

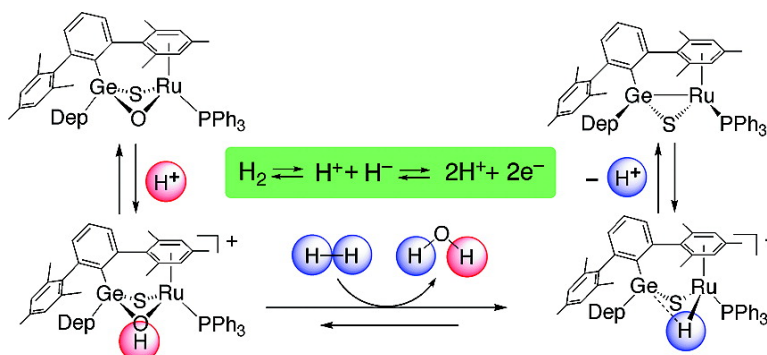
Communication

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A Functional Hydrogenase Model: Reversible Interconversion of H₂ and H₂O by a Hydroxo/Sulfido-Bridged Dinuclear Ruthenium–Germanium Complex

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The heterolytic activation of dihydrogen has been recognized as one of the fundamentally important reactions in organometallic chemistry and catalysis.¹ The heterolysis of dihydrogen on transition metals has also been claimed as a key step for the hydrogen metabolism in nature mediated by hydrogenases, where dihydrogen is reversibly transformed into two protons and two electrons via a heterolytic cleavage mechanism (eq 1).² Although there are many examples of heterolytic H₂ cleavage promoted by transition metal complexes,^{3–5} reports on the reversible transformation between dihydrogen and protons + electrons are limited.⁶



In the course of our studies of transition-metal/germanium mixed-metal complexes,⁷ we have reported that the S/O bridged dinuclear

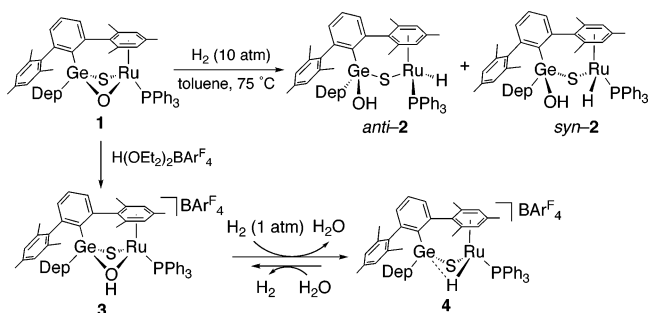
Ru–Ge complex $\text{Dmp}(\text{Dep})\text{Ge}(\mu\text{-S})(\mu\text{-O})\text{Ru}(\text{PR}_3)$ (**1**) activates dihydrogen heterolytically to afford two isomers, *anti*-**2** and *syn*-**2** (Scheme 1 (top), Dmp = 2,6-dimesitylphenyl, Dep = 2,6-diethylphenyl).^{7a} This reaction however occurs rather slowly even at 75 °C under 7.5–10 atm of H₂. Herein we report that the related

S/OH bridged dinuclear Ru–Ge complex cation, $[\text{Dmp}(\text{Dep})\text{Ge}(\mu\text{-S})(\mu\text{-OH})\text{Ru}(\text{PR}_3)](\text{BAR}^{\text{F}_4})$ (**3**), which was synthesized quantitatively by the protonation of **1** with $\text{H}(\text{OEt}_2)_2\text{BAR}^{\text{F}_4}$ ($\text{Ar}^{\text{F}} = 3,5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3$),^{7b} promotes *facile* and reversible H₂ activation leading to H₂O and the S/H bridged Ru–Ge complex cation $[\text{Dmp}(\text{Dep})\text{Ge}(\mu\text{-S})(\mu\text{-H})\text{Ru}(\text{PR}_3)](\text{BAR}^{\text{F}_4})$ (**4**).

