Dihydrogen Activation

DOI: 10.1002/anie.200704899

Heterolytic Dihydrogen Activation by a Sulfido- and Oxo-Bridged Dinuclear Germanium–Ruthenium Complex**

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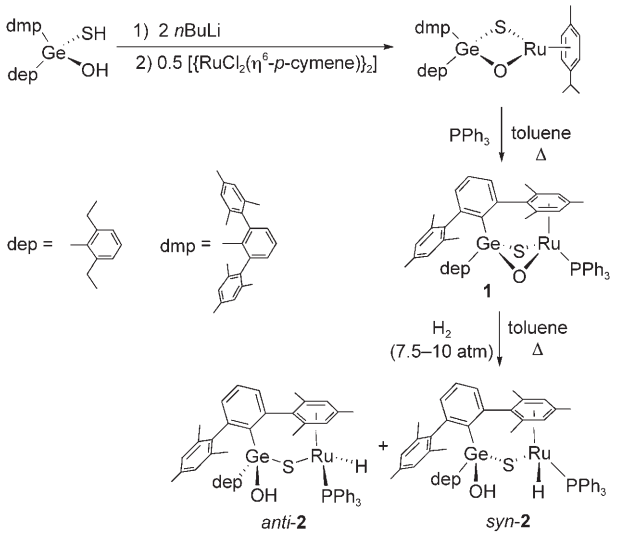
Heterolytic cleavage of dihydrogen on transition metal sulfides/thiolates has been regarded as the key reaction in hydrogen metabolism in nature[1] and in catalytic desulfurization of fossil fuel.[2] Although there are numerous reports of heterolytic dihydrogen activation,[3,4] that occurring at metal–sulfur bonds is still limited. A representative example is the reaction of $[\{Rh(triphos)\}_2(\mu\text{-}S)_2]^{2+}$ (triphos = tris(diphenylphosphanylethyl)methane) with H_2 to generate $[\{RhH(triphos)\}_2(\mu\text{-}SH)_2]^{2+}$.[4a,b] Heterolytic H_2 cleavage was also reported to be promoted by sulfido/thiolato-bridged dinuclear Mo–Mo,[4c–e] Ir–Ir,[4f] and W–Ir[4g] complexes and mononuclear sulfido/thiolato complexes of Ti,[4h-i] Ni, Ru, and Rh.[4j–n] In the course of our studies on transition metal sulfide/thiolate complexes,[5] we found that sulfido-bridged W–Ru complexes activate H_2 in a heterolytic manner.[5c]

Here we report heterolytic cleavage of H_2 by the sulfido- and oxo-bridged heterodinuclear germanium–ruthenium complex [(dmp)(dep)Ge(μ-S)(μ-O)Ru(PPh_3)] (**1**; dmp = 2,6-dimesitylphenyl, dep = 2,6-diethylphenyl). As we showed previously, the μ-S ligand of **1** prefers softer acids, and the μ-O ligand harder acids.[6] The synergetic μ-sulfide and μ-oxide pair plays an important role in H_2 heterolysis by **1**.

Heterodinuclear complex **1** was prepared from [(dmp)(dep)Ge(SH)(OH)], $[RuCl_2(\eta^6\text{-}p\text{-cymene})]$, and PPh_3 according to Scheme 1.[6] No H_2 activation by **1** took place under an atmospheric pressure of dihydrogen even at 90 °C. However, complex **1** was converted slowly to *anti* and *syn* isomers of hydroxy hydride complex **2** when heated to 75 °C in toluene under 10 atm of H_2 (Scheme 1, Table 1). As is obvious from the structures of *anti*-**2** and *syn*-**2**, H_2 was cleaved heterolytically by **1** into a hydroxy-bound proton on Ge and a hydride ligand on Ru.

Dihydrogen activation was examined under various conditions to obtain insight into the reaction mechanism. Intriguingly, *anti*-**2** is the favored product in the early stage of the reaction (Table 1, entry 1). The relative ratio of *syn*-**2** to *anti*-**2** slowly increases as the reaction proceeds, and eventually *syn*-**2** becomes the exclusive product at 90 °C after 3 days under 7.5 atm H_2 (Table 1, entry 5). The results suggest that the kinetically favored product is *anti*-**2**, which gradually isomerizes to the more thermodynamically stable *syn*-**2**.



Scheme 1. Synthesis of **1** and the H_2 activation.

