1360 *Inorg. Chem.* **1997**, *36*, 1360−1365

Sulfido−Persulfido Equilibria in Sulfur-Rich Metal Clusters: The Case of $(C_5Me_5)_3RhRu_2S_4{}^{2+}$

Anne Venturelli, Thomas B. Rauchfuss,* and Atul K. Verma

School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

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The reaction of $[(C_5Me_5)M(MeCN)_3](PF_6)_2$ with $(C_5Me_5)_2Ru_2S_4$ gives the cluster compounds $[(C_5Me_5)_3MRu_2S_4(MeCN)](PF_6)_2$, **1**$(PF_6)_2$ (M = Rh) and **3**$(PF_6)_2$ (M = Ir). Crystallographic studies of **1**$(PF_6)_2$ show that the dication consists of an asymmetric $RhRu_2S_4$ core containing an isosceles triangle of metal atoms with a Ru−Ru bond of 2.88 Å. The three metal atoms are joined by two μ_3-η^1:η^2:η^1−S_2 units, each persulfide being monodentate toward Rh. NMR studies show that $\mathbf{1}^{2+}$ is stereochemically nonrigid such that the two $Ru(C_5\mathit{Me}_5)$ resonances coalesce at higher temperatures. The dynamic processes involving $\mathbf{1}^{2+}$ are unaffected by added $(C_5Me_5)Rh(MeCN)_3{}^{2+}$, ruling out dissociation of the $(C_5Me_5)Rh$ center. Exchange of the $(C_5Me_5)Ru$ sites in $[(C_5Me_5)_2(C_5Me_4Et)RhRu_2S_4(MeCN)](PF_6)_2$, **2**$(PF_6)_2$, is associated with coalescence of the pairs of $C_5\mathit{Me}_4Et$ resonances, suggesting that the dynamics in $\mathbf{1}^{2+}$ involve racemization. It is proposed that these dynamics proceed via the "base-free" intermediate $[(C_5Me_5)_3RhRu_2S_4]^{2+}$, wherein one S−S bond has been cleaved. Solutions of $\mathbf{1}^{2+}$ react with acetone to give the *S*-acetonyl derivative $[(C_5Me_5)_3RhRu_2S_3(SCH_2COCH_3)]PF_6$, **4**$(PF_6)$. This species, which is not fluxional on the NMR time scale, is a rare example of a metal sulfido cluster with a trigonal prismatic M_3S_3 core. There is one metal−metal bond of 2.75 Å between the two Ru atoms, spanned by the acetonylthio ligand. The M−S distances are nearly equivalent at 2.33 Å while the S−S bonding distance is 2.12 Å. This reaction is reversed by acid to give $\mathbf{1}^{2+}$ and acetone.

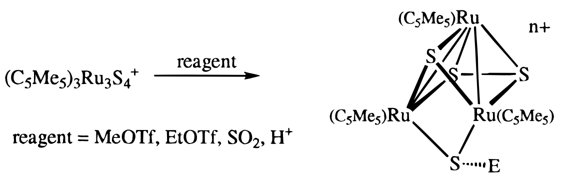
Introduction

We wish to report synthetic and structural studies on some M_3S_4 clusters that implicate the reversible breaking of S−S bonds. This process is not well precedented for metal sulfides although the irreversible scission of S−S bonds is of obvious relevance to the formation of metal sulfides from elemental sulfur. The corresponding reversible cleavage of O−O bonds in Cu_2O_2 complexes was discussed recently.[1]

Sulfido clusters where the S:M ratio exceeds unity can be described as sulfur-rich. For the late transition metals, sulfur-rich compounds feature S−S bonds, while, for earlier metals this is typically not the case since the early metals exist in higher oxidation states. This pattern borne out in solid state chemistry, where, for example, the structures of the metal disulfides, $M^{IV}(S^{2-})_2$ vs $M^{II}(S_2{}^{2-})$, can be explained in terms of the ionization potentials of the metals.[2] Early metals have low ionization potentials such that the d electrons of these metals lie above the S−S σ* energy; thus the S−S σ* levels are occupied, leading to S^{2-} and relatively oxidized metals centers. Conversely, the d electrons of later transition metal compounds are lower in energy and the S−S σ* levels remain unoccupied, viz. the persulfido centers of pyrite and marcasite. While these patterns are well established for minerals and related inorganic materials, the corresponding patterns for discrete clusters have received little attention. Through judicious selection of coligands, one should be able to design molecules where the M d levels and the S−S σ* levels are close, opening the way for highly reactive or bistable clusters.

The simplest family of sulfur-rich clusters has the core stoichiometry M_3S_4.[3] Clusters of this type are common for molybdenum. Mo_3S_4 clusters have been studied for several years,[4] and the area continues to be a fruitful one.[5] The M_3S_4 core of these species, typified by $Mo_3S_4(H_2O)_9{}^{4+}$, possesses idealized C_{3v} symmetry, consisting of three doubly bridging sulfido centers and one triply bridging sulfur atom. The M_3S_4 clusters of the late transition metals have been examined only for the case of Fe−S−SR systems. $Fe_3S_4(SR)_3$ clusters have been identified in nature and, recently, were stabilized in a protein-free environment.[6] The Fe centers in these species are high spin, indicative of the unimportance of the metal−metal bonding.

We recently described the 50 e^- cluster $(C_5Me_5)_3Ru_3S_4{}^+$ as well as some of its adducts (eq 1).[7] Crystallographic studies on salts of $(C_5Me_5)_3Ru_3S_4{\cdot}SO_2{}^+$ and $(C_5Me_5)_3Ru_3S_3(SEt)^{2+}$ established a persulfide-containing trimetal cluster with an unusual trigonal prismatic M_3S_3 core. Additionally, the persulfide ligands display unsually long S−S distances of ∼2.3 Å. The structure of $(C_5Me_5)_3Ru_3S_4{}^+$, be it a bis(persulfido) or



(1)

[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1997.

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(3) In this discussion, we define clusters as consisting of triangular arrays of metals. There are, however, a number of M_3S_4 species where the metals are collinear, an example being the tetrathiomolybdate derivative $MoS_4[Ru(C_5H_5)(PPh_3)]_2$ (Howard, K. E.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1988**, *27*, 1710).

