

g) were stirred together in 5 mL of benzene for 1 h. The resulting red-brown suspension was heated and the solution allowed to cool slowly to room temperature. This formed a deposit of irregular off-white lumps and red-orange needles of compound 3, which were manually separated to provide 0.093 g (55%) of pure compound 3.  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  -31.2, d (33) of t (12); 1.21, q; 2.76, m.  $\{^1\text{H}\}^{31}\text{P NMR}$ : 45.7, d (97).

**Structure Determinations.** Crystals of compound 1 were grown from THF solution according to method b above, crystals of compound 2 were grown from toluene at  $-30^\circ\text{C}$ , and crystals of compound 3 were obtained from a cooled benzene solution. Data for all of the structures were collected on a Syntex P3 diffractometer with the crystals cooled to  $-100^\circ\text{C}$  (graphite monochromator, Mo  $\text{K}\alpha$  radiation,  $\lambda = 0.71069 \text{ \AA}$ ). The crystal system, space group, and approximate unit cell dimensions of each crystal were determined during a preliminary investigation. The unit cell parameters were subsequently refined from the Bragg angles of at least 48 computer-centered reflections. A summary of the crystal data is given in Table I. The presence of two independent molecules in the asymmetric unit of compound 2, compounded by the fact that a pseudomonoclinic  $A$ -centered unit cell can be chosen,<sup>23</sup> raises the possibility that the material should be described in a higher-symmetry space group. But we have been unable to find any higher symmetry in the reflection intensities, and the final structure reveals significant differences in the orientations of the isopropyl groups such that the molecules cannot be related by symmetry.

Intensity data were collected using the  $\omega$ -scan technique with background measurements at both ends of the scan (total background time was equal to the scan time). The intensities of standard reflections were monitored periodically; none of the crystals showed any signs of decomposition but both showed some variation over the data collection period

(23) We thank a reviewer for noting this possibility.

and corrections were applied. Azimuthal scans also showed some variation in intensity for compound 1, and empirical corrections for absorption were made. The azimuthal scans for compounds 2 and 3 were relatively flat, and no corrections were applied.

The refinement and analysis of the two structures were carried out using a package of local programs.<sup>24</sup> The atomic scattering factors were taken from the tabulations of Cromer and Waber; anomalous dispersion corrections were by Cromer.<sup>25</sup> In the least-squares refinement, the function minimized was  $\sum w(|F_o| - |F_c|)^2$  with the weights,  $w$ , assigned as  $[\sigma^2(I) + 0.0009I^2]^{-1/2}$ .

The structures of compounds 1 and 2 were solved by direct methods (MULTAN);<sup>26</sup> the coordinates of 1 were used as a starting point for 3. All of the non-hydrogen atoms were refined with anisotropic thermal parameters; all hydrogens were refined with isotropic thermal parameters. Table I details the results of the various refinements. The atomic coordinates are given in Tables II-IV for compounds 1-3, respectively.

**Acknowledgment.** We thank P. Krusic for preliminary ESR measurements, and S. Hill, L. Lardear, W. Marshall, and L. J. Ayers for skilled technical assistance.

**Supplementary Material Available:** Tables of crystal structure information, anisotropic thermal parameters, hydrogen atom positional and thermal parameters, and complete interatomic distances and angles (20 pages); tables of structure factor amplitudes (34 pages). Ordering information is given on any current masthead page.

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## Aggregation of $\text{CpRu}(\text{PPh}_3)_2\text{SR}$ via Loss of $\text{PPh}_3$ ( $\text{R} = 1\text{-C}_3\text{H}_7$ , $\text{CHMe}_2$ ). Structure of $[\text{CpRuS-1-C}_3\text{H}_7]_3$ , a Molecule with Short C-H...S Distances

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The complexes  $\text{CpRu}(\text{PPh}_3)_2\text{SR}$ , where  $\text{R} = 1\text{-C}_3\text{H}_7$  and  $\text{CHMe}_2$ , lose both  $\text{PPh}_3$  ligands in refluxing toluene to give the trimers  $[\text{CpRuSR}]_3$  via intermediate dimers. The crystal structure for  $\text{R} = 1\text{-C}_3\text{H}_7$  was determined: space group  $P\bar{1}$ ,  $a = 10.554$  (1)  $\text{\AA}$ ,  $b = 14.033$  (2)  $\text{\AA}$ ,  $c = 18.243$  (2)  $\text{\AA}$ ,  $\alpha = 76.977$  (10) $^\circ$ ,  $\beta = 87.299$  (8) $^\circ$ ,  $\gamma = 89.009$  (11) $^\circ$ ,  $V = 2629.4$  (9)  $\text{\AA}^3$ , and  $Z = 4$ . The three thiolato ligands are all on the same side of the  $\text{Ru}_3$  triangle, each ligand bridging two ruthenium atoms. This leads to two of the  $1\text{-C}_3\text{H}_7$  groups occupying equatorial-like positions while the third is axial such that one proton on the  $\alpha$ -carbon is well within the van der Waals contact distance of the sulfur atoms across the triangle. The consequences of this close approach are characterized via NMR spectroscopy and discussed as a partial model for chemisorption of thiols on metal surfaces.

### Introduction

Our early attempts<sup>2</sup> to prepare the relatively simple complexes  $\text{CpRu}(\text{PPh}_3)_2\text{SR}$  via treatment of  $\text{CpRu}(\text{PPh}_3)_2\text{Cl}$  with  $\text{NaSR}$ , failed due to the generation of multiple side products which were suspected to include dimers and trimers. The desired monomers were eventually obtained by application of flash heating followed by rapid quenching of the reaction solution.<sup>2</sup> With the monomers in hand, their reactivity was attributed to activation via  $\pi$ -donation by the thiolato ligand and steric-accelerated loss of  $\text{PPh}_3$ .