Table 1: Product ratio for H_2 activation by **1**.

Entry	Reaction conditions				Product ratio[a]			
	T [°C]	*t* [h]	*p*(H_2) [atm]	Additive	**1**	*anti*-**2**	*syn*-**2**	*anti*-**2**/*syn*-**2**
1	75	6	10	–	32	52	16	3.3
2	75	6	10	PPh_3[b]	36	49	15	3.3
3	75	24	10	–	2	73	25	2.9
4	75	24	10	PPh_3[b]	2	71	27	2.6
5	90	72	7.5	–	0	0	100	0.0
6	90	72	7.5	PPh_3[b]	0	34	66	0.5

[a] The product ratio was estimated by ^{1}H NMR spectroscopy. Complexes **1** and/or *anti*-**2**, *syn*-**2** were exclusively observed by ^{1}H NMR spectroscopy. [b] 10 equiv PPh_3.

Addition of 10 equiv PPh_3 hardly affects the reaction of **1** with H_2. No significant deceleration of the consumption of **1** was observed, either for the reactions at 75 °C for 6 h (Table 1, entries 1 and 2) or for those at 24 h (Table 1, entries 3 and 4), that is, the rate-determining step does not include PPh_3 dissociation. On the other hand, the subsequent isomerization from *anti*-**2** to *syn*-**2** is clearly decelerated by addition of PPh_3, as is manifested in the results at 90 °C and 72 h (Table 1, entries 5 and 6). The isomerization appears to be accompanied by dissociation of PPh_3.

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[**] This work was supported by Grant-in-Aid for Scientific Research on Priority Areas (No. 18065013, "Chemistry of Concerto Catalysis") from Ministry of Education, Culture, Sports, Science and Technology (Japan).

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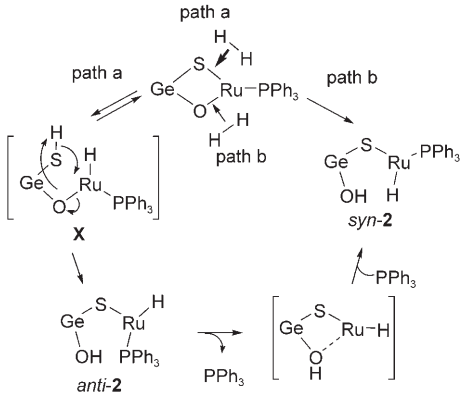
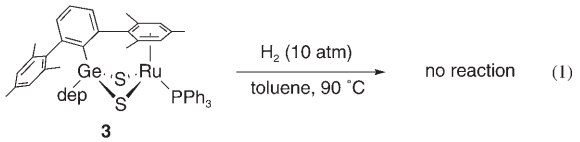
On the basis of these facts, we propose the mechanism of H_2 heterolysis summarized in Scheme 2. As a premise, H_2 activation between two molecules of **1** is excluded, because of the steric bulk of **1**.[6] The activation of H_2 may occur stepwise



Scheme 2. Proposed mechanism of H_2 heterolysis by **1**. Some of the substituents on Ge and Ru are omitted for clarity.

via initial coordination to the Ru atom with slippage of the η^6-arene and successive heterolytic cleavage.[7] On the other hand, the H_2 molecule could undergo a straightforward σ-bond metathesis.[8] We do not have any evidence to support either pathway.

If H_2 heterolysis occurs at the Ru–O bond (path b), it straightforwardly affords *syn*-**2**. However, path b does not account for the formation of *anti*-**2** as the kinetic product. The most conceivable pathway affording *anti*-**2** proceeds by H_2 heterolysis at the Ru–S bond (path a). This pathway should form **X**, which would be further transformed into *anti*-**2** by migration of the SH proton to the μ-oxo ligand with concomitant Ru–S bond formation and Ru–O bond dissociation. The proposed intermediate **X** has not been detected. We examined H_2 activation with a bis(μ-S) analogue of **1**, namely, [(dmp)(dep)Ge(μ-S)$_2$Ru(PPh$_3$)] (**3**), at 90 °C under 10 atm H_2, anticipating the formation of the μ-S analogue of **X**. However, complex **3** was recovered quantitatively [Eq. (1)]. This result suggests that H_2 activation at Ru–S bonds is reversible, and furthermore that intermediate **X** and its μ-S analogue are considerably less stable than **1** and **3**, respectively. It seems that the key to H_2 activation via path a is subsequent proton migration onto the hard μ-oxo ligand to generate stable *anti*-**2**.