(4) Shibahara, T. *Coord. Chem. Rev.* **1993**, *123*, 73.

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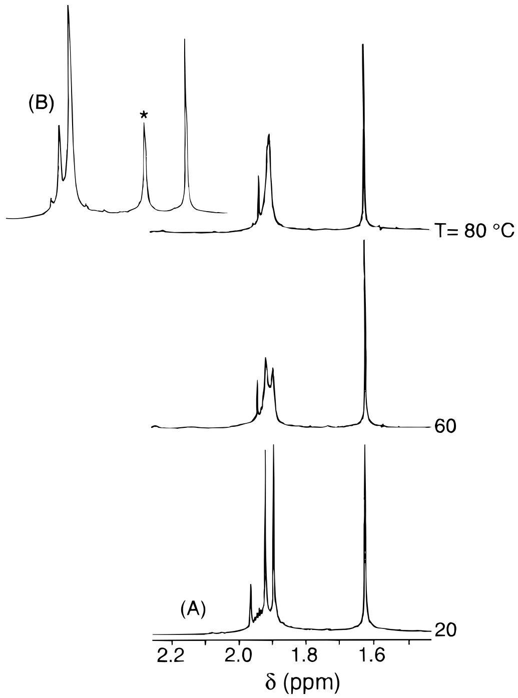
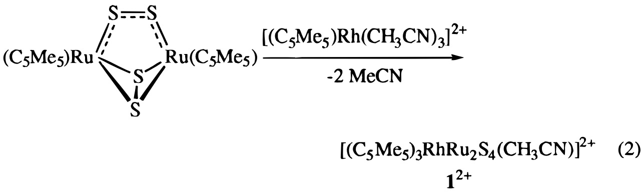


Figure 1. (A) Variable-temperature 400 MHz ^{1}H NMR spectra of $[(C_5Me_5)_3RhRu_2S_4(MeCN)](PF_6)_2$ (CD_3CN solution). (B) ^{1}H NMR spectrum of $[(C_5Me_5)_3RhRu_2S_4(MeCN)](PF_6)_2$ with added $(C_5Me_5)Rh(MeCN)_3{}^{2+}$ (C_5Me_5 indicated by *) (CD_3CN solution, 80 °C).

a disulfido–persulfido species, remains uncertain. In the present report, we describe the synthesis of related 52 e^- M_3S_4 clusters.

Results

Synthesis of $[(C_5Me_5)_3RhRu_2S_4(MeCN)]^{2+}$. Addition of yellow $[(C_5Me_5)Rh(MeCN)_3](PF_6)_2$[8] to a blue THF solution of $(C_5Me_5)_2Ru_2S_4$ results in the immediate formation of a red-brown solution. After recrystallization from MeCN–Et_2O, a product analyzing as $[(C_5Me_5)_3RhRu_2S_4(MeCN)](PF_6)_2$, **1**$(PF_6)_2$, was obtained in 85% yield (eq 2). The room-temperature ^{1}H NMR spectrum of a CD_3CN solution of $\mathbf{1}^{2+}$ consists of three equally intense singlets, showing that the three $(C_5Me_5)M$ centers are nonequivalent. An additional peak at δ 1.97 corresponds to $C\mathit{H}_3CN$, with one-fifth of the intensity of the $C_5\mathit{Me}_5$ peaks. We initially attributed this acetonitrile peak to an impurity; however, attempts to remove the MeCN by heating the solid in vacuo resulted in decomposition of the sample. We conclude that exchange between coordinated and bulk MeCN occurs in the time needed to prepare the NMR sample.



(2)

Variable-temperature ^{1}H NMR measurements revealed that $\mathbf{1}^{2+}$ is stereochemically nonrigid. At 85 °C, the signals at δ 1.92 and 1.90 coalesce into a singlet at δ 1.91 as a consequence of a dynamic process that interchanges the two $(C_5Me_5)Ru$ sites (Figure 1). A DNMR experiment was conducted on a solution containing both $[(C_5Me_5)Rh(MeCN)_3]^{2+}$ and $\mathbf{1}^{2+}$. At temperatures where the $(C_5\mathit{Me}_5)Ru$ singlets coalesce, the $[(C_5Me_5)Rh(MeCN)_3]^{2+}$ signal at δ 1.72 remains unchanged.

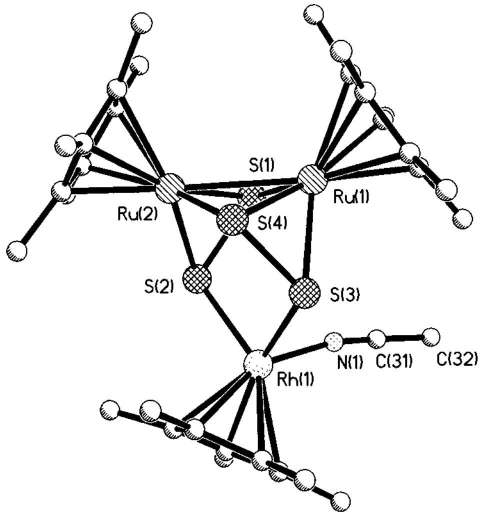


Figure 2. Structure of the dication in $[(C_5Me_5)_3RhRu_2S_4(MeCN)](SbF_6)_2$ (**1**$(SbF_6)_2$). Hydrogen atoms are omitted for clarity.

Table 1. Selected Bonding and Nonbonding Distances (Å) for $[(C_5Me_5)_3RhRu_2S_4(MeCN)](SbF_6)_2$ (**1**$(SbF_6)_2$)

Ru1–Ru2	2.884(1)	Ru1···Rh1	3.963(1)
Ru2···Rh1	4.025(1)	S1–S2	2.082(3)
S1···S3	3.482(3)	S1···S4	3.016(2)
S2···S3	3.315(3)	S2···S4	3.464(3)
S3–S4	2.099(3)	Rh1···S1	3.637(2)
Rh1–S2	2.346(2)	Rh1–S3	2.393(2)
Rh1···S4	3.707(2)	Ru1–S1	2.247(2)
Ru1···S2	3.520(2)	Ru1–S3	2.393(2)
Ru1–S4	2.340(2)	Ru2–S1	2.330(2)
Ru2–S2	2.381(2)	Ru2···S3	3.550(2)
Ru2–S4	2.258(2)	Rh1–N1	2.085(8)
C31–C32	1.451(14)	N1–C31	1.131(12)

The $^{13}C\{^1H\}$ NMR spectrum of $\mathbf{1}^{2+}$ is also consistent with an unsymmetrical cluster. For example, the signals for C_5Me_5 appear at δ 105.3, 104.1, and 103.9; the last is split into a doublet due to ^{103}Rh coupling (J = 24 Hz).