When a toluene solution of **3** was stirred at room temperature under an atmospheric pressure of H₂, the color of the solution turned from reddish yellow to light yellow, and the μ -hydride complex **4** was isolated quantitatively. Thus, in contrast to the sluggish activity of **1** toward H₂, protonation of the μ -O in **1** to produce **3** facilitates H₂ activation under much milder conditions, generating **4** and H₂O.⁸ The formation of H₂O was confirmed by monitoring the ¹H NMR of the reaction in benzene-*d*₆. In this reaction, a dihydrogen molecule is heterolytically cleaved by **3** and is converted to a hydride bridging Ru and Ge in **4** and to a proton trapped by the μ -OH of **3** to form H₂O which dissociates (Scheme 1 (bottom)). According to a kinetic study using ¹H NMR, the reaction under 1 atm H₂ obeys pseudo-first-order kinetics for **3**, namely, $-d[\mathbf{3}]/dt = k_{\text{H}}[\mathbf{3}]$, with a rate constant $k_{\text{H}} = 2.1(1) \times 10^{-4} \text{ s}^{-1}$ at 298 K. The rate was not affected by the presence of 5 equiv PPh₃. We have also monitored the reaction of **3** with 1 atm D₂ in benzene-*d*₆ by ¹H NMR. Signals for HD and H₂ appeared within 5 min, along with the signals of the μ -OD complex, **3-*d***₁ (D content 70%), and the μ -D complex **4-*d***₁ (D content 90%). Note that the reaction of **4** and D₂ in 5 min did not give HD.

The H₂ activation by **3** may be initiated by the coordination of H₂ to a vacant site at Ru, for example, created by dissociation of

Scheme 1



the Ru–OH bond, or a direct σ -bond metathesis mechanism may be operative between the Ru–O(H) bond and H₂. In either way, the weaker Ru–OH bond, relative to the Ru–O bond of **1**, could be a reason behind the facile H₂ activation by **3**.

The X-ray derived structure of **4** is shown in Figure 1.⁹ The Ru(1)–H(68) distance is understandably elongated compared to the terminal Ru–H bonds of *anti*-**2** [1.57(3) Å] and *syn*-**2** [1.55(2) Å],^{7a} and is similar to those of μ -hydride complexes such as $[(\eta^5\text{-C}_5\text{H}_3)_2\text{-}(\text{SiMe}_2)_2]\text{Ru}_2(\text{CO})_4(\mu\text{-H})(\text{BF}_4)$ [1.741(4), 1.768(5) Å] and $[(p\text{-cymene})\text{RuCl}]_2(\mu\text{-Cl})(\mu\text{-H})$ [1.75(2), 1.76(3) Å].¹⁰ The Ge(1)–H(68) distance is even longer than the Ru(1)–H(68) bond, but is shorter than that of $(\text{depe})_2(\text{CO})\text{Mo}(\eta^2\text{-H-GePh}_2\text{H})$ [2.08(6) Å],¹¹ indicating a weak bonding interaction between Ge and the hydride on Ru. The Ge(1)–Ru(1) distance of 2.5812(5) Å is somewhat longer than those of the Ru–Ge σ -bonds of $(\text{C}_6\text{H}_6)\text{Ru}(\text{CO})(\text{GeCl}_3)_2$ [2.408(2) Å] and *cis*- $\text{Ru}(\text{CO})_4(\text{GeCl}_3)_2$ [2.481(5) Å].¹²

The μ -hydride complex **4** was found to react slowly with excess H₂O, regenerating **3** and H₂. When a benzene-*d*₆ solution of **4** was heated to 80 °C in the presence of 10 equiv H₂O, 80% of **4** was converted to **3** in 17 h, and concomitant formation of H₂ was detected by ¹H NMR. Therefore, activation of H₂ by **3** occurs reversibly. The removal of H₂ is required to facilitate H₂ formation,

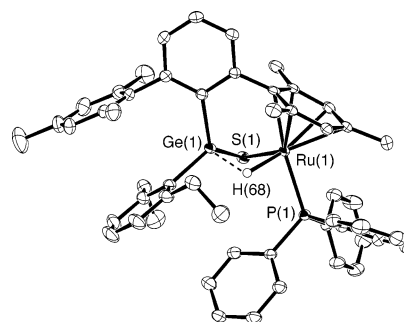
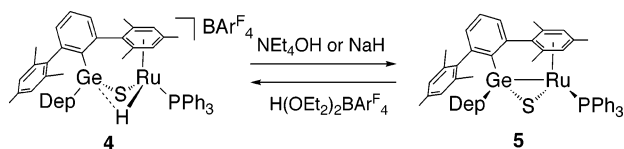


Figure 1. ORTEP drawings of **4**. Selected bond distances (Å) and angles (deg): (4) Ru(1)–S(1), 2.4611(7); Ru(1)–P(1), 2.3402(10); Ru(1)–H(68), 1.77(3); Ge(1)–H(68), 1.91(2); Ge(1)–S(1), 2.1594(10); Ru(1)–Ge(1), 2.5812(5); Ru(1)–S(1)–Ge(1), 67.56(2); Ge(1)–H(68)–Ru(1), 89.0(11).