The propensity of thiolato ligands to bridge metal atoms in organometallic complexes is well recognized. We have recently reported dimerization of  $\text{CpW}(\text{CO})_2(\text{PPh}_3)\text{SR}$  via loss of  $\text{PPh}_3$  to give thiolato-bridged dimers.<sup>3</sup> However, aggregation of  $\text{CpRu}(\text{PPh}_3)_2\text{SR}$ , where  $\text{R} = 1\text{-C}_3\text{H}_7$  or  $\text{CHMe}_2$ , is difficult to

Table I. Crystallographic Data for  $[\text{CpRuS-1-C}_3\text{H}_7]_3$

chem formula: $\text{C}_{24}\text{H}_{36}\text{Ru}_3\text{S}_3$	$f_w = 723.95$
$a = 10.554$ (1) $\text{\AA}$	space group: $P\bar{1}$ (No. 2)
$b = 14.033$ (2) $\text{\AA}$	$T = 22^\circ\text{C}$
$c = 18.243$ (2) $\text{\AA}$	$\lambda = 0.71069 \text{ \AA}$
$\alpha = 76.977$ (10) $^\circ$	$\rho_{\text{calc}} = 1.829 \text{ g cm}^{-3}$
$\beta = 87.299$ (8) $^\circ$	$\mu(\text{Mo K}\alpha) = 1.897 \text{ mm}^{-1}$
$\gamma = 89.009$ (11) $^\circ$	$R^a = 0.0304$
$V = 2629.4$ (9) $\text{\AA}^3$	$R_w^b = 0.0268$
$z = 4$	

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

stop at the dimer stage and easily proceeds to the trimers  $[\text{CpRuSR}]_3$ , wherein all the  $\text{PPh}_3$  ligands have been lost.<sup>4</sup>

Complexes of the type  $[\text{CpM}(\text{CO})]_3$ , where  $\text{M} = \text{Co}$  and  $\text{Rh}$ , have been studied as models for the chemisorption of  $\text{CO}$ , a

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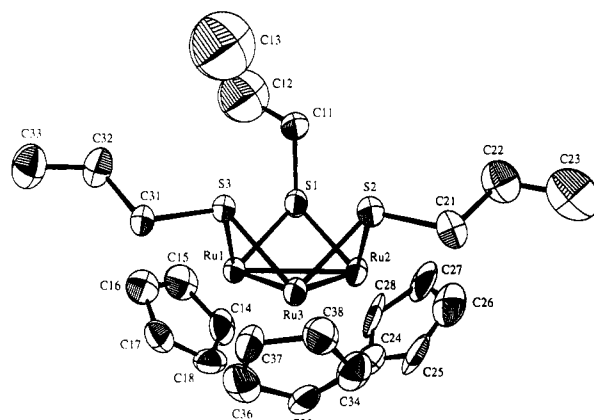
(4) Where  $\text{R} = \text{H}$ , the tetramer  $[\text{CpRuS}]_4$ , having a cuboidal structure, has been isolated; see: Amarasekera, J.; Rauchfuss, T. B.; Wilson, S. R. *J. Chem. Soc., Chem. Commun.* 1989, 14.

**Table II.** Atomic Coordinates ( $\times 10^4$ ;  $\times 10^5$  for Ru and S Atoms) and Equivalent Isotropic Temperature Factors ( $\text{\AA}^2 \times 10^3$ ;  $\text{\AA}^2 \times 10^4$  for Ru and S Atoms) for  $[\text{CpRuS-1-C}_3\text{H}_7]_3$ 

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>eq</sub> , $\text{\AA}^2$
Ru(1)	11997 (3)	336684 (2)	29335 (2)	322 (1)
Ru(2)	27144 (3)	46145 (3)	19233 (2)	372 (1)
Ru(3)	15007 (3)	52374 (2)	30754 (2)	322 (1)
S(1)	12172 (10)	36062 (8)	16475 (6)	408 (3)
C(11)	-204 (4)	4155 (4)	1198 (4)	56 (1)
C(12)	-1192 (6)	3366 (6)	1251 (5)	144 (3)
C(13)	-2349 (8)	3589 (7)	1173 (6)	230 (5)
S(2)	13350 (10)	59240 (8)	18152 (6)	401 (3)
C(21)	2230 (4)	7058 (3)	1526 (2)	48 (1)
C(22)	2278 (5)	7389 (4)	669 (3)	67 (1)
C(23)	3050 (6)	8282 (4)	389 (3)	100 (2)
S(3)	-3832 (9)	45060 (7)	29392 (6)	341 (2)
C(31)	-1338 (4)	4202 (3)	3823 (2)	38 (1)
C(32)	-2512 (4)	3648 (3)	3700 (3)	55 (1)
C(33)	-3447 (5)	3508 (4)	4372 (3)	73 (2)
C(14)	2503 (4)	2565 (3)	3763 (3)	53 (1)
C(15)	2489 (5)	2072 (3)	3163 (3)	61 (1)
C(16)	1246 (5)	1723 (3)	3149 (3)	63 (2)
C(17)	517 (5)	1984 (3)	3723 (3)	58 (1)
C(18)	1274 (5)	2509 (3)	4104 (3)	52 (1)
C(24)	4588 (4)	4059 (5)	2315 (3)	70 (2)
C(25)	4688 (4)	5044 (5)	2090 (2)	71 (2)
C(26)	4478 (4)	5321 (4)	1324 (4)	75 (2)
C(27)	4254 (5)	4489 (6)	1064 (4)	86 (2)
C(28)	4309 (5)	3680 (4)	1693 (4)	77 (2)
C(34)	2892 (5)	6170 (4)	3417 (3)	58 (1)
C(35)	3052 (5)	5217 (4)	3844 (3)	60 (1)
C(36)	1954 (5)	4947 (4)	4291 (3)	61 (1)
C(37)	1109 (5)	5743 (4)	4151 (3)	62 (1)
C(38)	1672 (4)	6499 (4)	3617 (3)	59 (1)
Ru(4)	38489 (3)	935 (2)	70247 (2)	345 (1)
Ru(5)	23537 (3)	7453 (3)	80648 (2)	377 (1)
Ru(6)	35556 (3)	20413 (2)	69274 (2)	330 (1)
S(4)	38687 (10)	-4577 (8)	83082 (6)	415 (3)
C(41)	5297 (4)	-198 (3)	8749 (3)	49 (1)
C(42)	6339 (5)	-940 (4)	8650 (4)	78 (2)
C(43)	7572 (5)	-723 (4)	8887 (4)	110 (2)
S(5)	37282 (10)	19483 (8)	81905 (6)	405 (3)
C(51)	2832 (4)	2933 (3)	8492 (2)	50 (1)
C(52)	2772 (5)	2758 (4)	9341 (3)	73 (2)
C(53)	2021 (6)	3484 (5)	9616 (3)	118 (3)
S(6)	54421 (9)	11844 (7)	70332 (6)	348 (2)
C(61)	6372 (4)	1423 (3)	6142 (2)	41 (1)
C(62)	7555 (4)	771 (4)	6217 (3)	63 (1)
C(63)	8465 (5)	1032 (4)	5537 (3)	79 (2)
C(44)	2523 (5)	-165 (4)	6209 (4)	73 (2)
C(45)	3728 (6)	-28 (4)	5853 (3)	66 (2)
C(46)	4512 (5)	-787 (4)	6193 (3)	69 (2)
C(47)	3833 (6)	-1389 (4)	6757 (4)	79 (2)
C(48)	2595 (5)	-1042 (4)	6798 (4)	73 (2)
C(54)	484 (5)	432 (7)	7688 (4)	86 (2)
C(55)	360 (5)	1284 (5)	7909 (5)	90 (2)
C(56)	590 (5)	1113 (6)	8682 (5)	92 (2)
C(57)	843 (5)	138 (7)	8929 (4)	98 (2)
C(58)	783 (5)	-285 (5)	8300 (6)	87 (2)
C(64)	3243 (5)	3635 (3)	6448 (3)	60 (1)
C(65)	2074 (5)	3156 (4)	6584 (3)	62 (1)
C(66)	2055 (5)	2482 (4)	6128 (3)	63 (1)
C(67)	3225 (6)	2549 (4)	5722 (3)	69 (2)
C(68)	3931 (5)	3272 (4)	5918 (3)	67 (1)

