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Preparation of the Hydrosulfido-Bridged Diruthenium Complex [(η^5-C_5Me_5)RuCl(μ-SH)$_2$Ru(η^5-C_5Me_5)Cl] and Its Transformation into a Cubane-Type Tetraruthenium Sulfido Cluster or Triangular Heterometallic $RhRu_2$ Sulfido Cluster

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The hydrosulfido-bridged diruthenium complex [Cp*RuCl(μ-SH)$_2$RuCp*Cl] (**4**; Cp* = η^5-C_5Me_5) was obtained by the reaction of either [(Cp*Ru)$_4$(μ_3-Cl)$_4$] (**1**) or [Cp*RuCl(μ-Cl)$_2$-RuCp*Cl] with excess H_2S gas, while the reactions of **1** with thiols resulted in the formation of the thiolato-bridged diruthenium complexes [Cp*RuCl(μ-SR)$_2$RuCp*Cl] (R = Et (**5a**), C_6H_4-Me-*p*). When a solution of **4** in toluene was heated at reflux, the cubane-type tetraruthenium sulfido cluster [(Cp*Ru)$_4$(μ_3-S)$_4$]Cl_2 (**6**) was produced. On the other hand, treatment of **4** with 2 molar equiv of [RhCl(PPh_3)$_3$] in THF at room temperature afforded the triangular heterometallic sulfido cluster [(Cp*Ru)$_2$(μ_2-H)(μ_3-S)$_2$RhCl$_2$(PPh_3)] (**10**). X-ray analyses have been undertaken to determine the detailed structures for **4**, **5a**, **6**, and **10**.

Introduction

Extensive studies in this and other laboratories have shown that the Ru(II) complex [(Cp*Ru)$_4$(μ_3-Cl)$_4$] (**1**) and the Ru(III) complex [Cp*RuCl(μ-Cl)$_2$RuCp*Cl] (**2**; Cp* = η^5-C_5Me_5) are quite versatile precursors in the preparation of polynuclear Ru−sulfur complexes containing two or more Cp*Ru units. These include a series of thiolato-bridged dinuclear complexes having a Ru(II)/Ru(II),[1] Ru(II)/Ru(III),[2] or Ru(III)/Ru(III) pair,[1b,3] sulfido-capped triruthenium clusters,[4] and a cubane-type tetraruthenium sulfido cluster.[5] This structural diversity of the products arises from the nature of the sulfur sources and reaction conditions as well as the choice of the Ru precursor. Furthermore, intriguing reactivities of diruthenium complexes such as [Cp*Ru(μ-SPr^i)$_2$RuCp*], [Cp*Ru(μ-SPr^i)$_3$RuCp*], and [Cp*RuCl(μ-SPr^i)$_2$RuCp*][OTf] (OTf = CF_3SO_3) toward terminal alkynes,[6] alkyl halides,[1,7] and hydrazines[8] have been demonstrated. These substrates undergo unique transformations at the diruthenium centers in these complexes with retention of the bimetallic core,[9] owing apparently to the presence of the firmly bound thiolato bridges. It might be emphasized that although the chemistry of transition-metal−sulfur complexes is progressing rapidly because of their relevance to the active sites of metalloproteins and heterogeneous hydrodesulfurization catalysts,[10] organic reactions and catalyses using transition-metal−sulfur complexes have still been poorly advanced.[11] Another important feature of these diruthenium complexes lies in their potential to serve as starting compounds for the preparation of homo- and heterometallic clusters with higher nuclearity. In this context, we have already reported the reactions of [Cp*Ru(μ-S_2)(μ-SPr^i)$_2$RuCp*], readily available from [Cp*RuCl(μ-SPr^i)$_2$RuCp*Cl], with [M(PPh_3)$_4$] (M = Pt, Pd), which lead to the formation of the heterometallic sulfido clusters [(Cp*Ru)$_2$(μ_2-SPr^i)$_2$(μ_2-S)$_2$Pt(PPh_3)$_2$] and [(Cp*Ru)$_2$(μ_3-S)$_2$Pd$_2$(μ_2-SPr^i)(SPr^i)(PPh_3)].[12]

In a previous paper dealing with a series of triruthenium sulfido clusters derived from **1**,[4a] we have briefly shown that the reaction of **1** with (Me_3Si)$_2$S in the presence of H_2O affords a mixture of the fully characterized triangular cluster [(Cp*Ru)$_3$(μ_3-S)$_2$(μ_2-H)] (**3**) and the diruthenium(III) complex [Cp*RuCl(μ-SH)$_2$RuCp*Cl] (**4**) determined by a preliminary X-ray diffraction study.

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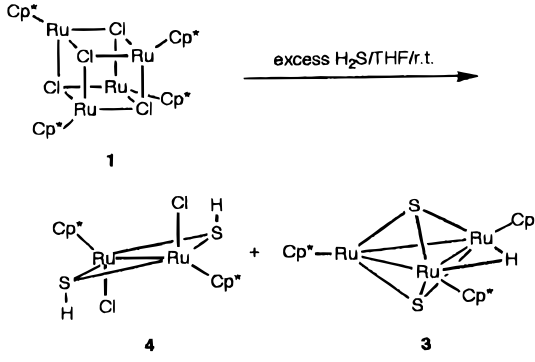
In this paper, we wish to report the details of the preparation and structure of this new hydrosulfido-bridged diruthenium complex **4** along with its reactions to give a cubane-type tetraruthenium sulfido cluster and a trimetallic $RhRu_2$ sulfido cluster. The X-ray structure of the thiolato-bridged diruthenium(III) complex $[Cp^*RuCl(\mu\text{-SEt})_2RuCp^*Cl]$ (**5a**) is also described in relation to that of **4**.