Crystallographic Studies on $[(C_5Me_5)_3RhRu_2S_4(MeCN)](SbF_6)_2$. X-ray quality crystals of $[(C_5Me_5)_3RhRu_2S_4(MeCN)](SbF_6)_2$ were obtained by slow diffusion of ether into an MeCN solution of **1**$(SbF_6)_2$. We attempted to grow crystals using other counteranions, including $PF_6{}^-$, $CF_3SO_3{}^-$, and $BF_4{}^-$, but these salts formed oils. The crystallographic study shows that the dication consists of an unsymmetrical $RhRu_2S_4$ core containing an isosceles triangle of metal atoms with one M–M bond of 2.88 Å (Figure 2, Table 1). The metal–metal bond is assigned as being between the two Ru atoms due to similarity of the ^{1}H NMR shifts for $(C_5Me_5)Ru$ ($\Delta\delta = 0.02$ ppm). These signals are unambiguously assigned to $(C_5Me_5)Ru$ because they coalesce at higher temperatures. The three metal atoms are joined by two μ_3-η^1:η^2:η^1-S_2 units. The persulfido distances are slightly long, at 2.08–2.10 Å, but not as long as 2.3 Å seen for the S–S bond in $(C_5Me_5)_3Ru_3(S_2)S(SEt)^{2+}$.[7] The S···S nonbonding contacts are unremarkable (3.31–3.46 Å). Each persulfide is monodentate toward Rh1, whose coordination sphere is completed with an η^5-C_5Me_5 and an MeCN molecule. The Rh–N distance of 2.09 Å is unexceptional; in $[\{(MeCN)_3[P(OMe)_3]_2Ru\}_2S_2]^{4+}$ the Ru–N bonds range from 2.02 to 2.14 Å.[9]

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(8) Russell, M. J. H.; White, C.; Yates, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1978**, 857.

(9) Matsumoto, T.; Matsumoto, K. *Chem. Lett.* **1992**, 1539.

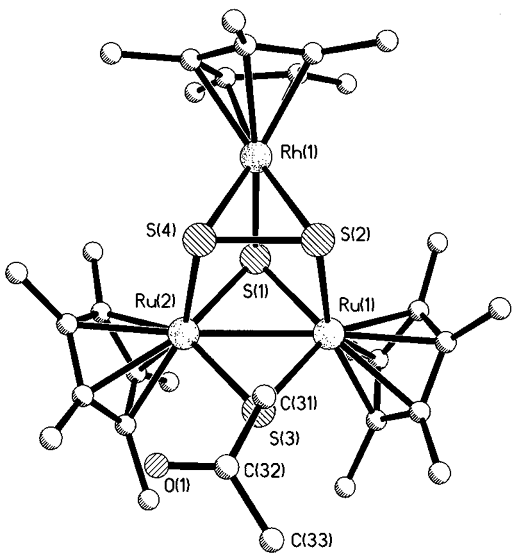

Figure 3. Structure of the cation in $[(C_5Me_5)_3RhRu_2S_3(SCH_2COCH_3)]BF_4$ (**4**(BF_4)). Hydrogen atoms are omitted for clarity.

Analogs of 1^{2+}. To better understand the stereodynamics in 1^{2+}, an analogous compound was prepared with $(C_5Me_4Et)Rh$ in place of $(C_5Me_5)Rh$. Using a synthetic procedure analogous to that leading to **1**(PF_6)$_2$, we obtained $[(C_5Me_4Et)(C_5Me_5)_2RhRu_2S_4(MeCN)](PF_6)_2$, **2**($PF_6$)$_2$, in good yield. The analytical data for this compound were only of marginal quality, but the spectroscopic data are clean. The room-temperature ^1H NMR spectrum of a CD_3CN solution of 2^{2+} consists of six $C_5Me_{5-x}Et_x$ ($x = 1, 0$) singlets in a 1:1:1:1:5:5 ratio in addition to the CH_2CH_3 resonances which appear as a quartet at δ 2.06 and a triplet at δ 1.07. A peak at δ 1.96 is again assigned to free MeCN, due to exchange with the deuterated solvent. At elevated temperatures, the ^1H NMR signals for $(C_5Me_5)Ru$ coalesce concomitantly with the partial collapse of the C_5Me_4-Et signals into two broadened singlets. Seven methyl signals are seen in the $^{13}C\{^1H\}$ NMR spectrum.

The preparation of the analog of 1^{2+} with Ir in place of Rh required relatively stringent conditions. Treatment of a blue THF solution of $(C_5Me_5)_2Ru_2S_4$ with an MeCN solution of $(C_5Me_5)Ir(MeCN)_3{}^{2+}$ results in a green solution. If this mixture is stirred at room temperature, as was done for 1^{2+}, one obtains only unreacted starting materials. The mixture was refluxed for 6 h and cooled to room temperature, and then the solvent was removed, giving a green-brown oily solid. Purification as for 1^{2+} gave a 38% yield of green $[(C_5Me_5)_3IrRu_2S_4(MeCN)](PF_6)_2$, **3**($PF_6$)$_2$. The ^1H and $^{13}C\{^1H\}$ NMR spectra are also indicative of an unsymmetrical cluster.

