Hydrosulfido-Bridged Titanium-Ruthenium Heterobimetallic Complex: Stepwise Construction of $Ti_2Ru_2S_4$ Cubane-Type Sulfido Cluster

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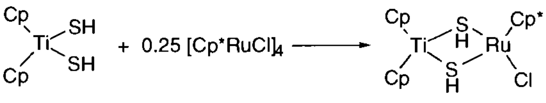
Reaction of $[Cp_2Ti(SH)_2]$ (Cp = η^5-C_5H_5) with $[(Cp^*Ru)_4(\mu_3\text{-}Cl)_4]$ (Cp* = η^5-C_5Me_5) afforded the hydrosulfido-bridged titanium-ruthenium heterobimetallic complex $[Cp_2Ti(\mu_2\text{-}SH)_2RuClCp^*]$ (**3**), which was further converted into the heterobimetallic cubane-type sulfido cluster $[(CpTi)_2(Cp^*Ru)_2(\mu_3\text{-}S)_4]$ (**4**) upon treatment with an excess of triethylamine. The structures of **3** and **4** have been determined by X-ray crystallography.

Hydrosulfido complexes have attracted much attention owing to their potential relevance to metal–sulfide catalysis in industrial hydrogenation and hydrodesulfurization[1] as well as metalloenzymes.[2] We have previously prepared a series of hydrosulfido-bridged dinuclear complexes $[Cp^*MCl(\mu_2\text{-}SH)_2MClCp^*]$ (M = Ru,[3a] Rh, Ir[3c,d]) and have studied their conversion into the cubane-type sulfido clusters $[(Cp^*M)_4(\mu_3\text{-}S)_4]$ through the α-elimination of hydrogen chloride.[3b–d] These hydrosulfido complexes also serve as versatile precursors to mixed-metal sulfide clusters with higher nuclearity.[3a,c,e] As an extension of these studies, we have now prepared the early-late heterobimetallic complex with bridging hydrosulfido ligands $[Cp_2Ti(\mu_2\text{-}SH)_2RuClCp^*]$ (**3**), which is readily transformed into the heterobimetallic cubane-type sulfido cluster $[(CpTi)_2(Cp^*Ru)_2(\mu_3\text{-}S)_4]$ (**4**) by triethylamine.

Treatment of $[Cp_2Ti(SH)_2]$[4] (**1**) with $[(Cp^*Ru)_4(\mu_3\text{-}Cl)_4]$[5] (**2**) in a Ti:Ru ratio of 1:1 cleanly afforded the hydrosulfido-bridged titanium-ruthenium complex **3** in 73% yield (eq 1).[6] A sharp singlet with the intensity of 2 H at 2.10 ppm in the ^1H NMR spectrum as well as the weak ν_{SH} band at 2492 cm^{-1} in the IR spectrum demonstrates the presence of the hydrosulfido ligands in **3**. The present reaction contrasts with the reaction of **2** with thiols (RSH) or H_2S gas giving the thiolato- or hydrosulfido-bridged diruthenium(III) complexes $[Cp^*RuCl(\mu_2\text{-}SR)_2RuClCp^*]$ (R = Et, p-$CH_3C_6H_4$, H),[3a] in which the ruthenium centers are oxidized and the S–H bond is cleaved. However, adduct formation of hydrosulfido complexes with Lewis acid metal complexes is known as a versatile method to prepare hydrosulfido-bridged complexes.[7,8]

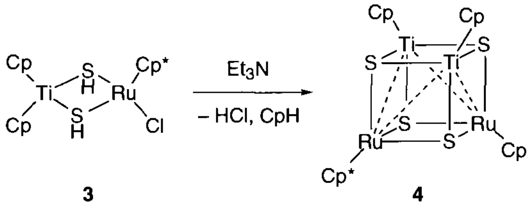


(1)

1 **2** **3**

The hydrosulfido-bridged heterobimetallic core in **3** has been confirmed by an X-ray analysis.[9] The two hydrosulfido hydrogen atoms, which have been found in the final difference Fourier map, lie in the *cis*-position with respect to the chloro ligand bound to the ruthenium atom with the S–H distances of 1.20 and 1.13 Å. The bond distances and angles in **3** show no significant difference from the related thiolato-bridged titanium-ruthenium complex $[Cp_2Ti(\mu_2\text{-}SPh)_2RuClCp^*]$.[10] Early-late heterobimetallic complexes have been the subject of increased attention.[11] However, hydrosulfido-bridged heterobimetallic complexes are still rare,[7,8,12] and, to our knowledge, **3** is the first structurally characterized early-late heterobimetallic complex with bridging hydrosulfido ligands.

When **3** was allowed to react with an excess of triethylamine in THF at –78 °C, the dark reddish brown solution immediately turned deep violet, which further changed to dark reddish brown as the solution was warmed to room temperature. Subsequent workup afforded the diamagnetic cubane-type sulfido cluster **4** in 63% yield (eq 2).[13] Figure 1 clearly demonstrates that **4** has a cubane-



(2)