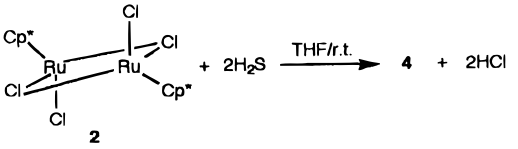
Results and Discussion

Preparation of $[Cp^*RuCl(\mu\text{-SH})_2RuCp^*Cl]$ (4). Previously we have found that the reaction of **1** with $(Me_3Si)_2S$ in THF at room temperature gives a mixture of the triruthenium sulfido clusters $[(Cp^*Ru)_3(\mu_3\text{-S})(\mu_3\text{-Cl})]$ and **3**.[4a] To confirm whether the hydrido ligand in **3** comes from the adventitious moisture in THF, we investigated the reaction of **1** with $(Me_3Si)_2S$ in the presence of either H_2O or D_2O. As expected, this led to the formation of **3** or its deuterido analog, and $[(Cp^*Ru)_3(\mu_3\text{-S})(\mu_3\text{-Cl})]$ was no longer observed in the reaction mixture. However, from this reaction another compound containing the Cp*Ru unit was also produced in moderate yield, which was subsequently characterized to be the hydrosulfido-bridged diruthenium complex **4** or its deuteriosulfido analog by the X-ray crystallography of **4** (vide infra). Since **4** seems to be formed by the reaction of **1** with H_2S generated in situ from $(Me_3Si)_2S$ and H_2O, the reaction of **1** with H_2S gas has been investigated.

When a suspension of **1** in THF was stirred for 15 h under an H_2S atmosphere at room temperature, both **3** and **4** were formed in an approximately 1:1 molar ratio. Evolution of H_2 gas accompanied by the formation of **4** from **1** and H_2S has been confirmed by the GLC analysis of the gaseous phase. Analytically pure **4** was isolated in 31% yield as dark brown crystals from the reaction mixture by fractional crystallization (eq 1). It has also been found that **4** can be prepared from **2** instead of **1** in 43% yield by analogous treatment of **2** with H_2S gas (eq 2).



(1)



(2)

Structure of 4. The structure of **4** has been unambiguously determined by a single-crystal X-ray analysis. The ORTEP drawing is shown in Figure 1, and the pertinent bond distances and angles are listed in Table 1.

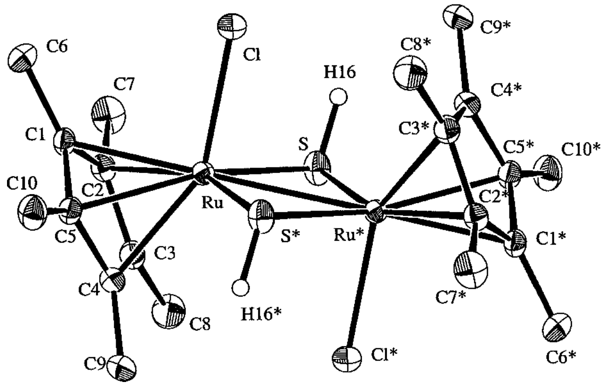


Figure 1. Molecular structure of **4** with atom-numbering scheme.

Table 1. Selected Bond Distances and Angles in 4 and 5a

Bond Distances (Å) in **4**			
Ru−Ru*	2.822(1)	Ru−Cl	2.441(2)
Ru−S	2.310(1)	Ru−S*	2.319(2)
Ru−C	2.197(5)−2.231(5)	S−H(16)	1.18
Bond Angles (deg) in **4**			
Ru*−Ru−Cl	88.34(4)	Ru*−Ru−S	52.58(4)
Ru*−Ru−S*	52.28(4)	Cl−Ru−S	89.09(6)
Cl−Ru−S*	88.89(6)	S−Ru−S*	104.86(5)
Ru−S−Ru	75.14(5)	Ru−S−H(16)	109.5
Ru*−S−H(16)	106.4		
Bond Distances (Å) in **5a**			
Ru(1)−Ru(2)	2.850(2)	Ru(1)−Cl(1)	2.424(4)
Ru(1)−S(1)	2.306(4)	Ru(1)−S(2)	2.324(4)
Ru(2)−Cl(2)	2.426(4)	Ru(2)−S(1)	2.321(4)
Ru(2)−S(2)	2.305(4)	Ru(1)−C	2.21(1)−2.31(1)
Ru(2)−C	2.18(1)−2.27(2)	S(1)−C(1)	1.79(1)
S(2)−C(3)	1.84(1)		
Bond Angles (deg) in **5a**			
Ru(2)−Ru(1)−Cl(1)	100.7(1)	Ru(2)−Ru(1)−S(1)	52.2(1)
Ru(2)−Ru(1)−S(2)	51.7(1)	Ru(1)−Ru(2)−Cl(2)	100.6(1)
Ru(1)−Ru(2)−S(1)	51.7(1)	Ru(1)−Ru(2)−S(2)	52.3(1)
S(1)−Ru(1)−S(2)	103.2(2)	S(1)−Ru(2)−S(2)	103.3(2)
Ru(1)−S(1)−Ru(2)	76.1(1)	Ru(1)−S(1)−C(1)	115.8(5)
Ru(2)−S(1)−C(1)	113.0(5)	Ru(1)−S(2)−Ru(2)	76.0(1)
Ru(1)−S(2)−C(3)	111.7(5)	Ru(2)−S(2)−C(3)	114.9(5)

The molecule consists of a crystallographically imposed inversion center at the midpoint of the Ru−Ru vector. The Ru−Ru distance of 2.822(1) Å suggests the presence of a Ru−Ru single bond and is comparable to those in the thiolato-bridged analogs $[Cp^*RuCl(\mu\text{-SR})_2RuCp^*Cl]$ (R = Et (**5a**; see below), Pr^i [13]) and the related thiolato-bridged complexes $[Cp^*RuR(\mu\text{-SPr}^i)_2RuCp^*R]$ (R = $C{\equiv}CC_6H_4Me$-*p* (Tol),[6f] CH_2CH_2Ph[14]) and $[Cp^*RuBr(\mu\text{-SPr}^i)_2RuCp^*(CH_2CH_2Ph)]$,[1a] which fall in the range 2.80−2.86 Å. This bonding interaction between the two Ru atoms accounts well for the diamagnetic nature of these complexes containing two Ru(III) centers. The plane defined by two Ru and two Cl atoms is almost perpendicular to the Ru_2S_2 plane, with a dihedral angle of 89.88(7)°. The other metrical parameters associated with the $Ru_2S_2Cl_2$ core are not unusual, and the position of the SH proton was located unequivocally in the final difference Fourier map. A significant difference in the structure of **4** from those of the thiolato-bridged complexes shown above is the mutually trans