Synthesis of $[(C_5Me_5)_3RhRu_2S_3(SCH_2COCH_3)]^+$. The high reactivity of 1^{2+} was initially suggested by FAB mass spectroscopic experiments which showed parent ion peaks for $m/z = (840 + \text{matrix}^+)$. Attempts to recrystallize the salt from an acetone solution gave microcrystals of $[(C_5Me_5)_3RhRu_2S_3(SCH_2COCH_3)]PF_6$, **4**($PF_6$). This product, which proved to be an *S*-acetonyl derivative, displays an ^1H NMR spectrum consisting of singlets at δ 3.93 (CH_2) and δ 2.50 (CH_3), along with two C_5Me_5 signals in a 2:1 ratio. This spectrum does not qualitatively change at lower temperatures, indicating that in contrast to its precursor, this acetonyl species is symmetrical. An ^1H NMR spectrum of 4^+ was also obtained in CD_3CN to establish the robustness of the acetonylthio complex in the absence of acetone. The signals are shifted somewhat upfield; however, the acetonyl resonances remain virtually unchanged.

The $^{13}C\{^1H\}$ NMR spectrum of 4^+ showed three signals ascribed to the acetonyl fragment at δ 206, 42.9, and 30.7, assigned to CO, CH_2, and CH_3, respectively. The assignment of the $-CH_2C(O)CH_3$ signals is based on the *J*-modulated spin-echo (APT) sequence where the number of coupled protons determines the phases of carbon signals.[10] The symmetrical nature of this complex was also demonstrated by its ^{13}C NMR spectrum. Its IR spectrum featured prominent bands at 840 (ν_{PF}) and 1705 cm^{-1} (ν_{CO}). Dissolution of the $IrRu_2$ cluster 3^{2+} in acetone resulted in a color change of the solution from green to red; however, the characterization of this product was not pursued.

Table 2. Selected Bonding and Nonbonding Distances (Å) for $[(C_5Me_5)_3RhRu_2S_3(SCH_2COCH_3)]BF_4$ (**4**(BF_4))

Ru1−Ru2	2.746(9)	Ru1···Rh1	3.597(1)
Ru2···Rh1	3.582(1)	S1···S2	3.007(2)
S1···S3	3.734(2)	S1···S4	3.016(2)
S2···S3	3.258(2)	S2−S4	2.124(3)
S3···S4	3.261(3)	Rh1−S1	2.361(2)
Rh1−S2	2.363(2)	Rh1···S3	4.779(2)
Rh1−S4	2.351(2)	Ru1−S1	2.315(2)
Ru1−S2	2.366(2)	Ru1−S3	2.314(2)
Ru1···S4	3.382(2)	Ru2−S1	2.332(2)
Ru2···S2	3.372(2)	Ru2−S3	2.311(2)
Ru2−S4	2.356(2)	O1−C32	1.214(11)
C31−C32	1.468(11)	C32−C33	1.411(14)
S3−C31	1.857(8)		

The formation of 4^+ from 1^{2+} formally results from the addition of the enolate of acetone to $[(C_5Me_5)_3RhRu_2S_4]^{2+}$. Independent of the mechanistic details, a balanced reaction would produce protons (eq 3). The reversibility of the alkylation was tested by treating **4**(PF_6) with acid. Addition of trifluoromethanesulfonic acid (HOTf) to an MeCN solution of **4**(PF_6) gives **1**(PF_6)(OTf) in 82% yield.

$$\underset{\mathbf{1}^{2+}}{(C_5Me_5)_3RhRu_2S_4(MeCN)^{2+}} \underset{MeCN}{\overset{Me_2CO}{\rightleftarrows}} \underset{\mathbf{4}^{+}}{(C_5Me_5)_3RhRu_2S_3(SCH_2C(O)Me)^+} + H^+ \quad (3)$$

Crystallographic Studies on $[(C_5Me_5)_3RhRu_2S_3(SCH_2COCH_3)]BF_4$. The monocation features a trigonal prismatic $RhRu_2S_3$ cluster with an $CH_3C(O)CH_2S$ group spanning the Ru−Ru edge (Figure 3, Table 2). The M_3S_4 core can also be viewed as an incomplete cubane. The BF_4^- counterion is well separated from the cluster molecule. Crystallographic symmetry was not imposed on the cation. Since crystallographic methods cannot distinguish the Rh from the Ru atoms, the positions of these atoms are based on the observation of a symmetric structure by ^1H and ^{13}C NMR spectroscopy. There is one metal−metal bond between the two Ru atoms of 2.75 Å, as in 1^+. The Ru···Rh nonbonding contacts are 3.60 Å. The M−S distances are nearly equivalent at 2.33−2.38 Å. The S2−S4 bonding distance is 2.12 Å; in $(C_5Me_5)_3Ru_3S_3SEt^{2+}$, the S−S bond distance is 2.14 Å.[7] The remaining S···S nonbonding contacts range from 3.00 Å (S1−S2) to 3.26 Å (S4−S3). The S3−C31 distance of 1.86 Å and the O1−C32 distance of 1.21 Å are normal.[11]

Discussion

The 52 e$^-$ cluster $(C_5Me_5)_3RhRu_2S_4(MeCN)^{2+}$ is a rare[7] example of a M_3S_4 cluster comprising of S_2 ligands.[12] The persulfido ligands are arranged in a μ_3-η^1:η^2:η^1 binding mode,

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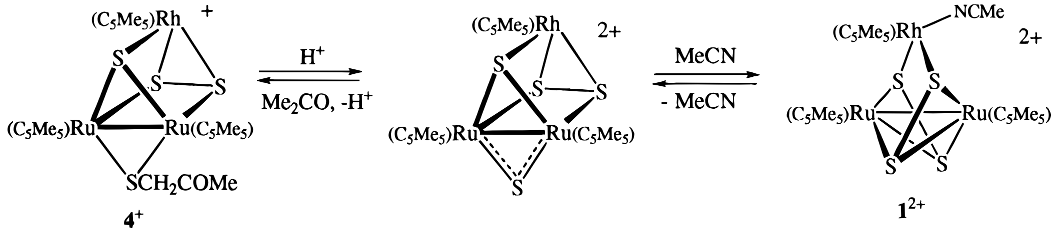
(10) Friebolin, H. *Basic One- and Two- Dimensional NMR Spectroscopy*; VCH: Weinheim, Germany, 1991; pp 167−181.

(11) *CRC Handbook of Chemistry and Physics*, 71st ed.; Weast, R. C., Ed.; CRC: Cleveland, OH 1990; p 9.

