A Tetranuclear Rhodium Complex with a μ_4-S Ligand, $[\{Cp^*{}_2Rh_2(\mu_2\text{-}CH_2)_2\}_2(\mu_4\text{-}S)]^{2+}$ ($Cp^* = \eta^5\text{-}C_5Me_5$), Obtained from Stepwise Abstraction of the SH^- Ligand from a Dinuclear Rhodium Dihydrosulfide Precursor by Ag^+

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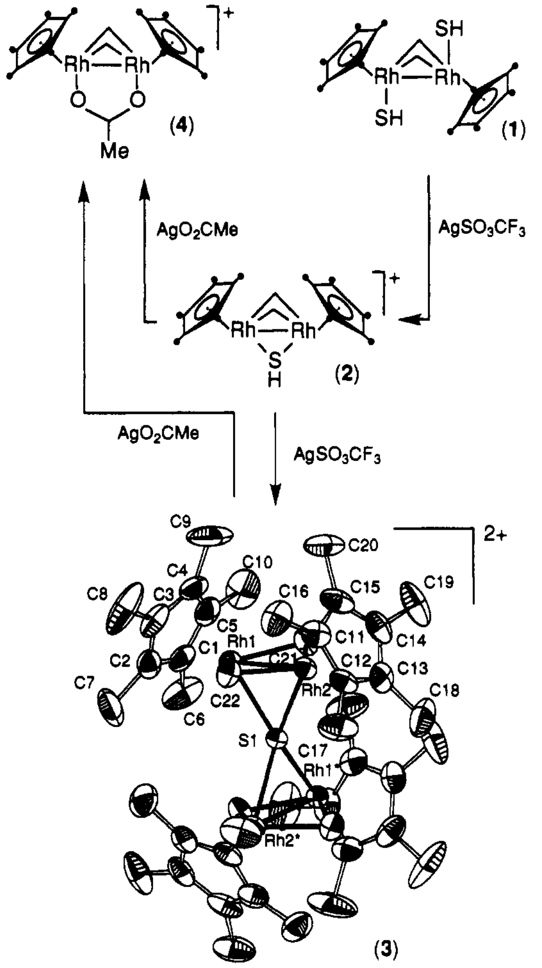
Transition-metal hydrosulfide complexes are currently under intensive investigation because of their interesting chemical behavior in oxidation,[2] deprotonation,[3] and nucleophilic reactions,[4] as well as their significance in biological,[5] mineralogical,[6] and industrial processes.[7] Recently our group reported the syntheses and X-ray structures of the terminal- and bridging-hydrosulfide rhodium dinuclear (Rh–Rh) complexes *trans*-$[Cp^*{}_2Rh_2(\mu_2\text{-}CH_2)_2(SH)_2]$ (**1**) and $[Cp^*{}_2Rh_2(\mu_2\text{-}CH_2)_2(\mu_2\text{-}SH)]^+$ (**2**).[8] In the presence of O_2 and excess H_2S, the latter complex undergoes an unusual oxidative coupling to yield the bridged S_4 derivative $[\{Cp^*{}_2Rh_2(\mu_2\text{-}CH_2)_2\}_2(\mu_4\text{-}S_4)]^{2+}$.[9] In the course of our investigation of the oxidation of **1**, we have found that a strong oxidant—Ag^+ in CH_2Cl_2—[10] instead of oxidation,[11] induces an intriguing partial abstraction of the terminal SH^- ligand in **1** to give **2** followed by abstraction of the bridging SH^- ligand in **2** to form a tetranuclear μ_4-S cationic complex $[\{Cp^*{}_2Rh_2(\mu_2\text{-}CH_2)_2\}_2(\mu_4\text{-}S)]^{2+}$ (**3**). Further abstraction of the μ_4-S ligand of **3** takes place slowly with formation of a completely S atom-abstracted product $[Cp^*{}_2Rh_2(\mu_2\text{-}CH_2)_2(\mu_2\text{-}O_2CMe)]^+$ (**4** in Scheme 1).

Reaction of *trans*-$[Cp^*{}_2Rh_2(\mu_2\text{-}CH_2)_2(SH)_2]$ with an equimolar amount of silver trifluoromethanesulfonate, $AgSO_3CF_3$, took place immediately in CH_2Cl_2 and was accompanied by a color change from red to orange-brown, the evolution of H_2S gas, and precipitation of Ag_2S. From the reaction mixture was isolated $[Cp^*{}_2Rh_2(\mu_2\text{-}CH_2)_2(\mu_2\text{-}SH)](SO_3CF_3)$ (**2**-SO_3CF_3)[12] in an 86% yield. The silver salt induces an elimination of one terminal SH ligand from **1** to give **2**-SO_3CF_3. The stoichiometry of the reaction is as follows (H_2S gas was identified by a H_2S detector tube but was not quantified):