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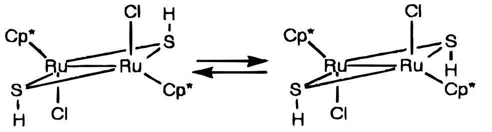
(14) Takahashi, A.; Mizobe, Y.; Tanase, T.; Hidai, M. *J. Organomet. Chem.* **1995**, *496*, 109.

configuration of the two Cp* ligands and the anti orientation of the two bridging SH ligands with respect to the Ru_2S_2 plane. In contrast, the thiolato complexes cited above generally contain mutually cis Cp* ligands together with syn-axial thiolato ligands with respect to the slightly puckered Ru_2S_2 ring.[15]

The IR spectrum of **4** shows a weak band at 2462 cm^{-1} characteristic of ν(SH), which shifts to 1792 cm^{-1} in the deuterio analog prepared from the reaction of **1** with $(Me_3Si)_2S/D_2O$ (see the Experimental Section). It is noteworthy that the ^1H NMR spectrum of **4** recorded for a $CDCl_3$ solution indicates the presence of two isomers in about 1:1 ratio in the solution state. One isomer exhibits one singlet Cp* resonance at 1.71 ppm with 30H intensity, while the other isomer shows two singlets at 1.68 and 1.74 ppm due to the Cp* ligand, both with 15H intensities. The SH protons in these isomers resonate at 5.11 and 5.13 ppm, each having 2H intensity. These ^1H NMR data may be interpreted in terms of the syn–anti isomerization associated with the bridging SH groups shown in eq 3. Such isomerization

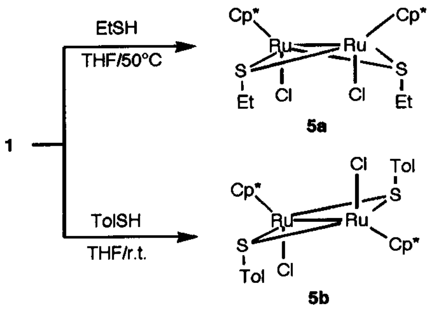


(3)

involving the sulfur inversion occurs ubiquitously in thiolato- or hydrosulfido-bridged complexes, which has been well documented already.[16] As for the related diruthenium complex [Cp*Ru(μ-SH)$_2$(μ-dppm)RuCp*] (dppm = $Ph_2PCH_2PPh_2$) prepared from the reaction of [Cp*Ru(μ-OMe)$_2$(μ-dppm)RuCp*] with H_2S, the presence of the syn and anti isomers in a 4:1 ratio in solution has been suggested from the ^1H NMR criteria.[17] Appearance of the SH resonances for **4** at unusually low field should be noteworthy, since the SH proton in transition-metal hydrosulfido complexes generally resonates in a much higher region, viz. a few ppm higher than TMS.[18]

Preparation of [Cp*RuCl(μ-SR)$_2$RuCp*Cl] (5) and X-ray Structure of 5a (R = Et). Treatment of **1** with excess EtSH in place of H_2S for 15 h in THF at 50 °C resulted in the formation of the Ru(III)/Ru(III) complex [Cp*RuCl(μ-SEt)$_2$RuCp*Cl] (**5a**), which was isolated as red-purple crystals in 51% yield. The reaction of **1** with TolSH in THF proceeded at room temperature, and the corresponding STol complex [Cp*RuCl(μ-STol)$_2$RuCp*Cl] (**5b**) was obtained as green crystals in 51% yield (Scheme 1). Complex **5a** was isolated previously from the reaction of **2** with Me$_3$SiSEt,[3,19] whereas **5b** was found to be available from the reaction of **1** with TolSSTol.[15] It is to be noted that the reaction of **2** with excess TolSH in CH_2Cl_2 results in the formation of the triply bridged diruthenium(III) complex [Cp*Ru(μ-STol)$_3$RuCp*]Cl.[3] Apart from the arenethiolato complex **5b** having the unexpected trans-anti structure,[15] it has been presumed that the diruthenium(III) complexes of this type containing two alkanethiolato bridges generally consist of mutually cis Cp* ligands and syn-axial thiolato groups (vide supra). However, full characterization of the complexes [Cp*RuX(μ-SR)$_2$RuCp*X] (R = alkyl, X = halide) by X-ray analysis has not yet been achieved. Now we have succeeded in preparing single crystals of **5a**, and therefore, an X-ray diffraction study has been undertaken.

Scheme 1



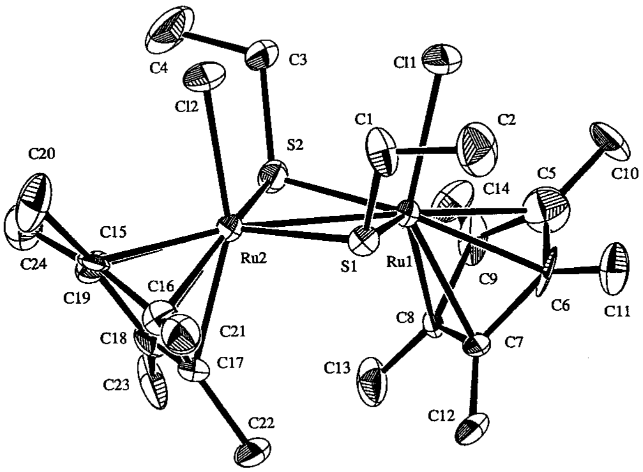


Figure 2. Molecular structure of **5a** with atom-numbering scheme.

The molecular structure of **5a** depicted in Figure 2 clearly shows that **5a** has mutually cis Cp* ligands and syn-axial SEt groups, as expected. Selected bond distances and angles are listed in Table 1. The Ru–Ru distance at 2.850(2) Å indicates the presence of a single bond between these two atoms, and the Ru_2S_2 ring is slightly puckered with a dihedral angle of 168.3(2)° around the Ru–Ru bond. Metrical parameters with respect to the $Ru_2S_2Cl_2$ core in **5a** are unexceptional, if compared with those in the other well-defined Ru(III)/Ru(III) complexes of this type.