**Table III.** Selected Bond Lengths ( $\text{\AA}$ ) and Angles (deg) for  $[\text{CpRuS-1-C}_3\text{H}_7]_3$ 

Ru(1)-Ru(2)	2.716 (1)	Ru(4)-Ru(5)	2.716 (1)
Ru(1)-Ru(3)	2.718 (1)	Ru(4)-Ru(6)	2.712 (1)
Ru(2)-Ru(3)	2.713 (1)	Ru(5)-Ru(6)	2.712 (1)
Ru(1)-S(1)	2.293 (1)	Ru(4)-S(4)	2.295 (1)
Ru(1)-S(3)	2.292 (1)	Ru(4)-S(6)	2.296 (1)
Ru(2)-S(1)	2.286 (1)	Ru(5)-S(4)	2.289 (1)
Ru(2)-S(2)	2.304 (1)	Ru(5)-S(5)	2.302 (1)
Ru(3)-S(2)	2.297 (1)	Ru(6)-S(5)	2.294 (1)
Ru(3)-S(3)	2.302 (1)	Ru(6)-S(6)	2.301 (1)
S(1)-C(11)	1.818 (4)	S(4)-C(41)	1.821 (5)
S(2)-C(21)	1.825 (4)	S(5)-C(51)	1.832 (5)
S(3)-C(31)	1.830 (4)	S(6)-C(61)	1.825 (4)
Ru(2)-Ru(1)-Ru(3)	59.9 (1)	Ru(5)-Ru(4)-Ru(6)	59.9 (1)
Ru(3)-Ru(1)-S(1)	100.4 (1)	Ru(6)-Ru(4)-S(4)	100.1 (1)
Ru(3)-Ru(1)-S(3)	53.9 (1)	Ru(6)-Ru(4)-S(6)	53.9 (1)
Ru(2)-Ru(1)-S(1)	53.5 (1)	Ru(5)-Ru(4)-S(4)	53.6 (1)
Ru(2)-Ru(1)-S(3)	93.8 (1)	Ru(5)-Ru(4)-S(6)	94.0 (1)
S(1)-Ru(1)-S(3)	92.1 (3)	S(4)-Ru(4)-S(6)	91.6 (1)
Ru(1)-Ru(2)-Ru(3)	60.1 (1)	Ru(4)-Ru(5)-Ru(6)	60.0 (1)
Ru(3)-Ru(2)-S(1)	100.8 (1)	Ru(6)-Ru(5)-S(4)	100.3 (1)
Ru(3)-Ru(2)-S(2)	53.8 (1)	Ru(6)-Ru(5)-S(5)	53.7 (1)
Ru(1)-Ru(2)-S(1)	53.7 (1)	Ru(4)-Ru(5)-S(4)	53.8 (1)
Ru(1)-Ru(2)-S(2)	94.8 (1)	Ru(4)-Ru(5)-S(5)	95.0 (1)
S(1)-Ru(2)-S(2)	93.4 (1)	S(4)-Ru(5)-S(5)	93.2 (1)
Ru(1)-Ru(3)-Ru(2)	60.0 (1)	Ru(4)-Ru(6)-S(5)	95.3 (1)
Ru(2)-Ru(3)-S(2)	54.0 (1)	Ru(4)-Ru(6)-S(6)	53.8 (1)
Ru(2)-Ru(3)-S(3)	93.7 (1)	S(5)-Ru(6)-S(6)	84.1 (1)
Ru(1)-Ru(3)-S(2)	94.9 (1)	Ru(4)-Ru(6)-Ru(5)	60.1 (1)
Ru(1)-Ru(3)-S(3)	53.5 (1)	Ru(5)-Ru(6)-S(5)	54.0 (1)
S(2)-Ru(3)-S(3)	83.5 (1)	Ru(5)-Ru(6)-S(6)	94.0 (1)
Ru(1)-S(1)-Ru(2)	72.8 (1)	Ru(4)-S(4)-Ru(5)	72.7 (1)
Ru(1)-S(1)-C(11)	116.2 (2)	Ru(4)-S(4)-C(41)	116.0 (2)
Ru(2)-S(1)-C(11)	118.4 (2)	Ru(5)-S(4)-C(41)	117.7 (2)
Ru(2)-S(2)-Ru(3)	72.3 (1)	Ru(5)-S(5)-Ru(6)	72.3 (1)
Ru(2)-S(2)-C(21)	109.2 (1)	Ru(5)-S(5)-C(51)	109.4 (1)
Ru(3)-S(2)-C(21)	111.8 (1)	Ru(6)-S(5)-C(51)	111.3 (1)
Ru(1)-S(3)-Ru(3)	72.6 (1)	Ru(4)-S(6)-Ru(6)	72.3 (1)
Ru(1)-S(3)-C(31)	110.3 (1)	Ru(4)-S(6)-C(61)	110.7 (1)
Ru(3)-S(3)-C(31)	112.1 (2)	Ru(6)-S(6)-C(61)	111.5 (1)

