3)	0.3509 (3)	2.6 (1)
O(11B)	-0.360 (1)	0.244 (1)	0.041 (1)	7.6 (6)*
O(13B)	-0.255 (1)	0.179 (1)	0.172 (1)	7.9 (6)*
O(21B)	-0.599 (1)	0.137 (1)	0.284 (1)	7.3 (6)*
O(23B)	-0.498 (1)	0.118 (1)	0.459 (1)	7.4 (5)*
O(31B)	-0.514 (1)	0.141 (1)	0.111 (1)	7.2 (5)*
O(32B)	-0.568 (1)	-0.006 (1)	0.301 (1)	8.4 (6)*
O(33B)	-0.397 (1)	0.037 (1)	0.127 (1)	9.1 (7)*
N(B)	-0.3727 (9)	0.111 (1)	0.329 (1)	4.5 (5)*
C(1B)	-0.329 (1)	0.167 (1)	0.371 (1)	3.7 (5)*
C(2B)	-0.286 (1)	0.167 (1)	0.427 (1)	3.9 (5)*
C(3B)	-0.280 (1)	0.108 (1)	0.438 (2)	5.5 (7)*
C(4B)	-0.320 (1)	0.054 (1)	0.395 (2)	5.7 (7)*
C(5B)	-0.369 (1)	0.050 (1)	0.342 (2)	6.1 (7)*
C(11B)	-0.351 (1)	0.245 (1)	0.109 (1)	4.5 (6)*
C(13B)	-0.286 (1)	0.205 (1)	0.189 (2)	5.6 (7)*
C(21B)	-0.538 (1)	0.168 (1)	0.293 (2)	5.2 (6)*
C(23B)	-0.478 (1)	0.157 (1)	0.403 (2)	5.0 (6)*
C(31B)	-0.486 (1)	0.128 (1)	0.159 (2)	5.2 (6)*
C(32B)	-0.517 (1)	0.041 (1)	0.275 (2)	5.4 (7)*
C(33B)	-0.413 (1)	0.066 (1)	0.170 (2)	5.9 (7)*
Ru(1C)	0.41030 (9)	0.80357 (9)	-0.0039 (1)	3.14 (5)
Ru(2C)	0.29745 (9)	0.72758 (9)	0.1101 (1)	3.26 (5)
Ru(3C)	0.3565 (1)	0.86703 (9)	0.0815 (1)	3.71 (5)
S(C)	0.2889 (3)	0.7277 (3)	-0.0301 (4)	3.3 (1)
O(11C)	0.558 (1)	0.915 (1)	0.020 (1)	7.0 (5)*
O(13C)	0.4114 (9)	0.8863 (9)	-0.137 (1)	6.0 (5)*
O(21C)	0.3284 (9)	0.7466 (9)	0.277 (1)	6.4 (5)*
O(23C)	0.177 (1)	0.745 (1)	0.151 (1)	7.6 (6)*
O(31C)	0.4657 (9)	0.8878 (9)	0.196 (1)	5.9 (4)*
O(32C)	0.2849 (9)	0.905 (1)	0.207 (1)	6.8 (5)*
O(33C)	0.455 (1)	1.011 (1)	0.021 (1)	7.5 (6)*
N(C)	0.2770 (9)	0.8384 (9)	-0.008 (1)	3.8 (4)*
C(1C)	0.254 (1)	0.782 (1)	-0.052 (1)	4.1 (6)*
C(2C)	0.207 (1)	0.764 (1)	-0.110 (1)	3.6 (5)*
C(3C)	0.181 (1)	0.808 (1)	-0.129 (1)	4.9 (6)*
C(4C)	0.205 (1)	0.868 (1)	-0.086 (2)	5.2 (7)*
C(5C)	0.249 (1)	0.881 (1)	-0.029 (2)	4.6 (6)*
C(11C)	0.501 (1)	0.873 (1)	0.015 (2)	5.7 (7)*
C(13C)	0.413 (1)	0.853 (1)	-0.085 (1)	4.0 (5)*
C(21C)	0.315 (1)	0.736 (1)	0.210 (2)	4.5 (5)*
C(23C)	0.222 (1)	0.734 (1)	0.131 (2)	5.1 (6)*
C(31C)	0.422 (1)	0.877 (1)	0.152 (1)	4.7 (6)*
C(32C)	0.312 (1)	0.890 (1)	0.158 (1)	4.4 (6)*
C(33C)	0.413 (1)	0.956 (1)	0.041 (2)	5.0 (6)*

<sup>a</sup> Starred values are for atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as  $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$ .