Scheme 1



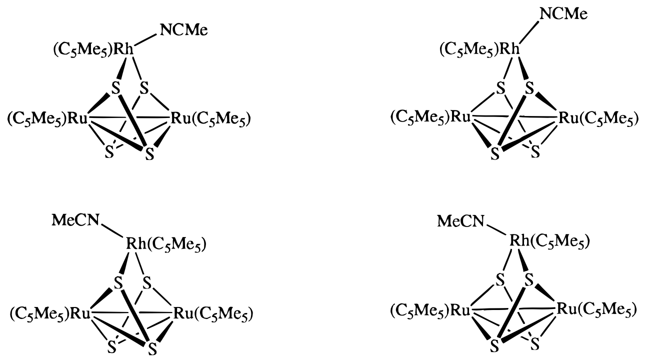
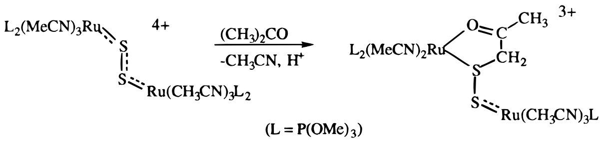


Figure 4. Isomers of $[(C_5Me_5)_3RhRu_2S_4(MeCN)]^{2+}$ ($\mathbf{1}^{2+}$). DNMR experiments on $\mathbf{1}^{2+}$ demonstrate that the Ru sites exchange. Related DNMR experiments on $[(C_5Me_4Et)(C_5Me_5)_2RhRu_2S_4(MeCN)]^{2+}$ demonstrate that this exchange involves racemization; thus all four isomers interconvert.

reminiscent of that found for $(C_5Me_5)_2Co_2S_4$ and for one of two isomers of $(C_5Me_5)_2Fe_2S_4$, where these ligands are μ_2-η^1:η^2.[13,14] The two $Ru(C_5Me_5)$ sites are similar but nonequivalent due to the orientation of the MeCN ligand on Rh. In MeCN solution, the two $(C_5Me_5)Ru$ sites exchange as demonstrated by variable-temperature NMR measurements. The mechanism of the dynamic process is constrained by DNMR studies on $[(C_5Me_4Et)(C_5Me_5)_2RhRu_2S_4(MeCN)]^{2+}$, an analog of $\mathbf{1}^{2+}$, which indicate that the rate of racemization is the same as the rate of exchange of the $(C_5Me_5)Ru$ sites. DNMR measurements also rule out pathways involving dissociation of $\mathbf{1}^{2+}$ to give $(C_5Me_5)_2Ru_2S_4$ and $[(C_5Me_5)Rh(MeCN)_3]^{2+}$, since added $[(C_5Me_5)Rh(MeCN)_3]^{2+}$ does not affect the site exchange. These findings indicate that the dynamics interconvert all four isomers of $\mathbf{1}^{2+}$ (Figure 4), initiated by dissociation of MeCN. Clues relevant to the nature of the MeCN-free intermediate were provided by the reaction of $\mathbf{1}^{2+}$ with acetone.

Solutions of $[(C_5Me_5)_3RhRu_2S_4(MeCN)]^{2+}$ react with acetone under mild conditions to give the 52 e^- acetonylthio derivative $[(C_5Me_5)_3RhRu_2S_3(SCH_2COCH_3)]^+$, an unusual example of a cluster with a trigonal prismatic M_3S_3 core. In this transformation, the metals remain in oxidation state III. The reaction of $\mathbf{1}^{2+}$ with acetone is unusual, as it formally represents C−H activation by a sulfido ligand. Acetone is known to react with inorganic ligands via sulfidation,[15] insertion into metal−dioxygen bonds,[16] and attack at linear nitrosyl ligands.[17,18] In the present case, however, we suggest that the acetone is activated as its enol. The equilibrium concentration of acetone enol in water (25 °C) is ~6 × 10^{-7} M.[19]

The S-alkylation process can be reversed with acid, presumably via protonation of the ketonic oxygen, which allows release of the enol of acetone.[20] The reverse of this process, the attachment of acetone enol at a sulfido ligand to give $\mathbf{4}^+$, requires that the (per)sulfido ligands be electrophilic. Electrophilic sulfido ligands have been observed in certain $Mo_2(\mu\text{-}S)_x$ and $Fe_2(\mu\text{-}S_2)$ centers.[21,22] Electrophilic persulfido ligands are well-known in 34 e^- Ru_2S_2 dimers; this aspect would explain the recently observed formation of an acetonylperthio complex (eq 4).[23] Little mechanistic information is available on this transformation.



(4)

The structure of $[(C_5Me_5)_3RhRu_2S_4]^{2+}$, formed upon dissociation of MeCN from $\mathbf{1}^{2+}$, has not been definitively established. This species is of special interest since it is likely the reactive cluster that binds the acetone enol. There are many structures possible for this 50 e^- species, one featuring a pair of M−M bonds (cf. eq 1) and another featuring a 4 e^- sulfido ligand (Scheme 1). The second option is appealing since the same trigonal prismatic cluster, $[(C_5Me_5)_3RhRu_2(\mu_3\text{-}S_2)(\mu_3\text{-}S)(\mu_2\text{-}S)]^{2+}$, would be generated by protonolysis of $\mathbf{4}^+$. Indeed, we demonstrated that $\mathbf{1}^{2+}$ is regenerated when $\mathbf{4}^+$ is protonated in MeCN solution.

Overall, this work and the previous study[7] show that high reactivity is associated with sulfur atoms in cationic clusters containing persulfido ligands. Such sulfur-rich clusters can be prepared in a rational manner by metalation of $(C_5R_5)_2M_2S_4$ precursors.

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Experimental Section

Materials. The hydrated trichlorides of iridium, rhodium, and ruthenium were obtained from PGM Ltd. $[(\mathrm{C_5Me_5})\mathrm{IrCl_2}]_2$,[24] $[(\mathrm{C_5Me_5})\mathrm{RhCl_2}]_2$,[24] and $(\mathrm{C_5Me_5})_2\mathrm{Ru_2S_4}$[25] were prepared according to literature methods. $[(\mathrm{EtC_5Me_4})\mathrm{RhCl_2}]_2$ was prepared analogously to $[(\mathrm{C_5Me_5})\mathrm{RhCl_2}]_2$ using $\mathrm{C_5Me_4EtH}$ in place of $\mathrm{C_5Me_5H}$. $\mathrm{HO_3SCF_3}$ was purchased from Aldrich. Acetonitrile and $\mathrm{Et_2O}$ were distilled from $\mathrm{CaH_2}$ and Na/K alloy, respectively. Acetone was deoxygenated before use.