Scheme 1



$$\begin{aligned} &trans\text{-}[Cp^*{}_2Rh_2(\mu_2\text{-}CH_2)_2(SH)_2] + AgSO_3CF_3 \rightarrow \\ &\quad [Cp^*{}_2Rh_2(\mu_2\text{-}CH_2)_2(\mu_2\text{-}SH)](SO_3CF_3) + \\ &\qquad {}^1/{}_2Ag_2S + {}^1/{}_2H_2S \quad (1) \end{aligned}$$

Upon similar treatment of **2**-SO_3CF_3 with 1 equiv of $AgSO_3CF_3$ in dichloromethane under Ar gas, dark grayish solids containing Ag_2S precipitated, and further ligand abstraction was observed, this time, of the μ_2-SH ligand. After subsequent workup $[\{Cp^*{}_2Rh_2(\mu_2\text{-}CH_2)_2\}_2(\mu_4\text{-}S)](SO_3CF_3)_2$ (**3**-SO_3CF_3) was isolated

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(12) Detailed experimental procedures and selected spectroscopic data for $[Cp^*{}_2Rh_2(\mu_2\text{-}CH_2)_2(\mu_2\text{-}SH)](SO_3CF_3)$ and $[Cp^*{}_2Rh_2(\mu_2\text{-}CH_2)_2(\mu_2\text{-}O_2CMe)]X$ (X = BPh_4, SO_3CF_3) are given in the supplementary material.

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in a 93% yield as an orange solid.[13] The reaction proceeds according to eq 2.

$$[Cp^*_2Rh_2(\mu_2\text{-}CH_2)_2(\mu_2\text{-}SH)](SO_3CF_3) + AgSO_3CF_3 \rightarrow {}^1/_2[\{Cp^*_2Rh_2(\mu_2\text{-}CH_2)_2\}_2(\mu_4\text{-}S)](SO_3CF_3)_2 + {}^1/_2Ag_2S + H^+ + CF_3SO_3^- \quad (2)$$

Upon recrystallization from water–methanol (1:1), **3**-$SO_3CF_3\cdot 3H_2O$ slowly precipitated as deep red crystals, which were used for structural characterization.[14] **3**-$SO_3CF_3\cdot 3H_2O$ consists of discrete ions and three water molecules of crystallization. An ORTEP diagram for the cationic part is included in Scheme 1. The sulfido ligand has tetrahedral geometry and a spiran μ_4-S type linkage with two metal–metal-bonded dinuclear units, analogous to structures having been found mainly in clusters of Fe and Ru metals.[15] This, however, is the first example of a μ_4-S spiran sulfido complex of rhodium. The torsional angle between the Rh(1)–Rh(2) and Rh(1)*–Rh(2)* bonds is 83.66(5)°. Each rhodium atom is coordinated by two μ_2-CH_2 ligands, one μ_4-S ligand, and one Cp* ligand to give a slightly puckered Rh_2C_2 ring (the dihedral angle between the planes passing through Rh(1), Rh(2), C(21) and Rh(1), Rh(2), C(22) is 14.2(5)°) and has a single Rh–Rh bond (2.5786(8) Å). The Rh–S bond length (average 2.372(3) Å) is shorter than that of **2**-BPh_4 (average 2.401(7) Å).[8] A very small value for the Rh–S–Rh angle (65.85(2)°) agrees well with that for **2**-BPh_4.[8] The ^1H and ^{13}C NMR spectra give evidence for preservation of the structure of $[\{Cp^*_2Rh_2(\mu_2\text{-}CH_2)_2\}_2(\mu_4\text{-}S)]^{2+}$ in solution. All of the Cp* ligands are equivalent, as are all of the carbon atoms in the μ_2-CH_2 groups. On the other hand, the two protons in each μ_2-CH_2 group are not equivalent and appear at δ 7.78 as a doublet (J_{H-H} = 3.2 Hz) and at δ 8.27 as a double triplet (J_{H-H} = 3.2 Hz, J_{H-Rh} = 1.5 Hz): only one of the two hydrogens of each CH_2 ligand is coupled to the two rhodiums.[16] **3**-SO_3CF_3 reacts with excess AgO_2CMe in dichloromethane to give a completely S atom-abstracted product $[Cp^*_2Rh_2(\mu_2\text{-}CH_2)_2(\mu_2\text{-}O_2CMe)](SO_3CF_3)$ (**4** in Scheme 1).[12,17] The reaction may proceed according to eq 3.

$$[\{Cp^*_2Rh_2(\mu_2\text{-}CH_2)_2\}_2(\mu_4\text{-}S)](SO_3CF_3)_2 + 2AgO_2CMe \rightarrow 2[Cp^*_2Rh_2(\mu_2\text{-}CH_2)_2(\mu_2\text{-}O_2CMe)](SO_3CF_3) + Ag_2S \quad (3)$$

In the reaction of **1** or **2** with an equimolar amount of $AgSO_3CF_3$ and the reaction of **3** with excess AgO_2CMe, we did not observe the generation of ethylene, which is a direct coupling product of the two μ_2-CH_2 units in the rhodium complexes. This is in contrast to results from the decomposition[18] of $[Cp^*_2Rh_2(\mu_2\text{-}CH_2)_2X_2]$ (X = Cl, Br, I) by oxidizing agents, such as I_2, $IrCl_6^{2-}$, and $AgBF_4$–MeCN, which gives ethylene under the conditions similar to those employed in our reactions.