**Table IV.** Selected Bond Lengths (Å) and Angles (deg) for  $[\text{Ru}_3\text{H}(\text{pyS})(\text{CO})_9]$  (1) and  $[\text{Ru}_3\text{H}(\text{pyS})(\text{CO})_7]_3$  (2)

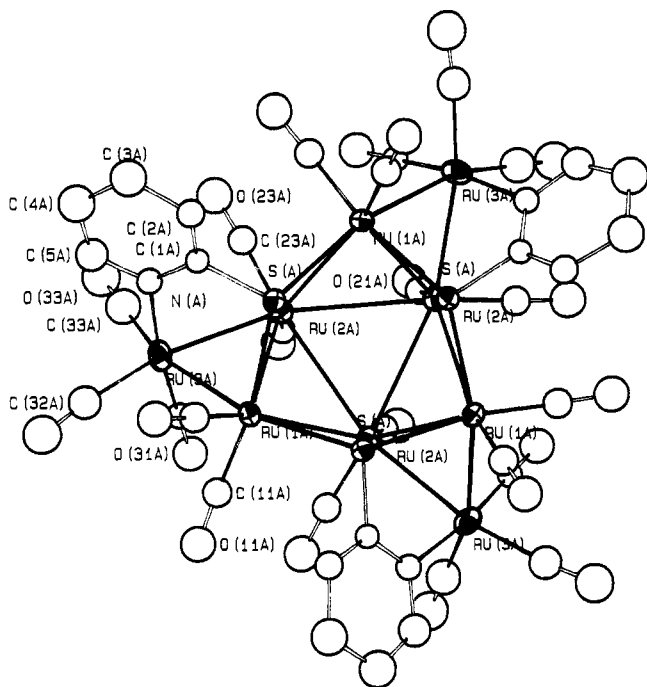
	compd 2			
	compd 1	A	B	C
Ru(1)–Ru(2)	2.841 (2)	2.970 (1)	2.957 (1)	2.975 (1)
Ru(2)–Ru(3)	2.774 (1)	2.751 (1)	2.702 (1)	2.760 (1)
Ru(1)–Ru(3)	2.790 (1)	2.705 (1)	2.757 (1)	2.714 (1)
Ru(2)–Ru(2')		3.300 (1)	3.262 (1)	3.289 (1)
Ru(1)–Ru(2')		3.202 (1)	3.164 (1)	3.194 (1)
Ru(1)–S	2.401 (3)	2.423 (2)	2.421 (3)	2.421 (3)
Ru(2)–S	2.398 (3)	2.427 (2)	2.432 (2)	2.429 (3)
Ru(1')–S		2.485 (3)	2.510 (3)	2.494 (3)
Ru(3)–N	2.174 (7)	2.183 (7)	2.171 (8)	2.197 (8)
S–C(1)	1.76 (1)	1.791 (9)	1.76 (1)	1.80 (1)
C(1)–C(2)	1.37 (2)	1.33 (1)	1.38 (1)	1.34 (1)
C(2)–C(3)	1.36 (2)	1.43 (1)	1.40 (2)	1.43 (1)
C(3)–C(4)	1.37 (2)	1.37 (2)	1.32 (2)	1.39 (2)
C(4)–C(5)	1.36 (2)	1.39 (2)	1.40 (2)	1.34 (1)
C(5)–N	1.35 (1)	1.33 (1)	1.41 (1)	1.41 (1)
Ru(1)–S–Ru(2)	72.6 (1)	75.50 (6)	75.11 (7)	75.68 (7)
Ru(3)–Ru(1)–S	79.7 (1)	80.25 (6)	79.67 (7)	80.33 (7)
Ru(3)–Ru(2)–S	80.1 (1)	79.26 (6)	80.61 (6)	79.27 (7)
Ru(1)–S–Ru(1')		139.7 (1)		139.3 (1)
Ru(2)–S–Ru(1')		81.30 (7)		80.8 (8)
Ru(2)–S–Ru(2')			139.3 (1)	
Ru(1)–S–Ru(2')			79.81 (9)	
Ru(1)–S–C(1)	106.8 (4)	106.2 (1)	104.8 (2)	106.5 (1)
Ru(2)–S–C(1)	107.9 (4)	105.8 (1)	105.7 (1)	106.0 (1)
Ru(1')–S–C(1)		111.6 (2)	111.5 (2)	111.7 (2)
S–C(1)–N	118.5 (7)	114.98 (8)	117.3 (1)	114.3 (7)
Ru(3)–N–C(1)	121.0 (6)	124.0 (1)	122.2 (1)	124.1 (1)
Ru(1)–Ru(3)–N	88.4 (2)	88.22 (7)	87.26 (8)	88.41 (8)
Ru(2)–Ru(3)–N	88.5 (2)	86.73 (7)	88.12 (8)	86.35 (7)

**Figure 1.** Molecular structure of the cluster  $[\text{Ru}_3(\mu\text{-H})(\mu_3\text{-pyS})(\text{CO})_9]$  (1).

be seen, there are major differences in Ru–Ru distances resulting from the conversion of 1 to 2. The hydride position in 1 was not determined from diffraction data but was calculated using HYDEX.<sup>12</sup> This atom lies in the expected position on a molecular symmetry plane passing through the pyS ligand. The CO positions and the Ru–Ru distances support the hydride position calculated in this way.