Conversion of Diruthenium Complex 4 into the Cubane-Type Tetraruthenium Cluster [(Cp*Ru)$_4$(μ_3-S)$_4$]Cl$_2$ (6). When a solution of **4** in toluene was heated under reflux conditions for 7 h, the cubane-type tetraruthenium sulfido cluster **6** precipitated as a black solid. Concurrent formation of H_2 gas has been confirmed by the GLC study. After recrystallization from MeCN/ether, **6**·MeCN has been isolated as dark brown

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[15] The X-ray analysis of [Cp*RuCl(μ-STol)$_2$RuCp*Cl] (**5b**) has revealed quite recently that this complex has an unexpected trans-anti structure: Matsuzaka, H.; Ogino, T.; Hidai, M. Unpublished results.

[16] See, for example: Abel, E. W.; Bhargava, S. K.; Orrell, K. G. *Prog. Inorg. Chem.* **1984**, *32*, 1.

[17] Koelle, U.; Hörnig, A.; Englert, U. *J. Organomet. Chem.* **1992**, *438*, 309.

[18] An SH resonance at exceptionally low field was previously observed for, e.g. [(η^5-MeC$_5$H$_4$)$_2$Ti(SH)$_2$] (3.1 ppm): Ruffing, C. J.; Rauchfuss, T. B. *Organometallics* **1985**, *4*, 524.

[19] We have recently found that the mixture from the reaction of **2** with EtSH also contains **5a** together with uncharacterizable byproduct(s), which is in contrast to our previous result that **5a** was not available from the reaction of **2** with EtSH.[3]

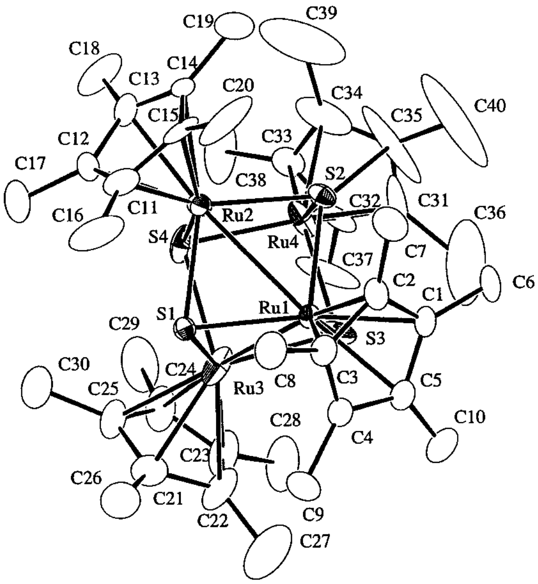


Figure 3. Structure of the cation in **6**·MeCN with atom-numbering scheme.

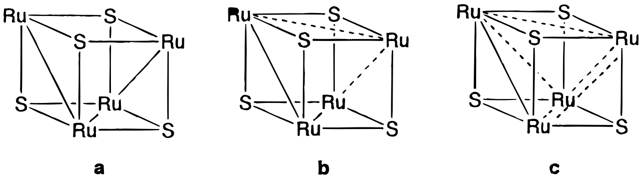
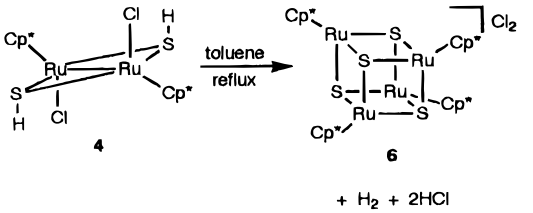


Figure 4. Bonding schemes in the $[(Cp'Ru)_4(\mu_3\text{-}S)_4]^{2+}$ cubane clusters: (a) **7**−**9**; (b) **6** in the solid state; (c) **6** in the solution state at −40 and −90 °C.

single crystals in 35% yield (eq 4),whose structure has



(4)

been established by the X-ray diffraction. The structure of the cation in **6** is shown in Figure 3, while the selected interatomic distances and angles are summarized in Table 2.

The chemistry of metal−sulfur cubane clusters is currently the subject of intense study, and a significant number of homo- and heterometallic clusters of this type are known.[20] For ruthenium, clusters of the type $[(Cp'Ru)_4(\mu_3\text{-}S)_4]^{n+}$ ($Cp' = \eta^5\text{-}C_5R_xH_{5-x}$, $n = 0, 2$) have already been prepared, and their structures have been determined in detail by Rauchfuss and his co-workers. Thus, the clusters $[\{(\eta^5\text{-}C_5H_4R)Ru\}_4(\mu_3\text{-}S)_4]$ (R = Me,[21] $SiMe_3$[21a]) have been synthesized by condensation of the monoruthenium complexes $[(\eta^5\text{-}C_5H_4R)Ru(PPh_3)_2(SH)]$, while $[(Cp^*Ru)_4(\mu_3\text{-}S)_4]$[5] has been obtained by treatment of **1** with NaSH. Cationic cubane clusters analogous to **6** have also been isolated: $[(Cp^*Ru)_4(\mu_3\text{-}S)_4][PF_6]_2$[5] and $[\{(\eta^5\text{-}C_5H_4R)Ru\}_4(\mu_3\text{-}S)_4]^{2+}$ (**7**, R = Me;[21a,22] **8**, R = $SiMe_3$[21a]) by oxidation of the corresponding neutral clusters and $[(CpRu)_2(Cp^*Ru)_2(\mu_3\text{-}S)_4]^{2+}$ (**9**)[23] from the reaction of $[(Cp^*Ru)_2S_4]$ with 2 molar equiv of $[CpRu(MeCN)_3]^+$. Reduction of **9** afforded another well-defined neutral cluster, $[(CpRu)_2(Cp^*Ru)_2(\mu_3\text{-}S)_4]$.[23]