Scheme 2



and only 5% of **4** was converted to **3** even after 12 h, when the reaction was conducted in a sealed NMR tube. Another important property of **4** is the characteristic protonic behavior of the μ -hydride. Complex **4** does not react with Brønsted acids such as $\text{H}(\text{OEt}_2)_2\text{BARF}_4$ and HOTf. On the other hand, the treatment with tetraethylammonium hydroxide or sodium hydride resulted in quantitative formation of $[\text{Dmp}(\text{Dep})\text{Ge}(\mu\text{-S})\text{Ru}(\text{PR}_3)]$ (**5**) (Scheme 2). Conversely, the protonation of **5** by $\text{H}(\text{OEt}_2)_2\text{BARF}_4$ in toluene gave **4**, again quantitatively. The molecular structure of **5**, determined by X-ray analysis, is shown in Figure 2. Upon deprotonation of **4**, the Ru–Ge distance is shortened by 0.153 Å, and the Ru–P bond length of **5** is also 0.035 Å shorter than that of **4**.

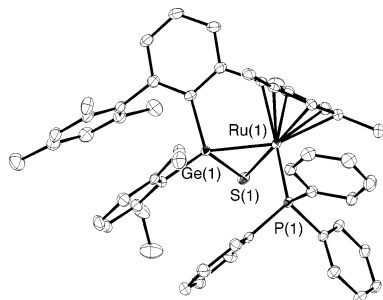
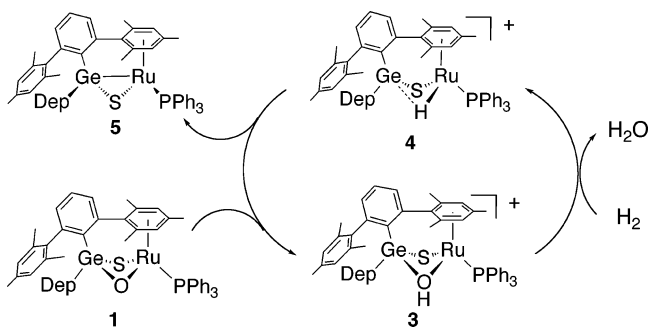


Figure 2. ORTEP drawing of **5**. Selected bond distances (Å) and angles (deg): Ru(1)–Ge(1), 2.4285(5); Ru(1)–S(1), 2.4860(5); Ru(1)–P(1), 2.3048(6); Ge(1)–S(1), 2.1877(5); Ru(1)–S(1)–Ge(1), 62.228(14).

Interestingly, the acidity of the μ -hydride of **4** is sufficiently high to transform **1** into **3**. When a C_6D_6 solution of **1** with a catalytic amount of $\text{H}(\text{OEt}_2)_2\text{BARF}_4$ (1 mol %) was heated to 70 °C for 24 h under an H_2 atmosphere, **5** and H_2O were formed in 95% yield. In this catalytic conversion of **1** to **5**, H_2 is consumed formally as two protons generating H_2O , and two electrons which are stored in **5** as the Ge–Ru bond or as Ru d-electrons (Scheme 3). Thus, activation of H_2 using Ge–Ru complexes as described in this paper provides an intriguing functional model of hydrogenases. In particular, it may mimic the interconversion among the various states

Scheme 3^a

^a The catalytic cycle is initiated by a trace of $\text{H}(\text{OEt}_2)_2\text{BARF}_4$ converting **1** to **3**.

of [NiFe] hydrogenase. The [NiFe] hydrogenase contains a dinuclear Ni–Fe framework bridged by two cysteine thiolates and an O-donor ligand in the inactive oxidized/reduced forms.² The O-donor ligand is absent in the active reduced form, and the nickel approaches the iron, either to form a direct Ni–Fe bond or a μ -hydride bridged metal pair.² In this regard, the μ -O complex **1**, the μ -OH complex **3**, and the μ -H complex **4** may respectively correspond to the *Ni-SU*, the *Ni-SI_r*, and the *Ni-SI_a* states of [NiFe] hydrogenase presumably with a common oxidation state.^{2a,c} Further, complex **5** could be a model of the active reduced *Ni-C* (or the *Ni-R*) state. Another important observation from our studies of this Ru–Ge system is that the μ -OH complex **3** reacts with H_2 much more readily than the μ -O complex **1**.

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Supporting Information Available: X-ray crystallographic data in CIF format for complexes **4** and **5** and the experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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