**Figure 1.** ORTEP drawing (50% probability level) of  $[\text{CpRuS-1-C}_3\text{H}_7]_3$ , (**1a**), showing the numbering scheme for molecule A. The *U*(eq) values were used for atoms C(12) and C(13).

## Results

The dark red trimers  $[\text{CpRuSR}]_3$ , where  $\text{R} = 1\text{-C}_3\text{H}_7$  (**1a**) and  $\text{CHMe}_2$  (**1b**), were obtained in 50% yield by refluxing toluene solutions of  $\text{CpRu}(\text{PPh}_3)_2\text{SR}^2$  for 4 h followed by standard workup involving chromatography (eq 1).



Complexes **1a,b** are soluble in THF, benzene, ether and hexanes. They are stable in solution, in air, for hours. The complexes were characterized by their NMR spectra and elemental analysis. Crystal data, atomic coordinates, and selected bond lengths and angles for **1a** are given in Tables I-III, respectively.

cluster/surface analogy<sup>5</sup> being invoked. The chemisorption of thiolato groups on surfaces may be an important step in the hydrodesulfurization process,<sup>6</sup> yet such interactions are difficult to study. Few model complexes exist with which to develop an appropriate cluster/surface analogy. We report the preparation and structure of potential model complexes of the type  $[\text{CpRuSR}]_3$  in which short  $\text{CH}\cdots\text{S}$  distances are observed in the crystal structure and are characterized via NMR spectroscopy.

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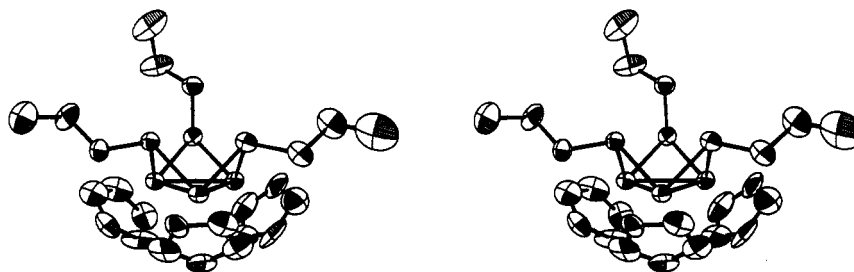


Figure 2. ORTEP stereoscopic drawing of [CpRuS-1-C<sub>3</sub>H<sub>7</sub>]<sub>3</sub> (**1a**) (molecule A).

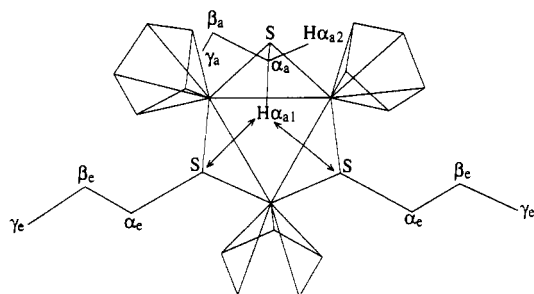


Figure 3. Line drawing of [CpRuS-1-C<sub>3</sub>H<sub>7</sub>]<sub>3</sub> (**1a**) illustrating the arrangement of the protons attached to the  $\alpha$ -carbon of the axial *n*-propyl group. The nonbonded H $\alpha_1$ -sulfur distances are as follows. Molecule A: H $\alpha_1$ -S<sub>2</sub>, 2.836 Å; H $\alpha_1$ -S<sub>3</sub>, 2.631 Å. Molecule B: H $\alpha_1$ -S<sub>5</sub>, 2.776 Å, H $\alpha_1$ -S<sub>6</sub>, 2.619 Å. The nonbonded sulfur-sulfur distance are as follows. Molecule A: S<sub>1</sub>-S<sub>2</sub>, 3.340 Å; S<sub>1</sub>-S<sub>3</sub>, 3.300 Å; S<sub>2</sub>-S<sub>3</sub>, 3.064 Å. Molecule B: S<sub>4</sub>-S<sub>5</sub>, 3.336 Å; S<sub>4</sub>-S<sub>6</sub>, 3.291 Å; S<sub>5</sub>-S<sub>6</sub>, 3.078 Å.