For the cationic cubane clusters, X-ray structures are available for **7**−**9**. These 66-electron clusters are all isostructural with respect to the Ru_4 tetrahedron containing the three relatively short Ru−Ru edges along with the three much longer Ru−Ru edges. The former, at ca. 2.8 Å, is diagnostic of a bonding contact, while the latter, at ca. 3.5 Å or more, is indicative of the absence of any bonding interaction (Figure 4a). The presence of three metal−metal bonds in these clusters corresponds well to the structure expected for an electron count of 66 from a simple EAN rule count. In contrast, as illustrated in Figure 4b, the Ru_4 tetrahedron in **6** consists of only two bonding Ru−Ru contacts (Ru(1)−Ru(2), 2.858(1) Å; Ru(1)−Ru(3), 2.849(1) Å). As for the remaining four Ru−Ru edges, two are apparently nonbonding Ru···Ru contacts (Ru(2)···Ru(3), 3.46 Å; Ru(1)···Ru(4), 3.47 Å) and the other two are significantly shorter than these two (Ru(2)···Ru(4), 3.25 Å; Ru(3)···Ru(4), 3.22 Å).

Table 2. Selected Interatomic Distances and Angles in 6·MeCN

Interatomic Distances (Å)			
Ru(1)−Ru(2)	2.858(1)	Ru(1)−Ru(3)	2.849(1)
Ru(1)−S(1)	2.269(2)	Ru(1)−S(2)	2.333(3)
Ru(1)−S(3)	2.329(3)	Ru(2)−S(1)	2.302(3)
Ru(2)−S(2)	2.265(3)	Ru(2)−S(4)	2.333(3)
Ru(3)−S(1)	2.303(2)	Ru(3)−S(3)	2.258(3)
Ru(3)−S(4)	2.358(3)	Ru(4)−S(2)	2.300(2)
Ru(4)−S(3)	2.293(3)	Ru(4)−S(4)	2.262(3)
Ru(1)−C	2.232(8)−2.287(9)	Ru(2)−C	2.170(9)−2.28(1)
Ru(3)−C	2.193(8)−2.28(1)	Ru(4)−C	2.16(1)−2.238(9)
Ru(1)···Ru(4)	3.47	Ru(2)···Ru(3)	3.46
Ru(2)···Ru(4)	3.25	Ru(3)···Ru(4)	3.22

Interatomic Angles (deg)			
S(1)−Ru(1)−S(2)	101.31(9)	S(1)−Ru(1)−S(3)	101.57(9)
S(2)−Ru(1)−S(4)	78.08(9)	S(1)−Ru(2)−S(2)	102.43(9)
S(1)−Ru(2)−S(4)	79.59(9)	S(2)−Ru(2)−S(4)	88.82(9)
S(1)−Ru(3)−S(3)	102.71(9)	S(1)−Ru(3)−S(4)	79.05(9)
S(3)−Ru(3)−S(4)	89.50(10)	S(2)−Ru(4)−S(3)	79.48(9)
S(2)−Ru(4)−S(4)	89.72(9)	S(3)−Ru(4)−S(4)	91.04(10)
Ru(1)−S(1)−Ru(2)	77.40(7)	Ru(1)−S(1)−Ru(3)	77.09(7)
Ru(2)−S(1)−Ru(3)	97.50(9)	Ru(1)−S(2)−Ru(2)	76.84(8)
Ru(1)−S(2)−Ru(4)	96.96(9)	Ru(2)−S(2)−Ru(4)	90.67(9)
Ru(1)−S(3)−Ru(3)	76.78(8)	Ru(1)−S(3)−Ru(4)	97.27(10)
Ru(3)−S(3)−Ru(4)	89.9(1)	Ru(2)−S(4)−Ru(3)	95.12(10)
Ru(2)−S(4)−Ru(4)	89.88(10)	Ru(3)−S(4)−Ru(4)	88.22(9)

Mobility of the metal−metal bonds in the mixed-valence cubane-type clusters has recently been demonstrated well for the formal $Ru^{III}_2Ru^{IV}_2$ clusters **7**,[21a,22] **8**,[21a] and **9**[23] as well as the $Ir^{III}_2Ir^{IV}_2$ cluster $[(Cp^*Ir)_4(\mu_3\text{-}S)_4]^{2+}$.[24] Also for **6**, with a formal $Ru^{III}_2Ru^{IV}_2$ core, the ^1H NMR spectrum in $CDCl_3$ recorded at room temperature exhibits one sharp singlet at 1.88 ppm due to the Cp* ligands, indicating that all Cp*Ru sites are equivalent under these conditions. This indicates that rapid migration of the metal−metal bonds in **6** is occurring in solution. When the temperature was lowered, this sharp singlet separated into two broad singlets. Thus, the spectra recorded at −40 and −55 °C in $CDCl_3$ and at −90 °C in CD_2Cl_2 all showed two

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[21] (a) Houser, E. J.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1993**, *32*, 4069. (b) Amarasekera, J.; Rauchfuss, T. B.; Wilson, S. R. *J. Chem. Soc., Chem. Commun.* **1989**, 14.

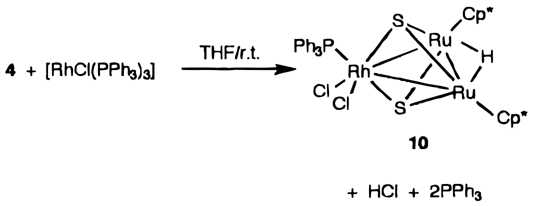
[22] Houser, E. J.; Amarasekera, J.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 7440.

[23] Feng, Q.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1995**, *117*, 4702.