Methods. Elemental analyses were performed by the University of Illinois Microanalytical Laboratory. Positive-ion fast atom bombardment mass spectra were recorded on a VG ZAB-SE. Solution ^{1}H and ^{13}C NMR spectra were recorded on Varian U400 spectrometer, except for variable-temperature measurements on the acetonylthio group, where we used a GE500 instrument. Infrared spectra were recorded on a Mattson Galaxy 3000 Fourier transform infrared spectrometer. Unless otherwise stated, preparative operations were performed under an atmosphere of nitrogen using standard Schlenk techniques.

$[(\mathrm{C_5Me_5})_3\mathrm{RhRu_2S_4(CH_3CN)}](\mathrm{PF_6})_2$ (1(PF$_6$)$_2$). A 150 mL Schlenk flask was charged with 0.32 g (0.513 mmol) of $[(\mathrm{C_5Me_5})\mathrm{RhCl_2}]_2$ and 0.55 g (2.15 mmol) of $\mathrm{AgPF_6}$, followed by 30 mL of MeCN. After 3 h, the yellow slurry was filtered through 2 g of Celite in a Schlenk filter to remove AgCl. The Celite was washed with 40 mL of $\mathrm{CH_3CN}$, and the yellow filtrate was added to a solution of 0.616 g (0.103 mmol) of $(\mathrm{C_5Me_5})_2\mathrm{Ru_2S_4}$ in 30 mL of THF. After the red-brown solution was stirred overnight, the solvent was removed, and the brown solid was extracted into 15 mL of MeCN. This extract was filtered from a dark-brown residue into 50 mL of $\mathrm{Et_2O}$, resulting in a red-brown powder. Two further recrystallizations from MeCN−$\mathrm{Et_2O}$ gave rust-colored **1**(PF$_6$)$_2$. Yield: 0.51 g (85%). ^{1}H NMR (CD$_3$CN, 25 °C): δ 1.96 (s, 3H), 1.92 (s, 15H), 1.90 (s, 15H), 1.63 (s, 15H). ^{1}H NMR (CD$_3$CN, 80 °C): δ 1.97 (3H), 1.94 (br s, 30H), 1.65 (s, 15H). ^{13}C{^{1}H} NMR (CD$_3$CN): δ 105.3 (s, $C_5\mathrm{Me}_5$), 104.1 (s, $C_5\mathrm{Me}_5$), 103.9 (d, $C_5\mathrm{Me}_5$, J = 24 Hz), 11.48 (s, C_5Me_5), 11.34 (s, C_5Me_5), 9.52 (s, C_5Me_5). FAB MS: *m/z* 840 (M$^+$). IR (KBr): ν_{PF} = 840 cm^{-1}. Anal. Calcd for $\mathrm{C_{32}H_{48}F_{12}NP_2RhRu_2S_4}$: C, 32.85; H, 4.14; N, 1.19. Found: C, 32.67; H, 4.43; N, 0.80.

$[(\mathrm{C_5Me_4Et})(\mathrm{C_5Me_5})_2\mathrm{RhRu_2S_4(MeCN)}](\mathrm{PF_6})_2$ (2(PF$_6$)$_2$). A 150 mL Schlenk flask was charged with 0.100 g (0.155 mmol) of $[(\mathrm{C_5Me_4Et})\mathrm{RhCl_2}]_2$, 0.164 g (0.650 mmol) of $\mathrm{AgPF_6}$, and 20 mL of MeCN. After 3 h, the lemon-yellow slurry was filtered through Celite to remove AgCl. The Celite was washed with 40 mL of MeCN, and the yellow filtrate was transferred to a solution of 0.186 g (0.310 mmol) of $(\mathrm{C_5Me_5})_2\mathrm{Ru_2S_4}$ in 30 mL of THF, resulting in a red-brown solution. After 12 h, the solvent was removed. The red-brown solid was extracted into 7 mL of MeCN, and this solution was filtered away from a small amount of a brown-black solid. The red-brown filtrate was transferred by cannula into 40 mL of $\mathrm{Et_2O}$. The resulting brown solid was purified by extraction into 7 mL of MeCN, followed by addition of this solution to 37 mL of $\mathrm{Et_2O}$ to give the dark-brown solid $[(\mathrm{C_5Me_4Et})(\mathrm{C_5Me_5})_2\mathrm{RhRu_2S_4(MeCN)}](\mathrm{PF_6})_2$. Yield: 0.160 g (87%). ^{1}H NMR (CD$_3$CN, 20 °C): δ 2.06 (q, 2H), 1.96 (s, 3H), 1.92 (s, 15H), 1.89 (s, 15H), 1.66 (s, 3H), 1.64 (s, 3H), 1.63 (s, 3H), 1.61 (s, 3H), 1.07 (t, 3H). ^{1}H NMR (CD$_3$CN, 80 °C): δ 2.10 (q, 2H), 1.96 (3H), 1.92 (s, 30H), 1.68 (s, 6H), 1.66 (s, 6H), 1.07 (t, 3H). ^{13}C{^{1}H} NMR (CD$_3$CN): δ 106.5−104.1 (unresolved $C_5\mathrm{R}_5$ signals), 18.0 (s, $C\mathrm{H_2CH_3}$), 12.5 (s, $\mathrm{CH_2}C\mathrm{H_3}$), 11.50 (s, C_5Me_5), 11.34 (s, C_5Me_5), 9.53 (s, $\mathrm{C}_5Me_4\mathrm{Et}$), 9.48 (s, $\mathrm{C}_5Me_4\mathrm{Et}$), 9.40 (s, $\mathrm{C}_5Me_4\mathrm{Et}$), 9.32 (s, $\mathrm{C}_5Me_4\mathrm{Et}$). FAB MS (matrix = 3-nitrobenzyl alcohol): *m/z* 853 (M$^+$), 1007 (M$^+$ + 3-NBA). Anal. Calcd for $\mathrm{C_{33}H_{50}F_{12}NP_2RhRu_2S_4}$: C, 33.47; H, 4.26; N, 1.18. Found: C, 32.41; H, 3.93; N, 1.31.