Two independent but very similar molecules of **1a** were found in the unit cell, only one of which (molecule A) is depicted in Figure 1.<sup>7</sup> The molecule, which is more easily visualized by means of the stereoscopic projection presented in Figure 2, consists of a triangle of ruthenium atoms with all of the Cp ligands on the same side of the plane. The three thiolato groups bridge two metal atoms each and are grouped on the other side of the triangular plane. Two of the three 1-C<sub>3</sub>H<sub>7</sub> groups occupy equatorial-like positions relative to the Ru<sub>3</sub>S<sub>3</sub> "basket" while the third group is axial. The Ru<sub>3</sub>S<sub>3</sub> unit is tightly bonded in comparison to two other complexes: [Ru<sub>3</sub>H(CO)<sub>10</sub>SCH<sub>2</sub>CO<sub>2</sub>H]<sup>8</sup> (**2**) and [Ru<sub>3</sub>(SPh)(H)(CO)<sub>8</sub>Me<sub>2</sub>PCH<sub>2</sub>PMe<sub>2</sub>]<sup>9</sup> (**3**). The average Ru-S bond length in **1a** (2.296 Å) is shorter than that found in **2** (2.388 Å) and **3** (2.391 Å). Likewise the average Ru-Ru bond distance in **1a** (2.715 Å) is shorter than that found in **2** and **3** (2.839 and 2.867 Å, respectively).

A most interesting aspect of the structure of **1a** is depicted in Figure 3, which presents the molecule viewed from above the plane formed by the three sulfur atoms. The protons on the  $\alpha$ -carbon of the axial 1-C<sub>3</sub>H<sub>7</sub> group are shown in their calculated positions as H $\alpha_1$  and H $\alpha_2$ . The distances between H $\alpha_1$  and the sulfur atoms (Figure 3) are shorter than the sum of the appropriate van der Waal distances (3.05 Å) and are within "hydrogen-bonding" distance as defined by Raston and White.<sup>10</sup>

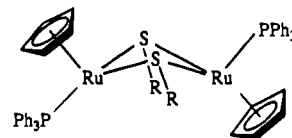
The NMR spectra of **1a,b** are consistent with the structure of **1a**. There are two signals for the Cp protons in the ratio 2:1. The resonances due to the 1-C<sub>3</sub>H<sub>7</sub> groups of **1a** are also divided into two types, one due to the two equatorial groups and the other due to the axial group in a 2:1 ratio. The multiplet due to the methylene protons of the  $\alpha$ -carbon of the axial group appears at 3.05 ppm, somewhat downfield from normal (2.6–2.4 ppm),<sup>2</sup> while the peaks due to the other protons are in the normal range. Two COSY NMR experiments on **1a** in CDCl<sub>3</sub> and C<sub>6</sub>D<sub>6</sub> permitted the assignment of the peaks as listed in the Experimental Section. The diastereotopic nature of the methylene protons of the  $\alpha$ -

carbons of the equatorial groups was clearly revealed by these experiments. The peaks due to the methyl groups of **1b** appear as three doublets consistent with the presence of one axial CHMe<sub>2</sub> group and two equatorial groups wherein the methyl groups are diastereotopic. The peak due to the methyne proton of the axial group also has an unusual downfield displacement (4.97 ppm) while that due to the methyne proton of the equatorial groups has an unusual upfield displacement (0.80 ppm). These shifts suggest the presence of a ring current associated with the Ru<sub>3</sub> and S<sub>3</sub> planes. The NMR spectrum (toluene-*d*<sub>8</sub>) of **1a** was invariant with temperature in the range -20 to +100 °C.

When the conversion of CpRu(PPh<sub>3</sub>)<sub>2</sub>S-1-C<sub>3</sub>H<sub>7</sub> was performed in C<sub>6</sub>D<sub>6</sub> and monitored by NMR spectroscopy, peaks due to an intermediate appeared which decreased in intensity as peaks due to the trimer grew. After 4 h, the peaks due to the trimer reached constant intensity, corresponding to 50% of the integrated intensity in the Cp region. A red complex, **4**, was prepared by heating the monomer in boiling toluene for 5 min followed by chromatographic workup. Although it was impure, as shown by its NMR spectrum, it was clearly the major intermediate observed above. The NMR spectrum of **4** showed two Cp signals in a 1:1 ratio and a single environment for the 1-C<sub>3</sub>H<sub>7</sub> group. Attempts to isolate a similar intermediate observed in the formation of **1b** were not successful.

## Discussion

It appears that the formation of **1a,b** is stepwise via dimeric intermediates such as **4**. Although **4** was not isolated in pure form, its NMR spectrum is consistent with its formulation as the dimer [CpRu(PPh<sub>3</sub>)- $\mu$ -SR]<sub>2</sub>. There are six possible geometric isomers for complexes of this type.<sup>3</sup> The Cp rings could be *cis* or *trans* with respect to the M-M vector, and each of the propyl groups could be axial or equatorial with respect to a nonplanar M<sub>2</sub>S<sub>2</sub> "butterfly" ring.<sup>11</sup> Only two of these (*trans-ee*, pictured below, and *trans-aa*) are consistent with the NMR spectrum of **4**, having two Cp environments and one environment for the propyl groups. Isomers where the R groups are both axial are sterically impractical;<sup>12</sup> therefore, the *trans-ee* structure is assigned to **4**.



The aggregation of CpRu(PPh<sub>3</sub>)<sub>2</sub>SR via facile loss of two PPh<sub>3</sub> ligands is consistent with earlier observations that one PPh<sub>3</sub> group is easily substituted by a CO molecule.<sup>2,13</sup> In the absence of added ligand one might expect thiolato bridged dimers to be formed. Therefore, the further aggregation via loss of the second PPh<sub>3</sub> group to give the trimers **1a,b** is notable.<sup>4</sup> The observed reactivity is probably due to a combination of steric and electronic effects. The presence of two bulky PPh<sub>3</sub> groups and a thiolato ligand would be expected to favor ligand loss via steric acceleration. Molecular orbital calculations<sup>14</sup> on CpFe(CO)<sub>2</sub>SH suggest that the HOMO is antibonding, involving the sulfur p and metal d orbitals.

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Consequently the lone pairs on the sulfur atom destabilize such molecules with respect to ligand loss. On the other hand calculations on  $\text{CpFe}(\text{CO})\text{SH}^{14}$  suggest the lone pair now stabilizes such 16-electron species, and some, such as  $\text{CpMo}(\text{NO})(\text{SPh})_2^{15}$  have been isolated.