[24] Venturelli, A.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1994**, *116*, 4824.

broad signals at 1.75 and 1.90 ppm with almost the same intensities. This finding is not consistent with a solid structure having three types of Cp*Ru units (Figure 4b) and probably suggests that cluster **6** has the structure shown in Figure 4c, containing only one relatively rigid Ru−Ru bond as a transient, at least in this temperature region, although the details are still uncertain. This difference in the structure of the Ru_4 core observed for **6** from the other cationic Ru_4S_4 cubanes presumably arises from the steric repulsion between the four Cp* ligands in **6**, which may be significantly greater than that in **7** and **8**, containing the monosubstituted cyclopentadienyl ligands exclusively, and in **9**, having two nonsubstituted Cp ligands and two Cp* ligands. It should be noted that the repulsive interactions between the Cp* ligands have previously been invoked to account for the Ru−Ru bonding distances observed in the selenide cubane cluster $[(Cp^*Ru)_4(\mu_3\text{-Se})_4]$ being longer than those in the telluride cluster $[\{(MeC_5H_4)Ru\}_4(\mu_3\text{-Te})_4]$, despite the fact that the Ru−Se distances are shorter than the Ru−Te distances by ca. 8%, owing to the chalcogen sizes.[5]

Preparation and X-ray Structure of the Triangular $RhRu_2$ Sulfido Cluster $[(Cp^*Ru)_2(\mu_2\text{-H})(\mu_3\text{-S})_2RhCl_2(PPh_3)]$ (10). Oxidative addition of an S−H bond to a low-valent transition-metal center is one of the general methods of preparing thiolato or hydrosulfido complexes. Reactions of certain low-valent noble-metal complexes with **4** containing bridging SH groups have therefore been investigated to synthesize new mixed-metal sulfido clusters. Now we have found that the reaction of 2 molar equiv of $[RhCl(PPh_3)_3]$ (**11**) with **4** readily affords a triangular $RhRu_2$ cluster with two capped sulfido ligands, **10**, in moderate yield (eq 5),whose structure has been verified by an X-ray diffraction study using a single crystal of **10**·THF. From the reaction of a stoichiometric amount of **11** with **4**, a mixture of several products, including **10**, was obtained; however, isolation of **10** from this mixture in a pure form was unsucessful. Oxidative addition of H_2S to **11** has previously been demonstrated to give the dirhodium complex $[RhCl(H)(\mu\text{-SH})(PPh_3)_2]_2$.[25]



(5)

An ORTEP drawing of **10** is shown in Figure 5, and selected bond distances and angles are collected in Table 3. Cluster **10** has a triangular $RhRu_2$ core, for which two Rh−Ru distances at 2.790(3) and 2.756(3) Å as well as the Ru−Ru distance at 2.707(3) Å are all consistent with the metal−metal bond order of unity. This core structure is diagnostic of the diamagnetic nature of **10**, containing one Rh(III) and two Ru(III) centers. The $RhRu_2$ plane is capped from both sides by the μ_3-sulfido ligands almost symmetrically, but the M−S bond lengths are all somewhat shorter for S(2) than for S(1). Neglecting the two Rh−Ru bonds, the geometry around the Rh atom is trigonal bipyramidal with the P and S(1) atoms in two apical positions. The Rh−Cl, Rh−S, and Rh−P bond distances are all unexceptional. Two Cp* ligands bind to two Ru atoms, where both Cp* planes are almost perpendicular to the $RhRu_2$ plane. In addition to the triruthenium cluster **3**, the *closo* trirhodium cluster with two μ_3-sulfido ligands $[(Cp^*Rh)_3(\mu_3\text{-S})_2]^{2+}$ has been reported recently.[26] However, to our knowledge, the $RhRu_2(\mu_3\text{-S})_2$ core observed for **10** is unprecedented.

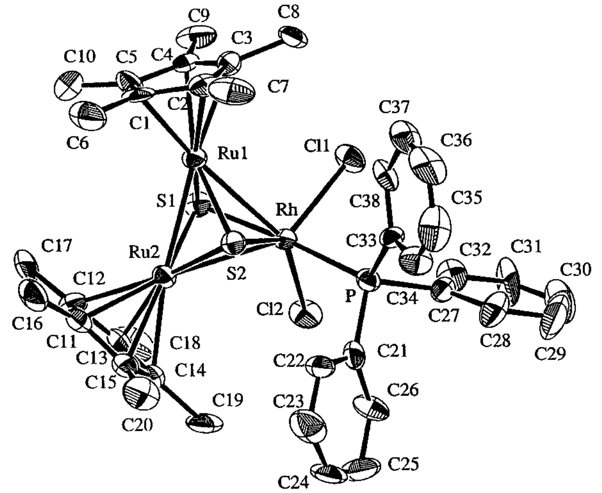


Figure 5. Molecular structure of **10** with atom-numbering scheme. The solvating THF molecule is omitted for clarity.

Table 3. Selected Bond Distances and Angles in 10

Bond Distances (Å)

Rh−Ru(1)	2.790(3)	Rh−Ru(2)	2.756(3)
Rh−Cl(1)	2.435(6)	Rh−Cl(2)	2.420(6)
Rh−S(1)	2.301(6)	Rh−S(2)	2.256(6)
Rh−P	2.320(7)	Ru(1)−Ru(2)	2.707(3)
Ru(1)−S(1)	2.276(7)	Ru(1)−S(2)	2.259(6)
Ru(2)−S(1)	2.291(6)	Ru(2)−S(2)	2.279(6)
Ru(1)−C	2.17(3)−2.24(3)	Ru(2)−C	2.15(2)−2.26(3)

Bond Angles (deg)

Ru(1)−Rh−Ru(2)	58.43(7)	Cl(1)−Rh−Cl(2)	95.9(2)
Cl(1)−Rh−S(1)	92.8(2)	Cl(1)−Rh−S(2)	129.9(2)
Cl(1)−Rh−P	91.4(2)	Cl(2)−Rh−S(1)	91.7(2)
Cl(2)−Rh−S(2)	133.8(2)	Cl(2)−Rh−P	88.1(2)
S(1)−Rh−S(2)	91.4(2)	S(1)−Rh−P	175.8(2)
S(2)−Rh−P	85.6(2)		
Rh−Ru(1)−Ru(2)	60.15(7)	Rh−Ru(1)−S(1)	52.8(2)
Rh−Ru(1)−S(2)	51.8(2)	Ru(2)−Ru(1)−S(1)	53.9(2)
Ru(2)−Ru(1)−S(2)	53.7(2)	S(1)−Ru(1)−S(2)	92.0(2)
Rh−Ru(2)−Ru(1)	61.42(6)	Rh−Ru(2)−S(1)	53.3(2)
Rh−Ru(2)−S(2)	52.2(1)	Ru(1)−Ru(2)−S(1)	53.4(2)
Ru(1)−Ru(2)−S(2)	53.1(2)	S(1)−Ru(2)−S(2)	53.1(2)

In the ^1H NMR spectrum of **10**, the resonance due to the Cp* methyl protons appeared as one singlet, indicating the equivalent nature of the two Cp* ligands. This is in accordance with the solid-state structure having a mirror plane that bisects the Ru−Ru bond. The ^1H NMR spectrum has also demonstrated the presence of one hydrido ligand in **10**. Although the position of the hydrido ligand could not be located by X-ray crystallography, the singlet nature of the hydrido resonance as well as the equivalence of the two Cp*Ru units

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(25) Mueting, A. M.; Boyle, P.; Pignolet, L. H. *Inorg. Chem.* **1984**, *23*, 44.