We have examined the reaction of **2** with different silver salts. Reactions with $AgBF_4$ and $AgPF_6$ salts containing so-called noncoordinating anions, give the μ_4-S complex, although AgO_2CMe yields, of course, the completely S atom-abstracted product $[Cp^*_2Rh_2(\mu_2\text{-}CH_2)_2(\mu_2\text{-}O_2CMe)]^+$.[12,17]

Such an abstraction of hydrosulfide ligands resembles that of halides or pseudohalides by silver salts. Apparently, abstraction of ligands by silver salts is not restricted only to halides and pseudohalides. R^- abstraction from $[Cp_2ZrR_2]$[19] and $[PbR_4]$[20] and S atom abstraction from thioacetamide[21] by Ag^+ have been observed. To our knowledge, however, no other example of the stepwise abstraction of SH and S ligands, such as that described here, has been reported to date.

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Supplementary Material Available: Text giving detailed experimental procedures and listings of crystallographic data, atomic positional parameters, anisotropic thermal parameters, bond distances, bond angles, and dihedral angles for **3** (10 pages). Ordering information is given on any current masthead page.

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(13) The anhydrous form, $[\{Cp^*_2Rh_2(\mu_2\text{-}CH_2)_2\}_2(\mu_4\text{-}S)](SO_3CF_3)_2$, was used for elemental analysis and NMR measurements. Anal. Calcd for $C_{46}H_{68}F_6O_6Rh_4S_3$: C, 41.27; H, 5.12. Found: C, 41.51; H, 4.72. FAB mass spectrum: *m/e* 1189 for $[[\{Cp^*_2Rh_2(\mu_2\text{-}CH_2)_2\}_2(\mu_4\text{-}S)](SO_3CF_3)]^+$. IR (in mineral oil): 1274 (s, br), 1230 (s, br), 1154 (s), 1020 (s) cm^{-1}. These bands are characteristic for the uncoordinated trifluoromethanesulfonate ion (Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17). ^1H NMR (CD_2Cl_2, 23 °C): δ 8.27 (dt, J_{H-H} = 3.2 Hz, J_{H-Rh} = 1.5 Hz, μ_2-CH_2, 4H), 7.78 (d, J_{H-H} = 3.2 Hz, μ_2-CH_2, 4H), 1.90 (s, C_5Me_5, 60H). ^{13}C NMR (CD_2Cl_2, 25 °C): δ 163.6 (t, J_{C-Rh} = 22.9 Hz, μ_2-CH_2), 121.5 (quart, J_{C-F} = 322 Hz, CF_3), 103.9 (d, J_{C-Rh} = 8 Hz, C_5Me_5), 11.4 (s, C_5Me_5). Details of the preparation and purification are presented in the supplementary material.

(14) A detailed X-ray analysis and crystallographic data are given in the supplementary material. Crystal data for $[\{Cp^*_2Rh_2(\mu_2\text{-}CH_2)_2\}_2(\mu_4\text{-}S)](SO_3CF_3)_2\cdot 3H_2O$: $C_{46}H_{74}F_6O_9Rh_4S_3$ (fw = 1392.88); monoclinic, space group *C2/c* (No. 15) a = 17.169(2) Å, b = 14.572(2) Å, c = 23.008(2) Å, β = 112.863(7)°, V = 5489(1) Å^3, Z = 4, ρ_{calcd} = 1.685 g cm^{-3}; μ(Mo Kα) = 13.7 cm^{-1}, crystal size 0.6 × 0.4 × 0.3 mm. The full-matrix refinements of 308 least-squares parameters for all non-hydrogen atoms and 4268 reflections converged at R (R_w) = 0.054 (0.073). Selected bond lengths (Å) and angles (deg): Rh(1)–Rh(2), 2.5786(8); Rh(1)–S(1), 2.369(1); Rh(2)–S(1), 2.375(1); Rh(1)–C(21), 2.057(8); Rh(1)–C(22), 2.073(9); Rh(2)–C(21), 2.058(8); Rh(2)–C(22), 2.042(8); Rh(1)–S(1)–Rh(2), 65.85(2); Rh(1)–Rh(2)–S(1), 56.96(5); Rh(2)–Rh(1)–S(1), 57.19(5); Rh(1)–S(1)–Rh(2)*, 134.29(2); Rh(1)–S(1)–Rh(1)*, 132.2(1); Rh(2)–S(1)–Rh(2)*, 138.2(1); Rh(1)–C(21)–Rh(2), 77.6(3); Rh(1)–C(22)–Rh(2), 77.6(3). (Atoms labeled with an asterisk have equivalent coordinates $-x, y, {}^1/_2 - z$. The molecule possesses a 2-fold axis of symmetry passing through the S(1) atom as defined by equivalent atoms shown in **3** in Scheme 1.)

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