The disposition of one of the alkyl groups of **1a,b** in the axial position and the other two in the equatorial is only one of the possible arrangements. However, there is no evidence for the presence of any of the other possible isomers for **1a** or **1b**. Moreover, the VT-NMR study of **1a** suggests that the lower limit for axial-equatorial interconversion is about  $85 \text{ kJ mol}^{-1}$ .<sup>16</sup> This lower limit exceeds the range ( $40\text{--}80 \text{ kJ mol}^{-1}$ )<sup>17,18</sup> observed for inversion at bridging sulfur atoms for a variety of dimers. Thus the axial alkyl group is, to a certain degree, locked into the position observed in the crystal with one proton directed towards the center of the  $\text{S}_3$  triangle. With respect to the two  $\alpha$ -protons on this axial group, the room-temperature COSY experiments show a single environment resonating at 3.50 ppm. The two protons  $\text{H}_{\alpha_1}$  and  $\text{H}_{\alpha_2}$  (Figure 3) are in rapid equilibrium on the NMR time scale. We conclude that the structure of the trimer is rigid in terms of axial-equatorial exchange, while the alkyl group is free to rotate at least to the degree that each  $\text{H}_{\alpha}$  proton alternatively interacts with the two sulfur atoms across the ring.

Minimal steric hindrance of the alkyl groups would probably be best achieved by an all-equatorial arrangement. The observed structural and NMR spectroscopic properties of **1a,b** are probably due to the close proximity of the three sulfur atoms. The observed orientation of the alkyl groups may simply minimize lone pair repulsions which would occur if all three of the groups were equatorial. Hydrogen bonding between the proton(s) of the  $\alpha$ -carbon atom of the axial group may also contribute to locking the axial group in position.

One can regard complexes **1a,b** as a model for thiolate ligand chemisorption to a metal surface. The three ruthenium atoms form a truncated metal surface upon which the three sulfur atoms are densely packed. Complexes **1a,b** illustrate possible consequences of such an architecture.

### Experimental Section

All experiments were performed under nitrogen in appropriately-sized Schlenk tubes or three-necked round-bottom flasks. Tetrahydrofuran, hexanes, and toluene were distilled over sodium/benzophenone prior to use. The compound  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  was kindly supplied by PGM Chemicals Ltd., New Germany, South Africa. The complexes  $\text{CpRu}(\text{PPh}_3)_2\text{SR}$ , where  $\text{R} = 1\text{-C}_3\text{H}_7$  and  $\text{CHMe}_2$ , were prepared via treatment of  $\text{CpRu}(\text{PPh}_3)_2\text{Cl}$  with the appropriate lithium thiolate, as reported.<sup>2</sup> Solvents and other liquid reagents were transferred by means of syringes.

Nuclear magnetic resonance (NMR) spectra were recorded on a Varian XL-200 or XL-300 spectrometer. All NMR samples were prepared under  $\text{N}_2$  atmosphere using benzene- $d_6$ , degassed by freeze-thaw degassing under vacuum. Chemical shifts are reported in ppm relative to tetramethylsilane, used as an internal standard, and the multiplicities are reported as m, d, t, dm, and ABq (multiplet, doublet, triplet, diastereotopic multiplet and AB quartet respectively). The COSY experiment was performed at 300 MHz in a 5 mm tube. Elemental analyses were performed by Spang Microanalytical Laboratories, Eagle Harbor, MI. Melting points were obtained on a Thomas Hoover capillary melting point apparatus in a sealed capillary tube under a nitrogen atmosphere and are uncorrected.

**1,1'1''-Tris(cyclopentadienyl)tris( $\mu$ -1-propanethiolato)triruthenium(II),  $[\text{CpRuS-1-C}_3\text{H}_7]_3$  (**1a**).** A solution of  $\text{CpRu}(\text{PPh}_3)_2\text{S-1-C}_3\text{H}_7$  (0.69 g, 0.91 mmol) in toluene (40 mL) was refluxed for 4 h. The cool reaction solution was reduced in volume (vacuum) to about 3 mL and placed on a chromatography column (Alumina, 2.5 cm  $\times$  23 cm). Elution with hexanes gave a fraction containing  $\text{PPh}_3$ . Elution with 20–30% THF in hexanes gave an orange-red band, which was collected and stripped to

dryness. The dark residue was recrystallized from hot THF/hexanes (3:10) to give dark red crystals (0.11 g, 51%; mp  $125\text{--}127^\circ\text{C}$ ).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  4.59 (s, 5 H, Cp), 4.55 (s, 10 H, Cp), 3.50 (m, 2 H,  $\text{CH}_2\text{-C}_3\text{H}_7$  axial), 1.97 (m, 2 H,  $\text{CH}_2\text{CH}_2\text{CH}_3$  axial), 1.50 (m, 6 H,  $1/2\text{CH}_2\text{CH}_2\text{CH}_3$  equatorial and  $\text{CH}_2\text{CH}_2\text{CH}_3$  equatorial), 1.33 (m, 2H,  $1/2\text{CH}_2\text{CH}_2\text{CH}_3$  equatorial), 1.20 (t, 3 H,  $\text{CH}_2\text{CH}_2\text{CH}_3$  axial,  $J(\text{H-H}) = 7.3 \text{ Hz}$ ), 0.87 (t, 6 H,  $\text{CH}_2\text{CH}_2\text{CH}_3$  equatorial,  $J(\text{H-H}) = 7.2 \text{ Hz}$ ). Anal. Calcd for  $\text{C}_{24}\text{H}_{36}\text{Ru}_3\text{S}_3$ : C, 39.82; H, 5.01; S, 13.29. Found: C, 40.07; H, 5.08; S, 13.15.