In view of our previous studies on the pyS ligand in clusters,<sup>7,8</sup> we believed that the thermolysis of 1 would lead to C–S bond cleavage to give a cluster such as  $[\text{Ru}_3(\mu\text{-H})(\mu\text{-2-pyridyl})(\mu_3\text{-S})(\text{CO})_9]$ . There is precedent for this in the conversion of  $[\text{Os}_3(\mu\text{-H})(\mu_3\text{-RN}=\text{CHS})(\text{CO})_9]$  into  $[\text{Os}_3(\mu\text{-H})(\mu\text{-RN}=\text{CH})(\mu_3\text{-S})(\text{CO})_9]$ .<sup>17</sup> A refluxing cyclohexane solution of cluster 1 changed from orange to dark red over 3 h, and deep red crystals

(17) Adams, R. D.; Dawoodi, Z.; Foust, D. F.; Segmüller, B. E. *Organometallics* 1983, 2, 315.

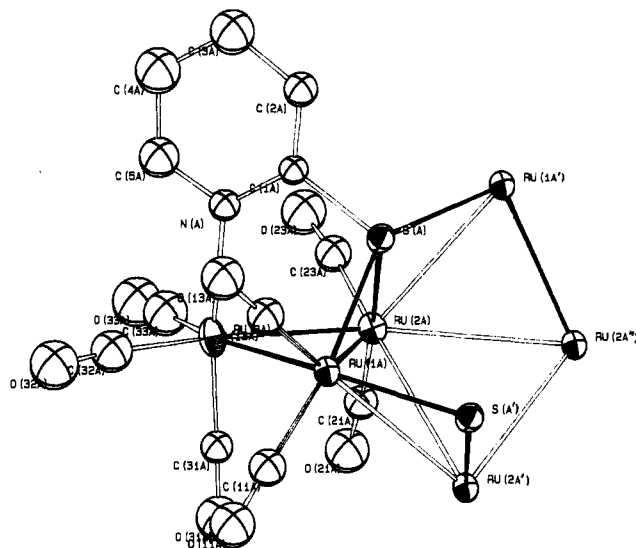


**Figure 2.** Molecular structure of the independent molecule A of the cluster  $[\text{Ru}_3(\mu_3\text{-H})(\mu_4\text{-pyS})(\text{CO})_7]_3$  (**2**). Atoms of the asymmetric unit are labeled as well as symmetry-related Ru and S atoms. The other two independent molecules in the unit cell are either entirely equivalent to A (molecule C) or enantiomeric with it (molecule B).

of **2** were isolated by TLC on silica. The  $^1\text{H}$  NMR spectrum showed that the hydride ligand and the 2-pyridyl group were still present, but we could not tell whether the C–S bond had been cleaved or not. Analytical data were consistent with the formula  $[\text{Ru}_3\text{H}(\text{pyS})(\text{CO})_7]_x$ , but a mass spectrum (EI or FAB) to establish  $x$  could not be obtained.

Previously, decarbonylation of  $[\text{Ru}_3(\mu\text{-H})_2(\mu_3\text{-S})(\text{CO})_9]$  has been shown to give  $[\text{Ru}_3(\mu\text{-H})_2(\mu_4\text{-S})(\text{CO})_8]_3$ , in which the three  $\text{Ru}_3$  cluster units are linked through  $\mu_4\text{-S}$  bridges to give a six-membered  $\text{Ru}_3\text{S}_3$  ring in the chair conformation.<sup>18</sup> By analogy, we thought that a C–S bond cleavage and a double decarbonylation had occurred to give  $[\text{Ru}_3(\mu\text{-H})(\mu\text{-2-pyridyl})(\mu_4\text{-S})(\text{CO})_7]_3$ , which would be an electron-precise tricluster system linked through  $\mu_4\text{-S}$  bridges as in the reported case. An observation that seemed to be incompatible with this was that **2** was reconverted to **1**, albeit in low yield (20%), on treatment with CO. It seemed unlikely to us that the C–S bond, once cleaved, would be re-formed on carbonylation. A single-crystal X-ray structure of **2** resolved the problem in a remarkable and unexpected way.