3 **4**

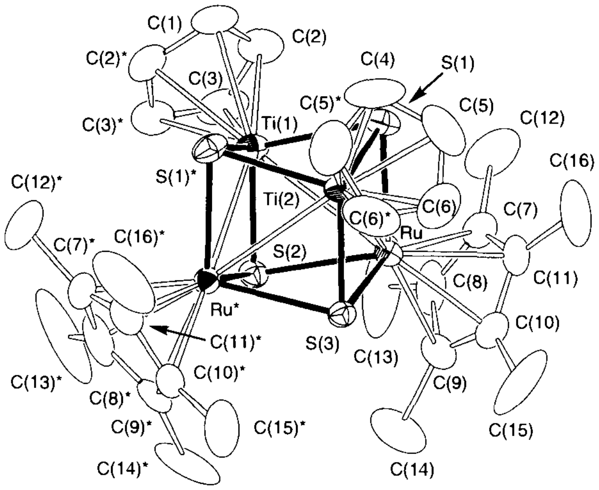


Figure 1. Molecular structure of **4**. The molecule has a crystallographically imposed mirror plane containing Ti(1), Ti(2), S(2), S(3), C(1), and C(4), which bisects the $Ti_2Ru_2S_4$ cube. Selected interatomic distances (Å): Ti(1)–Ti(2), 3.060(1); Ti(1)–Ru, 2.9440(8); Ti(2)–Ru, 2.9269(8); Ru–Ru*, 3.547(1); Ti(1)–S(1), 2.351(1); Ti(1)–S(2), 2.257(2); Ti(2)–S(1), 2.350(1); Ti(2)–S(3), 2.261(2); Ru–S(1), 2.356(1); Ru–S(2), 2.3956(9); Ru–S(3), 2.385(1).

type core with an approximate C_{2v} symmetry.[14] The long Ru–Ru distance of 3.547(1) Å precludes any direct metal–metal bonding. The Ti–Ti distance in **4** (3.060(1) Å) is considerably longer than the shortest edge of the nonbonding contacts in oxygen- or nitrogen-bridged Ti(IV)–Ti(IV) centers (2.724(1)–2.82(mean) Å).[15] The distance is, however, somewhat shorter than the nonbonding distances found in the sulfido-bridged dititanium(IV) complexes (3.141(3)–3.244(1) Å),[16–18] and falls in the range of the Ti–Ti distances in the cubane-type sulfido cluster with four skeletal electrons $[(Cp'Ti)_4(\mu_3\text{-}S)_4]$ (2.927(13)–3.008(10) Å; Cp' = η^5-C_5H_4Me)[19] and the clusters with three skeletal electrons $[\{CpTi(OC_6H_3Pr^i{}_2\text{-}2,6)\}_3(\mu_3\text{-}S)_3TiCp]$[16] and $[(CpTi)_5(\mu_3\text{-}S)_6]$[20] (3.076(5)–3.214(5) Å). These observations imply a weak Ti–Ti interaction in **4**. The four Ti–Ru distances of 2.9269(8) and 2.9440(8) Å are significantly shortened from that in **3** (3.138(1) Å) and we tentatively describe these interactions as a dative bond from the ruthenium atom to the titanium atom.[21]

Generation of terminal[22] or bridging[3a–d] sulfido species through α-elimination from hydrosulfido complexes has already been demonstrated. Interestingly, formal α-elimination of CpH also occurred in the reaction of **3** with triethylamine.[23] This sharply contrasts with the simple deprotonation of the hydrosulfido-bridged heterobimetallic complex $[Cp_2Ti(\mu_2\text{-}SH)_2Mo(CO)_4]$ upon treatment with base.[7] However, loss of cyclopentadienyl ligands from titanocene fragments during the formation of polynuclear titanium sulfido complexes has some precedents.[17,20,24] A closely related example is the formation of the sulfido-bridged dititanium complex $Na_2[CpTi(\mu_2\text{-}S)S]_2$ from the reaction of **1** with one equiv of NaH;[18] this reaction also may be recognized as a result of α-elimination of CpH from **1**.

Most of mixed-metal cubane-type sulfido clusters have been prepared by a spontaneous self-assembly of the mononuclear species, or incorporation of heterometals into di- or trinuclear homometallic sulfide precursors;[25] dimerization of the sulfido-bridged heterobimetallic fragments is a limited approach so far.[26] However, we believe that stepwise construction of cubane-type sulfido clusters by the latter method provides a rational and versatile pathway for cubane-type sulfido clusters. Actually, this has been successfully applied to the synthesis of the mixed-metal cubane-type cluster **4**, a rare example of mixed-metal sulfido clusters of titanium.[24c,27] Further studies on syntheses of hydrosulfido-bridged heterobimetallic complexes and their transformation into cubane-type sulfido clusters through this synthetic strategy are now in progress.

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9 Crystallographic data for **3**: $C_{20}H_{27}ClRuS_2Ti$, M = 515.98, orthorhombic, $P2_12_12_1$, a = 15.800(2), b = 16.424(4), c = 8.073(2) Å, V = 2095.1(6) Å^3, Z = 4, d_c = 1.636 g cm^{-3}, F_{000} = 1048, μ (Mo Kα) = 14.30 cm^{-1}. Full-matrix least-squares refinements of 227 parameters obtained by using 1919 reflections ($I > 3\sigma(I)$) collected on a Rigaku AFC7R diffractometer gave residuals of R = 0.028 and R_w = 0.022.

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13 **4**: ^{1}H NMR ($CDCl_3$): δ 5.58 (s, 10 H, C_5H_5), 1.54 (s, 30 H, C_5Me_5). Anal. Found: C, 43.61; H, 4.95%. Calcd for $C_{30}H_{40}Ru_2S_4Ti_2$: C, 43.58; H, 4.88%.

14 Crystallographic data for **4**: $C_{30}H_{40}Ru_2S_4Ti_2$, M = 826.83, orthorhombic, $Pnma$, a = 16.799(1), b = 19.335(2), c = 10.035(1) Å, V = 3259.4(5) Å^3, Z = 4, d_c = 1.685 g cm^{-3}, F_{000} = 1664, μ (Mo Kα) = 16.57 cm^{-1}. Refinements of 182 parameters obtained by using 2723 reflections ($I > 3\sigma(I)$) gave residuals of R = 0.032 and R_w = 0.024.

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