**1,1'1''-Tris(cyclopentadienyl)tris( $\mu$ -2-propanethiolato)triruthenium(II),  $[\text{CpRuSCHMe}_2]_3$  (**1b**).** A solution of  $\text{CpRu}(\text{PPh}_3)_2\text{SCHMe}_2$  (1.88 g, 2.45 mmol) in toluene (50 mL) was refluxed for 4.5 h. The cool solution was stripped to dryness, the residue dissolved in THF (5 mL), and this solution chromatographed (Alumina 2.5 cm  $\times$  20 cm). Elution with hexanes (300 mL) gave a dark brown band, which was collected and stripped to dryness. The residue was washed with hexanes ( $5 \times 2 \text{ mL}$ ) and recrystallized from THF/hexanes (1:1) at  $-20^\circ\text{C}$  to give the title complex as dark red crystals which served as the analytical sample (0.020 g, mp  $260\text{--}261^\circ\text{C}$ ). Eluting the column with THF/hexanes (1:4) gave a second band, which was stripped to dryness to give the title complex in high purity (90% by NMR) as a red crystalline powder (0.27 g, combined yield 49%).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  4.97 (septet, 1 H,  $\text{CHMe}_2$  axial), 4.58 (s, 5 H, Cp), 4.50 (s, 10 H, Cp), 1.55 (d, 6 H,  $\text{CHMe}_2$  axial,  $J(\text{H-H}) = 6.7 \text{ Hz}$ ), 1.51, 1.09 (dd, 12 H,  $\text{CHMe}_2$  equatorial,  $J(\text{H-H}) = 6.5 \text{ Hz}$ ), 0.78 (septet, 2 H,  $\text{CHMe}_2$  axial). Anal. Calcd for  $\text{C}_{24}\text{H}_{36}\text{Ru}_3\text{S}_3$ : C, 39.82; H, 5.01; S, 13.29. Found: C, 39.89; H, 5.12; S, 13.27.

**1,1'-Bis(cyclopentadienyl)-1,1'-bis(triphenylphosphene)bis( $\mu$ -1-propanethiolato)diruthenium(II),  $[\text{CpRu}(\text{PPh}_3)_2\text{S-1-C}_3\text{H}_7]_2$  (**4**).** A solution of  $\text{CpRu}(\text{PPh}_3)_2\text{S-1-C}_3\text{H}_7$  (0.17 g, 0.22 mmol) in toluene, (2 mL) in a Schlenk tube, was heated for 5 min by immersing the tube in a beaker of boiling toluene. Thereafter, the solution was immediately stripped to dryness. The residue, suspended in hexanes, was chromatographed on an alumina column (2.5 cm  $\times$  25 cm). Elution with hexanes gave a band containing  $\text{PPh}_3$ . Elution with THF/hexanes (1:1) gave an orange band, which was collected and concentrated under vacuum to about 3 mL in volume. Cooling at  $-20^\circ\text{C}$  overnight gave an obvious mixture whose composition, determined by its NMR spectrum, was colorless crystals of  $\text{PPh}_3$ , orange crystals of  $\text{CpRu}(\text{PPh}_3)_2\text{Cl}$  (a contaminant in  $\text{CpRu}(\text{PPh}_3)_2\text{S-1-C}_3\text{H}_7$ ), and dark red crystals of the title complex (total yield, 30 mg).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.49 (m, 12 H,  $\text{PPh}_3$ ), 7.01 (m, 18 H,  $\text{PPh}_3$ ), 4.41 (s, 5 H, Cp), 4.16 (s, 5 H, Cp), 2.78, 2.54 (dm, 4 H,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.70 (m, 4 H,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 0.89 (t, 6 H,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ,  $J(\text{H-H}) = 5.7 \text{ Hz}$ ).

**X-Ray Structure Determination for **1a**.** A dark, red, plate-shaped crystal (0.34 mm  $\times$  0.27 mm  $\times$  0.06 mm) was used for the structure determination. The unit cell dimensions were determined by a least-squares fit to the positions of 25 accurately centered reflections with  $7.71 \leq \theta \leq 19.75^\circ$ , and intensity measurements were made using an Enraf-Nonius CAD4F four-circle diffractometer with graphite-crystal-monochromatized  $\text{Mo K}\alpha$  radiation. A total of 11 430 reflections with  $3 \leq \theta \leq 27^\circ$  ( $h = 0$  to  $+12$ ,  $k = -17$  to  $+17$ ,  $l = -23$  to  $+23$ ) were measured using the  $\omega/2\theta$  scan mode with a variable scan speed: maximum  $0.0915^\circ \text{ s}^{-1}$  in  $\omega$ , maximum time 50 s/reflection, and a scan width of  $(0.52 + 0.34 \tan \theta)^\circ$  in  $\omega$ . The scan width was extended by 25% on each side for background measurements. Three standard reflections (1,5,16; 2,0,8; 4,3,4) were measured every 60 min. Since these showed an average total change in intensity of only  $-1.1\%$  over the 65.8-h X-ray exposure time, decay corrections were not applied. Semiempirical absorption corrections<sup>19</sup> based on azimuth scans of nine reflections were applied to the data, giving the following corrections: maximum, 0.9999; minimum, 0.8498; average, 0.9620. A total of 9276 reflections with  $F_o \geq 6\sigma(F_o)$  were used in the refinement. The structure was solved by direct methods using SHELXS-86,<sup>20</sup> and was refined by blocked-matrix (two blocks) weighted least-squares methods [ $w = \sigma^{-2}(F_o)$  (based on counting statistics)], the function minimized was  $\sum w(|F_o| - |F_c|)^2$  using SHELXL-76.<sup>21</sup> Complex neutral-atom scattering factors<sup>22</sup> were used for all atoms. Atoms C(12) and C(13) could not be refined anisotropically to give reasonable off-diagonal temperature tensor elements. All hydrogen atoms were added in calculated positions ( $d_{\text{C-H}} = 0.95 \text{ \AA}$ ). Four isotropic temperature

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factors were refined for the hydrogen atoms: one for the three *n*-propyl groups and one for the three cyclopentadienyl ligands for each of the two independent molecules in the asymmetric unit. The refinement converged with  $R = 0.0304$  and  $R_w = 0.0268$ . A total of 545 parameters were refined, giving an observation to parameter ratio of 17.0; the largest shift/error in the final cycles was 0.068. A final difference electron density map showed no significant residual features:  $\partial\rho_{\max}$ ,  $0.80 \text{ e } \text{\AA}^{-3}$ ;  $\partial\rho_{\min}$ ,  $-0.69 \text{ e } \text{\AA}^{-3}$ .