The hard nature of the μ-oxo ligand of **1** was demonstrated by μ-O-protonation of **1**.[6] The preference for path a could be due to the softness of the μ-S compared to the μ-O moiety, as was also observed in the reaction of **1** with MeOTf.[6]

Isomerization of *anti*-**2** to *syn*-**2** proceeds via dissociation of the phosphine ligand. Although the mechanism of this isomerization process is not entirely clear, it may involve weak H_2 coordination at Ru to compensate for PPh_3 dissociation. In fact, isomerization of preformed *anti*-**2** is even slower in the absence of H_2, for example, requiring 9 days in toluene at 90 °C. A basis for the relative thermodynamic stability of *syn*-**2** compared to that of *anti*-**2** can be deduced from their crystal structures (Figure 1).[9] The

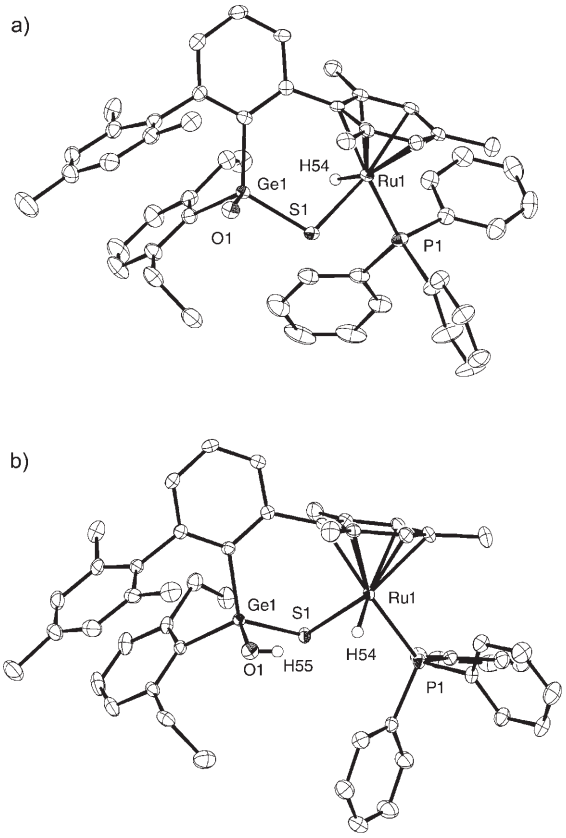


Figure 1. ORTEP drawings of a) *anti*-**2** and b) *syn*-**2**.

strained *m*-terphenyl arrangement of dmp in *anti*-**2** is reflected in the significantly smaller dihedral angle of 67° between the central arene ring of dmp and its Ru-coordinated mesityl ring, while those for both **1** and *syn*-**2** are 87°. The strained dmp conformation in *anti*-**2** is attributable to intramolecular steric congestion between the triphenylphosphine ligand and the hydroxy group, whereas the conformational strain in dmp is relieved in the structure of *syn*-**2**. The GeOH···HRu interaction for *syn*-**2** also contributes to its relative thermodynamic stability. The H···H interaction is indicated by the H54–H55 and O1–H54 distances of 2.25(3) and 2.95(2) Å, respectively, as derived from X-ray data.[10] This nonclassical hydrogen bonding is also manifested in the ^{1}H NMR spectrum. An nOe measurement on *syn*-**2** showed 17% enhancement of GeO*H* at $\delta = 2.73$ ppm on irradiation of Ru*H* at $\delta = -9.04$ ppm in C_6D_6. In the IR spectrum, the lower frequency of the Ru–H stretching band of *syn*-**2** at

1940 cm^{-1} relative to that of *anti*-**2** at 2015 cm^{-1} may also indicate a nonclassical hydrogen-bonding interaction.

In conclusion, the S/O-bridged dinuclear germanium–ruthenium complex **1** activates H_2 heterolytically at the ruthenium–chalcogen bonds. Cooperation of the μ-S and μ-O atoms is significant in the mechanism of H_2 activation.

Received: October 23, 2007
Revised: November 23, 2007
Published online: January 25, 2008

Keywords: germanium · heterometallic complexes · oxo ligands · ruthenium · sulfido ligands

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[9] The metric parameters are included in the Supporting Information. CCDC-610035 (*anti*-**2**) and -610036 (*syn*-**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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