$[(\mathrm{C_5Me_5})_3\mathrm{RhRu_2S_3(SCH_2COCH_3)}]\mathrm{PF_6}$ (3(PF$_6$)). A 100 mL Schlenk flask was charged with 0.100 g (0.088 mmol) $[(\mathrm{C_5Me_5})_3\mathrm{RhRu_2S_4(MeCN)}](\mathrm{PF_6})_2$ and 30 mL of acetone. After 4 h of stirring, the solvent was removed and the red solid was extracted into 10 mL of acetone. This red solution was filtered from a brown residue. The filtrate was concentrated to ∼2 mL and diluted with 20 mL of $\mathrm{Et_2O}$ to give red microcrystals of $[(\mathrm{C_5Me_5})_3\mathrm{RhRu_2S_3(SCH_2COCH_3)}]\mathrm{PF_6}$. Yield: 0.070 g (76%). ^{1}H NMR ((CD$_3$)$_2$CO): δ 3.93 (s, 2H), 2.50 (s, 3H), 1.88 (s, 15H), 1.80 (s, 30H). ^{1}H NMR (CD$_3$CN): δ 3.78 (s, 2H), 2.44 (s, 3H), 1.78 (s, 15H), 1.71 (s, 30H). ^{13}C{^{1}H} NMR (CD$_3$CN): δ 205.9 (s, CO), 97.8 (s, $C_5\mathrm{Me}_5$), 97.6 (d, $C_5\mathrm{Me}_5$, J = 24), 42.9 (s, $C\mathrm{H_2COCH_3}$), 30.7 (s, $\mathrm{CH_2CO}C\mathrm{H_3}$), 11.2 (s, C_5Me_5), 10.1 (s, C_5Me_5). FAB MS: *m/z* 897 (M$^+$). IR (KBr): ν_{PF} = 841 cm^{-1}, ν_{CO} = 1705 cm^{-1}. Anal. Calcd for $\mathrm{C_{33}H_{50}F_6OPRhRu_2S_4}$: C, 38.05; H, 4.90. Found: C, 37.68; H, 4.88. An 8 × 10^{-3} M solution of **1**$^{2+}$ was completely converted within 30 min, while a 2.4 × 10^{-2} M solution required 5 h. A saturated solution of **1**$^{2+}$ (∼1.5 M) required days to convert to the acetonyl derivative.

Table 3. Crystal Data for $[(\mathrm{C_5Me_5})_3\mathrm{RhRu_2S_4(MeCN)}](\mathrm{SbF_6})_2$ (**1**(SbF$_6$)$_2$)

formula	$\mathrm{C_{32}H_{48}F_{12}NRhRu_2S_4Sb_2}$
fw	1351.50
space group	$P\bar{1}$
a, Å	8.3401(6)
b, Å	13.2413(10)
c, Å	20.1748(16)
α, deg	84.898(1)
β, deg	89.620(1)
γ, deg	84.720(1)
V, Å^3	2209.74
Z	2
d_{calc}, g/cm^3	2.031
μ, cm^{-1}	25.0
radiation (monochromated in incident beam)	Mo Kα (λ = 0.710 73 Å)
temp, °C	198(2)
R_1[a]	0.0476
wR_2[b]	0.1048

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $\mathrm{w}R_2 = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

Reaction of $[(\mathrm{C_5Me_5})_3\mathrm{RhRu_2S_3(SCH_2COCH_3)}]\mathrm{PF_6}$ with HOTf. To a solution of 0.020 g (0.0191 mmol) of $[(\mathrm{C_5Me_5})_3\mathrm{RhRu_2S_3(SCH_2COCH_3)}]\mathrm{PF_6}$ in 2 mL of MeCN was added 0.003 mL (0.0341 mmol) of HOTf. Within 30 min, the solution color changed from red to red-brown. After a further 30 min, the solution was concentrated to ∼1 mL and added to 10 mL of $\mathrm{Et_2O}$ to give a brown powder of $[(\mathrm{C_5Me_5})_3\mathrm{RhRu_2S_4(MeCN)}](\mathrm{PF_6})(\mathrm{OTf})$ in 82% yield. The ^{1}H NMR spectrum of a CD$_3$CN solution of this species matched that found for **1**(PF$_6$)$_2$.

$[(\mathrm{C_5Me_5})_3\mathrm{IrRu_2S_4(MeCN)}](\mathrm{PF_6})_2$ (4(PF$_6$)$_2$). A 150 mL Schlenk flask was charged with 0.151 g (0.190 mmol) of $[(\mathrm{C_5Me_5})\mathrm{IrCl_2}]_2$, 0.200 g (0.796 mmol) of $\mathrm{AgPF_6}$, and 30 mL of MeCN. After 2 h, the pale yellow slurry was filtered through 2 g of Celite in a Schlenk filter to remove AgCl. The Celite was washed with 60 mL of MeCN, and the MeCN solution was added to a solution of 0.228 g (0.380 mmol) of $(\mathrm{C_5Me_5})_2\mathrm{Ru_2S_4}$ in 30 mL of THF. The resulting green-brown solution was heated at reflux for 6 h. After the solution cooled to room temperature, the solvent was removed. The product was purified by extraction into 7 mL of MeCN, followed by the addition of this solution to 30 mL of $\mathrm{Et_2O}$ to give a green powder. Yield: 0.090 g (38%). ^{1}H NMR (CD$_3$CN): δ 1.96 (s, 3H), 1.92 (s, 15H), 1.90 (s, 15H), 1.70 (s, 15H). ^{13}C{^{1}H} NMR (CD$_3$CN): δ 105.0 (s, $C_5\mathrm{Me}_5$), 103.9 (s, $C_5\mathrm{Me}_5$), 97.8 (s, $C_5\mathrm{Me}_5$), 11.53 (s, C_5Me_5), 11.43 (s, C_5Me_5), 9.05 (s, C_5Me_5). FAB MS: *m/z* 929 (M$^+$), 1080 (M$^+$ + 3-nitrobenzyl alcohol). Anal. Calcd for $\mathrm{C_{32}H_{48}F_{12}IrNP_2Ru_2S_4}$: C, 30.52; H, 3.84; N, 1.11. Found: C, 29.71; H, 4.02; N, 0.60.