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University, concerning the X-ray structural analysis are gratefully acknowledged.

**Registry No.** 1a, 139041-61-5; 1b, 139041-62-6; 4, 139041-63-7;  $\text{CpRu}(\text{PPh}_3)_2\text{S-1-C}_3\text{H}_7$ , 126899-34-1;  $\text{CpRu}(\text{PPh}_3)_2\text{SCHMe}_2$ , 126899-35-2.

**Supplementary Material Available:** An ORTEP drawing of  $[\text{CpRuS-1-C}_3\text{H}_7]_3$  showing the numbering scheme for molecule B (Figure 4), a full-length table of crystallographic data (Table IV), a table of anisotropic temperature factors (Table V), a table of calculated atomic coordinates and common isotropic temperature factors of the hydrogen atoms of  $[\text{CpRuS-1-C}_3\text{H}_7]_3$  (Table VI), and a table of bond lengths and angles (Table VII) (13 pages); a table of observed and calculated structure factors (Table VIII) (55 pages). Ordering information is given on any current masthead page.

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## Neutral Catecholate Derivatives of Manganese and Iron: Synthesis and Characterization of the Metal-Oxygen Cubane-like Species $\text{M}_4(\text{DBCat})_4(\text{py})_6$ ( $\text{M} = \text{Mn, Fe}$ ), the Trinuclear Complex $\text{Mn}_3(\text{DBCat})_4(\text{py})_4$ , and the Dimers $\text{M}_2(\text{DBCat})_2(\text{py})_n$ ( $\text{M} = \text{Mn, } n = 6; \text{M} = \text{Fe, } n = 4, 6$ )

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The synthesis and characterization of several new catecholate derivatives of manganese and iron are described. The reaction of 3,5-di-*tert*-butylcatechol ( $\text{DBCatH}_2$ ) with the amides  $\text{M}[\text{N}(\text{SiMe}_3)_2]_2$  ( $\text{M} = \text{Mn, Fe}$ ) in the presence of pyridine (py) affords the title compounds in high yield. The dimers  $\text{Mn}_2(\text{DBCat})_2(\text{py})_6$  (**1**) and  $\text{Fe}_2(\text{DBCat})_2(\text{py})_n$  ( $n = 4$  (**4a**),  $6$  (**4b**)) are obtained by treatment of catechol with the appropriate amide in pyridine. In hexane or toluene, this reaction gives the tetrametallic species  $\text{M}_4(\text{DBCat})_4(\text{py})_6$  ( $\text{M} = \text{Mn}$  (**2**),  $\text{Fe}$  (**5**)) upon the addition of 2 equiv of pyridine or, in the case of **2**, by recrystallization of the dimer from toluene.  $\text{Mn}_3(\text{DBCat})_4(\text{py})_4$  (**3**) is obtained by slow air oxidation of **2** or by addition of  $1/3$  equiv of 3,5-di-*tert*-butyl-*o*-benzoquinone to the reaction of  $\text{Mn}[\text{N}(\text{SiMe}_3)_2]_2$  with  $\text{DBCatH}_2$  in hexane with subsequent addition of pyridine. Compounds **1-5** were characterized by infrared, UV-visible,  $^1\text{H}$  NMR, and EPR spectroscopy and X-ray crystallography. The crystal structures of **1**, **4a**, and **4b** (which cocrystallize as **4**) consist of centrosymmetric dimeric units in which both catecholate ligands bridge the two metal centers by one doubly bridging and one terminal oxygen. Three pyridine ligands per metal complete the distorted octahedral geometry in **1** and **4a**. In **4b** two pyridines are bound to each iron which have distorted trigonal bipyramidal geometry at the metal. The structure of **2** possesses a  $\text{Mn}_4\text{O}_6$  core composed of four doubly bridging oxygens, two triply bridging oxygens, and four manganese atoms. Further coordination by pyridine ligands gives rise to two manganese centers with trigonal bipyramidal geometry and two with distorted octahedral geometry. The overall geometry of the complex gives **2** a basket-like appearance. Compound **5** has an  $\text{Fe}_4\text{O}_4$  distorted cubane core, with each iron bound to three triply bridging oxygens and one terminal oxygen. As in **2**, the six pyridine ligands are arranged to give two octahedral and two trigonal bipyramidal metal centers. The structure of **3** consists of two five-coordinate Mn(III) centers (one square pyramidal and one trigonal bipyramidal), each bound by two doubly bridging catecholate oxygens to a central pseudooctahedral Mn(II) ion. The cis arrangement of the bridging units imposes a bent geometry on the compound. Spectroscopic studies suggest that complex **3** undergoes intramolecular electron transfer on dissolution in toluene to give the all-Mn(II) semiquinone form  $\text{Mn}_3(\text{DBSQ})_2(\text{DBCat})_2(\text{py})_4$ .

Interest in the chemistry of manganese and iron catecholate and semiquinonate complexes has greatly increased in recent years.<sup>1-5</sup> One reason for this has been the recognition of the important role of quinone- and catechol-containing groups in biology. For instance, the use of catecholate-containing sequestering agents<sup>2</sup> by various organisms to concentrate  $\text{V}^{4+}$  and  $\text{Fe}^{3+}$  ions has been established<sup>3-5</sup> and successfully modeled in recent years.<sup>6-8</sup> Manganese and iron plastoquinone complexes have been

implicated as the electron-accepting center in photosystem II<sup>9-11</sup> in plants and some photosynthetic bacteria, as well as many other biological electron-transport chains.<sup>13,14</sup> Catechol dioxygenase enzymes containing iron or copper are known to oxidize catechol

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