(26) Nishioka, T.; Isobe, K. *Chem. Lett.* **1994**, 1661. The related Rh(III) cluster $[Rh_3(\mu_3\text{-S})_2(\mu_2\text{-S})(\mu_2\text{-Cl})_2(PEt_3)_6]^+$ is also known, which contains a $Rh_3(\mu_3\text{-S})_2$ core without direct Rh−Rh interactions.[27]

(27) Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Orlandini, A.; Vacca, A.; Ramirez, J. A. *Inorg. Chim. Acta* **1989**, *155*, 5.

Table 4. X-ray Crystallographic Data for 4, 5a, 6·MeCN, and 10·THF

	4	**5a**	**6**·MeCN	**10**·THF
(a) Crystal Data				
formula	$C_{20}H_{32}Cl_2S_2Ru_2$	$C_{24}H_{40}Cl_2S_2Ru_2$	$C_{42}H_{63}NCl_2S_4Ru_4$	$C_{42}H_{54}OCl_2PS_2RhRu_2$
fw	609.6	665.8	1185.4	1045.9
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/a$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
cryst color	dark brown	dark brown	dark brown	dark brown
cryst dimens, mm	0.2 × 0.3 × 0.4	0.1 × 0.3 × 0.9	0.3 × 0.3 × 0.5	0.15 × 0.15 × 0.25
a, Å	9.466(1)	11.192(4)	12.146(2)	18.910(4)
b, Å	13.985(1)	15.448(4)	26.166(6)	10.860(5)
c, Å	9.589(1)	8.707(3)	14.840(2)	21.775(3)
α, deg	90.00	106.32(3)	90.00	90.00
β, deg	116.33(1)	112.88(3)	101.41(1)	97.86(1)
γ, deg	90.00	80.84(3)	90.00	90.00
V, Å^3	1137.8(3)	1328.9(9)	4623(1)	4429(2)
Z	2	2	4	4
D_{calc}, g cm^{-3}	1.779	1.664	1.703	1.568
F(000), e	612	676	2384	2180
μ(Mo Kα), cm^{-1}	17.49	15.05	16.08	13.22
(b) Data Collection				
diffractometer	Rigaku AFC7R			
monochromator	graphite			
radiation (λ, Å)	Mo Kα (0.7107)			
temp	room temp			
scan type	$\omega-2\theta$			
scan rate, deg min^{-1}	16.0			
$2\theta_{max}$, deg	55.0	55.0	55.0	50.0
rflns measd	$+h,+k,\pm l$	$+h,\pm k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$
no. of unique rflns	2720	6112	10 888	6846
transmissn factors	0.790−1.00	0.555−1.00	0.832−1.00	0.801−1.00
(c) Solution and Refinements				
no. of data used ($I > 3.0\sigma(I)$)	2252	3610	5584	2912
no. of variables	118	271	478	460
R	0.029	0.068	0.060	0.067
R_w	0.042	0.058	0.035	0.062
max residual, e Å^{-3}	0.92	2.1	2.0	1.4

suggests that the hydrido ligand bridges the Ru−Ru bond. The chemical shift observed for this hydride is comparable to that in the sulfido-capped triruthenium cluster **3**[4a] (**10**, δ −22.2; **3**, δ −22.3), although the Ru−Ru bond supported by the hydride bridge in **10** (2.707(3) Å) is considerably shorter than that in **3** (2.851(3) Å).

Experimental Section

General Considerations. All manipulations were carried out under an atmosphere of nitrogen by the use of Schlenk techniques. Solvents were dried by common procedures and degassed before use. IR and ^{1}H NMR spectra were recorded on Shimadzu FTIR-8100M and JEOL EX-270 spectrometers, respectively. Evolution of H_2 gas has been verified by GLC analysis using a Shimadzu GC-8A gas chromatograph equipped with a Molecular Sieve 13X column. Elemental analyses were done with a Perkin-Elmer 2400II CHN analyzer. Complexes **1**,[28] **2**,[29] and **11**[30] were prepared according to the literature methods, while organic and inorganic reagents were used as received. The yields of the compounds below have been calculated by (mol of Ru in the product)/(mol of Ru charged).

Preparation of [Cp*RuCl(μ-SH)$_2$RuCp*Cl] (4). (a) Hydrogen sulfide gas was passed through a suspension of **1** (110 mg, 0.101 mmol) in THF (10 mL) for 5 min, and the mixture was continuously stirred for 15 h at room temperature under H_2S. The GLC analysis of the gaseous phase revealed the evolution of H_2 gas during the reaction. From the resulting mixture all the volatile materials were removed in vacuo. The ^{1}H NMR spectrum of the residue revealed the presence of **4** and **3** as the major products in a ca. 1:1 molar ratio. The residue was extracted with THF (20 mL), and the extract was concentrated. Addition of hexane (10 mL) yielded **4** as dark brown crystals (38 mg, 31%). ^{1}H NMR ($CDCl_3$): δ 1.68 (s, 15H, Cp*), 1.71 (s, 30H, Cp*), 1.74 (s, 15H, Cp*), 5.11 (s, 2H, SH), 5.13 (s, 2H, SH). IR (KBr): ν(SH) 2462 cm^{-1} (w). Anal. Calcd for $C_{20}H_{32}S_2Ru_2$: C, 39.40; H, 5.29. Found: C, 39.04; H, 5.23.