Crystallography of $[(\mathrm{C_5Me_5})_3\mathrm{RhRu_2S_4(MeCN)}](\mathrm{SbF_6})_2$. Crystals of $[(\mathrm{C_5Me_5})_3\mathrm{RhRu_2S_4(MeCN)}](\mathrm{SbF_6})_2$ were grown by vapor diffusion of ether into an acetonitrile solution of $[(\mathrm{C_5Me_5})_3\mathrm{RhRu_2S_4(MeCN)}](\mathrm{SbF_6})_2$. The platelike yellow data crystal was mounted to a thin glass fiber using Paratone-N oil (Exxon). The sample was bound by faces (100), $(\bar{1}00)$, (011), $(0\bar{1}\bar{1})$, $(01\bar{1})$, $(0\bar{1}1)$, and $(10\bar{3})$. Distances from the crystal center to these facial boundaries were 0.240, 0.200, 0.140, 0.080, 0.010, 0.010, and 0.090 mm, respectively. Data were collected on a Siemens 3-circle platform with a CCD area detector. Crystal and refinement details are given in Table 3. Systematic conditions suggested the ambiguous space group $P1$ or $P\bar{1}$; on the basis of E statistics, the latter was chosen. Standard intensities monitored during frame collection showed no decay. Intensity data were reduced by

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3d-profile analysis using SAINT[26] and corrected for Lorentz−polarization effects and for absorption (ψ-scan absorption correction). One reflection with a poor resolution (10 Å) was suppressed. Scattering factors and anomalous dispersion terms were taken from standard tables.[27]

The structure was solved using direct methods.[28] Subsequent cycles of isotropic least-squares refinement followed by an unweighted difference Fourier synthesis revealed positions for the remaining non-H atoms. The assignment of Rh and Ru atoms were based on the structure of the starting material and NMR studies of the trinuclear complex. Methyl H atom positions were optimized by rotation about R−C bonds with idealized C−H and H···H distances. Remaining H atoms were included as fixed idealized contributors. H atom U's were assigned as 1.2 times the U_{eq} values of adjacent C atoms. Non-H atoms were refined with anisotropic thermal coefficients. Successful convergence of the full-matrix least-squares refinement on F^2 was indicated by the maximum shift/error for the last cycle.[29] One of the SbF_6 anions was found to be disordered. The disordered F atoms were subjected to the restraints of being individually equidistant from the Sb center as well as from each other. The U's of the atoms in the disordered anion were constrained to be similar within a standard deviation of 0.02 and 0.04. Because the disorder in the anion did not affect the cation, this disorder was not addressed further. The highest peaks in the final difference Fourier map were in the vicinity of the Sb atoms; the final map had no other significant features. A final analysis of variance between observed and calculated structure factors showed no dependence on amplitude or resolution.

Crystallography of $[(C_5Me_5)_3RhRu_2S_3(SCH_2COCH_3)]BF_4$. Crystals of $[(C_5Me_5)_3RhRu_2S_3(SCH_2COCH_3)]BF_4$ were grown by diffusion of hexanes into an acetone solution of $[(C_5Me_5)_3Rh(MeCN)Ru_2S_4](BF_4)_2$. The platelike dark-red data crystal was mounted to a thin glass fiber using Paratone oil (Exxon) with scattering planes roughly normal to the spindle axis. The data crystal was bound by the (100), $(\bar{1}00)$, $(01\bar{1})$, $(0\bar{1}1)$, (021), and $(0\bar{2}\bar{1})$ faces. Distances from the crystal center to these facial boundaries were 0.02, 0.02, 0.34, 0.34, 0.36, and 0.36 mm, respectively. Data were measured at 198 K on an Enraf-Nonius CAD4 diffractometer. Crystal and refinement details are given in Table 4. Systematic conditions suggested the space group $P2/c$; refinement confirmed the presence of a symmetry center. Three standard intensity data were reduced by profile analysis[30] and corrected for Lorentz−polarization effects and for absorption.[26] Scattering factors and anomalous dispersion terms were taken from standard tables.[27]

Table 4. Crystal Data for $[(C_5Me_5)_3RhRu_2S_3(SCH_2COCH_3)]BF_4$ (**4**(BF_4))

formula	$C_{33}H_{50}BF_4ORhRu_2S_4$
fw	982.83
space group	$P2/c$
a, Å	11.846(3)
b, Å	19.859(4)
c, Å	16.304(5)
α, deg	90
β, deg	101.70(2)
γ, deg	90
V, Å^3	3756(2)
Z	4
d_{calc}, g/cm^3	1.738
μ, cm^{-1}	14.97
radiation (monochromated in incident beam)	Mo Kα (λ = 0.710 73 Å)
temp, °C	198(2)
R_1[a]	0.0364
wR_2[b]	0.0896

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

The structure was solved by direct methods;[28] correct positions for Rh and Ru atoms were deduced from an E map. Further cycles of isotropic least-squares refinement followed by an unweighted difference Fourier synthesis revealed positions for other non-hydrogen atoms. Methyl hydrogen atom positions, $R-CH_3$, were optimized by rotation about R−C bonds with idealized C−H and H--H distances. The remaining hydrogen atoms were included as fixed idealized contributors. Hydrogen atom U's were assigned as 1.2 times the U_{eq} values of adjacent non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic thermal coefficients. Successful convergence of the full-matrix least-squares refinement on F^2 was indicated by the maximum shift/error for the last cycle. The highest peak in the final difference Fourier map was in the vicinity of the H33A, Rh, and Ru atoms. The final map had no other significant features. A final analysis of variance between observed and calculated structure factors showed no dependence on amplitude or resolution.

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Supporting Information Available: Tables of atomic coordinates, thermal parameters, bond lengths, bond angles, torsion angles, nonbonding distances of core atoms, and least-squares planes (43 pages). Ordering information is given on any current masthead page.

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