Crystals of **2** are trigonal with  $Z = 6$ . There are three independent molecules of  $[\text{Ru}_3\text{H}(\mu_4\text{-pyS})(\text{CO})_7]_3$  (A, B, C) and a total of 54 Ru atoms in the unit cell. Figure 2 shows the molecular structure of molecule A, which is identical to molecule C, while molecule B is enantiomeric with these. The crystals actually contain equal amounts of the two enantiomeric molecules, i.e., a racemic mixture. As we suspected, trimerization has occurred with the cluster linked through sulfur bridges, but this has occurred without cleavage of the C–S bond; the  $\mu_4\text{-pyS}$  ligands are 7-electron donors, and to our knowledge this mode of bridging has not been reported previously. Each molecule contains a 3-fold rotation axis relating the three  $\text{Ru}_3$  components of each molecule. Two equatorial CO ligands trans to the Ru–Ru bonds have been lost from atoms Ru(1) and Ru(2) of cluster **1** in the formation of cluster **2**. Unsaturation at one of these atoms is removed by the formation of an Ru–S bond to the pyS ligand of an adjacent

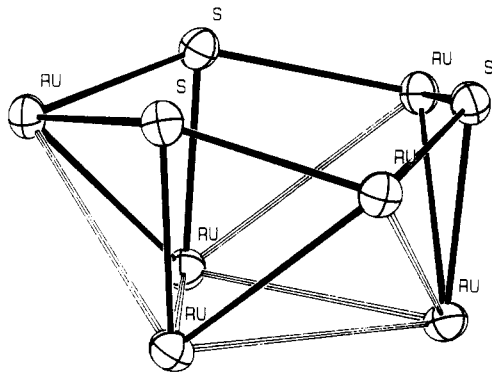


**Figure 3.** One  $\text{Ru}_3$  component of molecule A of the cluster  $[\text{Ru}_3(\mu_3\text{-H})(\mu_4\text{-pyS})(\text{CO})_7]_3$  (**2**) showing the coordination environments of the atoms Ru(1) and Ru(2), which are those linked through to the other  $\text{Ru}_3$  units. Ru–Ru contacts above 3.0 Å are shown as open lines.

$\text{Ru}_3$  cluster. Depending upon whether it is Ru(1) or Ru(2) of the original molecule (**1**) that is involved in this bond, the enantiomeric form A or B is produced (molecules A and C are equivalent). It can be seen from Figure 2 that the pyridyl rings extend outward as propeller blades around the central  $\text{RuSRuSRuS}$  ring, which is in the chair conformation. The right- or left-handedness of this propeller depends upon whether Ru(1) or Ru(2) forms the new bond to sulfur. As the reaction of **1** proceeds by the loss of CO and the formation of Ru–S bonds, all three  $\text{Ru}_3$  clusters need to have the same configuration for cyclic trimerization to occur. This has a low probability unless the configuration of the first link that is made induces the same configuration at the second and final linkages so that ring closure rather than linear polymerization is favored. Alternatively, if the new Ru–S bonds are formed reversibly, only when the appropriate configurations needed for the cyclic trimer are established does cyclization occur. Presumably, its stability relative to that of acyclic oligomers ensures that there is a reasonably high yield (65%). If the configurations of the Ru–S links were formed randomly and irreversibly, there would be only a 25% probability of forming the cyclic trimer even if we assume a 100% conversion.

Although the six-membered puckered  $\text{RuSRuSRuS}$  ring is similar to that in  $[\text{Ru}_3\text{H}_2(\mu_4\text{-S})(\text{CO})_8]_3$ ,<sup>18</sup> the formation of three Ru–S bonds is insufficient to produce coordinative saturation in **2**. Saturation is achieved by the formation of six further Ru–Ru contacts between  $\text{Ru}_3$  units (Ru–Ru distances of 3.2–3.3 Å) which are long for Ru–Ru bonds, normally between 2.8 and 3.0 Å, but somewhat short relative to expected van der Waals contacts (approximately 3.4 Å). A simple electron-pair model for Ru–Ru bonding would require only three Ru–Ru bonds linking the  $\text{Ru}_3$  units to ensure saturation; the formation of six weak long Ru–Ru bonds seems to be an interesting alternative adopted in this case. Figure 3 shows just one  $\text{Ru}_3$  component of molecule A and the coordination environments of the metal atoms. The bond Ru(1A)–S(A) between clusters, equivalent by symmetry to Ru(1A)–(SA'), is similar in length to the other Ru–S bonds in the molecule and to those in **1**. Atom Ru(2A') is 3.202 (1) Å from Ru(1A) and 3.300 (1) Å from Ru(2A) and lies closely in the plane defined by Ru(1A), Ru(2A), and the trans CO ligands C(13A)O(13A) and C(23A)O(23A). It therefore appears to occupy a normal coordination site at these metal atoms. Likewise Ru(2A'') occupies the site of the equatorial CO ligand lost from Ru(2A) of cluster **1**. Ru–Ru distances within the trinuclear units change considerably on going from **1** to **2**. Bond lengths to Ru(3) have decreased slightly but significantly [Ru(1)–Ru(3) = 2.790