(b) After H_2S gas was bubbled through a suspension of **2** (434 mg, 0.706 mmol) in THF (30 mL) for 5 min, the mixture was stirred for 15 h at room temperature under H_2S. The mixture was dried in vacuo, and the residue was extracted with benzene (50 mL). Addition of hexane (30 mL) to the concentrated extract afforded **4** as dark brown crystals (186 mg, 43%).

Preparation of the Deuterio Analog of 4. To a suspension of **1** (98.3 mg, 0.0905 mmol) in THF (10 mL) was added D_2O (4.8 μL, 0.24 mmol) and $(Me_3Si)_2S$ (51 μL, 0.24 mmol), and the mixture was stirred for 15 h at room temperature. The resulting mixture was evaporated to dryness in vacuo, and the residue was extracted with THF (20 mL). Addition of hexane to the concentrated filtrate gave the product as dark brown crystals (45.1 mg, 41%). IR and ^{1}H NMR spectra have shown that the product contains the SD and SH groups in an approximately 1:1 ratio. IR (KBr): ν(SH) 2462 (w); ν(SD) 1792 cm^{-1} (w). ^{1}H NMR ($CDCl_3$): δ 1.68 (s, 15H, Cp*), 1.71 (s, 30H, Cp*), 1.74 (s, 15H, Cp*), 5.11 (s, 1H, SH), 5.13 (s, 1H, SH).

Preparation of [Cp*RuCl(μ-SEt)$_2$RuCp*Cl] (5a). To a suspension of **1** (127 mg, 0.117 mmol) in THF (5 mL) was added EtSH (150 μL, 2.88 mmol), and the mixture was stirred at 50 °C for 15 h. The resultant red-purple suspension was filtered and hexane (10 mL) was added to the filtrate, giving **5a** as red-purple crystals (79 mg, 51%). The product was characterized by comparing its ^{1}H NMR spectrum with that of the authentic compound.[3a]

Preparation of [Cp*RuCl(μ-STol)$_2$RuCp*Cl] (5b). A suspension containing **1** (121 mg, 0.111 mmol) and TolSH (55

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mg, 0.44 mmol) in THF (7 mL) was stirred for 15 h at room temperature. The green suspension obtained was filtered off, and the remaining green solid was crystallized from CH_2Cl_2/hexane (3 mL/10 mL); yield 81 mg (51%). The ^1H NMR spectrum was identical with that of the authentic compound, which was fully characterized by an X-ray diffraction study.[15]

Preparation of $[(Cp^*Ru)_4(\mu_3\text{-}S)_4]Cl_2\cdot MeCN$ (6·MeCN). A yellow-brown solution of **4** (66 mg, 0.11 mmol) in toluene (20 mL) was heated at reflux for 7 h. The black solid that deposited was filtered off and recrystallized from MeCN/ether (5 mL/10 mL), affording **6**·MeCN as dark brown crystals (22 mg, 35%). ^1H NMR ($CDCl_3$, room temperature): δ 1.88 (s, 60H, Cp*); see also the test. Anal. Calcd for $C_{42}H_{63}NS_4Cl_2Ru_4$: C, 42.56; H, 5.36; N, 1.18. Found: C, 42.90; H, 5.50; N, 0.80.

Preparation of $[(Cp^*Ru)_2(\mu_2\text{-}H)(\mu_3\text{-}S)_2RhCl_2(PPh_3)]\cdot THF$ (10·THF). A solution containing **4** (22 mg, 0.036 mmol) and **11** (67 mg, 0.072 mmol) in THF (15 mL) was stirred at room temperature for 15 h, and the resultant red solution was filtered. Addition of hexane (10 mL) to the concentrated filtrate afforded **10**·THF as dark brown crystals (29 mg, 76%). ^1H NMR (C_6D_6): δ 1.62 (s, 30H, Cp*), 6.5−7.5 (m, 15H, PPh), 1.45 and 3.60 (m, 4H each, THF), −22.2 (s, 1H, RuHRu). Anal. Calcd for $C_{42}H_{54}OS_2Cl_2Ru_2Rh$: C, 48.23; H, 5.20. Found: C, 48.23; H, 5.24. The presence of both Ru and Rh in **10** has been confirmed by electron-probe microanalysis (EPMA) using a Kevex μX 7000 energy dispersive type X-ray analyzer.

X-ray Diffraction Studies. Single crystals of **4**, **5a**, **6**·MeCN, and **10**·THF prepared as described above were sealed in glass capillaries under N_2 and transferred to a Rigaku AFC7R diffractometer equipped with a graphite-monochromatized Mo Kα source. Diffraction studies were carried out at room temperature. Orientation matrices and unit cell parameters were determined by least-squares treatment of 25 reflections with $35 < 2\theta < 40°$. The intensities of 3 check reflections were monitored every 150 reflections during data collection, which revealed no significant decay for all crystals. Intensity data were corrected for Lorentz and polarization effects and for absorption (ψ scans). Details of crystal and data collection parameters are summarized in Table 4.

Structure solution and refinements were carried out by using the teXsan program package.[31] The positions of the non-hydrogen atoms were determined by Patterson methods and subsequent Fourier syntheses (DIRDIF PATTY),[32] which were refined anisotropically by full-matrix least-squares techniques. The hydrogen atom of the SH group in **4** was found in the final difference Fourier map, while all other hydrogen atoms were placed at calculated positions, except for those in the solvating THF for **10**·THF, which were included in the final stages of refinements with fixed parameters.

Acknowledgment. Financial support by the Ministry of Education, Science, and Culture of Japan is appreciated.

Supporting Information Available: Tables containing atom coordinates, anisotropic temperature factors of non-hydrogen atoms, and extensive bond distances and angles and figures giving the full views, including hydrogen atoms, for **4**, **5a**, **6**·MeCN, and **10**·THF (30 pages). Ordering information is given on any current masthead page.

OM960193S

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(31) teXsan: Crystal Structure Analysis Package, Molecular Structure Corp. (1985 and 1992).

(32) PATTY: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF Program System; Technical Report of the Crystallography Laboratory; University of Nijmegen, Nijmegen, The Netherlands, 1992.