(18) Adams, R. D.; Männig, D.; Segmüller, B. E. *Organometallics* **1983**, *2*, 149.

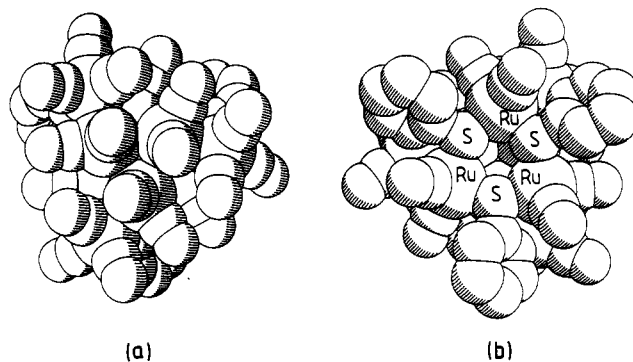


**Figure 4.** Central  $\text{Ru}_6\text{S}_3$  unit linking the three  $\text{Ru}_3$  cluster components of **2**. Ru–Ru bonds above 3.0 Å are shown open.

(1) and  $\text{Ru}(2)\text{--Ru}(3) = 2.744$  (1) Å in **1**, decreasing to 2.705 (1), 2.751 (1), and 2.702 (1) Å and to 2.757 (1), 2.714 (1), and 2.760 (1) Å in molecules A, B, and C of **2**. The other Ru–Ru bond length has increased markedly [ $\text{Ru}(1)\text{--Ru}(2) = 2.841$  (2) Å in **1**, increasing to 2.970 (1), 2.957 (1), and 2.975 (1) Å in **2**]. We offer no interpretation of these bond length differences except that they must be in response to the changed environments at Ru(1) and Ru(2).

The remaining problem is the position of the bridging hydride ligand in **2**, which was not located from diffraction data. Placing the hydride at the intersection of the C(13)–Ru(1) and C(23)–Ru(2) vectors would position it close to the center and in the plane of the Ru(1)Ru(2)Ru(2') triangle with approximately equal distances from the three metal atoms. We feel that the triply-bridging site is the most likely, as there is no other obvious position for the hydride in the molecule. However,  $\mu_3$ -hydrides are normally out of the trimetallic plane in capping positions. Application of HYDEX<sup>12</sup> gave two possible hydride positions, both well out of the  $\text{Ru}_3$  plane and both with unfavorable energy minima. Because of this, we feel that these results from HYDEX are probably not appropriate in this case and the hydride position remains an open question.

Figure 4 shows the geometric relation between the central Ru and S atoms; the Ru–Ru bonds  $<3.0$  Å are filled and those  $>3.0$



**Figure 5.** Space-filling diagrams of **2** showing that there is effective close-packing of CO ligands on the face containing the intracluster  $\text{Ru}_3$  triangular unit (a) and the more open arrangement on the face containing the  $\text{Ru}_3\text{S}_3$  ring in the chair conformation (b).

Å are open. The  $\text{Ru}_3\text{S}_3$  ring in the chair arrangement lies above the intercluster  $\text{Ru}_3$  triangle. The packing of the carbonyl groups at the triangular base of this torus is shown in Figure 5a. It can be seen that the CO ligands are essentially touching and that there is no room to incorporate any more. If there were incorporation of a CO ligand at each of the three Ru atoms of the bottom triangle shown in Figure 4, the whole torus would be required to expand. Since the Ru–Ru bonds above 3.0 Å are no longer required, this is feasible. The packing on the top face of the molecule shown in Figure 5b would be barely affected. The treatment of cluster **2** with CO did not lead, however, to any isolable material other than regenerated cluster **1**. This was only isolated in low yield, so we cannot be sure that there are not other products which we could not isolate.

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**Supplementary Material Available:** Tables of complete crystallographic data, distances and angles, and anisotropic temperature factors (14 pages). Ordering information is given on any current masthead page.