Dicationic Thiolate-Bridged Diruthenium Complexes for Catalytic Oxidation of Molecular Dihydrogen

Masahiro Yuki,[†] Ken Sakata,*,[‡] Kazunari Nakajima,[†] Syoma Kikuchi,[‡] Shinobu Sekine,[§] Hiroyuki Kawai,[§] and Yoshiaki Nishibayashi*,[†]

[†]Department of Systems Innovation, School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
[‡]Faculty of Pharmaceutical Sciences, Hoshi University, Ebara, Shinagawa-ku, Tokyo 142-8501, Japan
[§]Fuel Cell System Engineering & Development Division, Toyota Motor Corporation, Mishuku, Susono, Shizuoka 410-1193, Japan

Ⓢ *Supporting Information*

ABSTRACT: Dicationic thiolate-bridged diruthenium complexes bearing sterically bulky alkane substituents on the thiolate ligands such as $[Cp*Ru(\mu\text{-}S^iPr)_2Ru(OH_2)Cp*](OTf)_2$ have been found to work as effective catalysts toward oxidation of molecular dihydrogen into protons and electrons in protic solvents such as water and methanol. DFT calculations indicate that the sterically bulky alkane substituent in the complex plays an important role in facilitating the reaction step of the coordination of molecular dihydrogen.
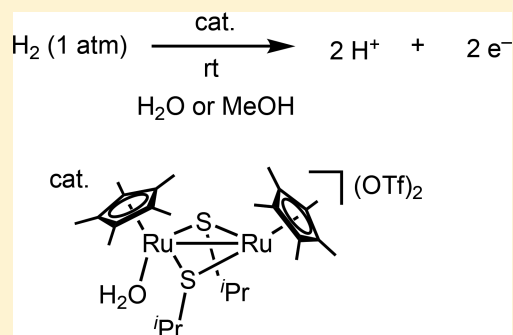
INTRODUCTION

Molecular dihydrogen is one of the promising candidates for the storage of renewable energy.[1] A polymer electrolyte fuel cell (PEFC) generates electricity from molecular dihydrogen at low temperature for the use of automobiles and portable devices. However, a major obstacle to hydrogen-based systems is that the state of the art PEFC employs the most precious metal platinum as an electrocatalyst. As a result, to avoid the use of platinum, the exploration of alternative catalysts is an important subject in the research field of PEFCs.

In nature, hydrogenase enzymes interconvert molecular dihydrogen to protons and electrons efficiently under ambient conditions. These hydrogenases are classified as [NiFe] and [FeFe] hydrogenases in terms of the metal composition of active sites. Recently, crystallographic, spectroscopic, and electrochemical investigations have been carried out to disclose relationships between the structures and functions of hydrogenases.[2] The active sites of the hydrogenase enzymes are sulfur-bridged bimetallic cores deeply buried in the protein matrix. These [NiFe] and [FeFe] bimetallic cores are interfaced to the outer sphere of the enzyme through three precisely organized pathways: namely, a hydrogen bond network for proton relay,[3] iron–sulfur clusters for electron transfer,[4] and hydrophobic cavities for dihydrogen delivery.[5]

The sophisticated catalytic system of the hydrogenase enzymes has inspired the design of artificial catalysts.[6] However, successful examples of molecular catalysts capable of performing oxidation of molecular dihydrogen have been limited until now.[7−18] DuBois and co-workers developed a series of mononuclear nickel complexes as mononuclear functional models of the hydrogenase enzymes.[7−14] In this system, a precisely positioned amine moiety in the complexes promoted proton relays and the interconversion of molecular dihydrogen into protons and electrons.[7] At present, this nickel system is the most active organometallic catalyst and its electrocatalytic performance as the immobilized catalyst has become close to that of the conventional platinum catalyst under relevant fuel-cell conditions.[7c,k,m,o] Similarly, some iron and manganese complexes have been reported as mononuclear functional models of the hydrogenase enzymes.[8,9] Some research groups found bimetallic mimics of the hydrogenase enzymes.[15−18] Ogo and co-workers reported the preparation of thiolate-bridged nickel−ruthenium, −iron, and −iridium complexes as mimics of [NiFe] hydrogenase enzyme and their reactivity toward oxidation of molecular dihydrogen,[15a−e] although a thiolate-bridged nickel−iron complex had a substoichiometric activity toward molecular dihydrogen.[15f] Rauchfuss and co-workers demonstrated that the use of a thiolate-bridged diiron complex bearing a ferrocene derivative as an electron reservoir promoted the oxidation of molecular dihydrogen catalytically.[16]

In an extensive study on the development of a novel catalytic activity of thiolate-bridged dinuclear ruthenium complexes,[19,20] we found that thiolate-bridged diruthenium complexes bearing a triarylphosphine[21] and pendant ethers[22] on the thiolate ligand (1 and 2, respectively; Chart 1) worked as effective catalysts toward the oxidation of molecular dihydrogen. The catalytic activity reached up to 10000 TON (turnover number) when 1

Chart 1. Oxidation of Molecular Dihydrogen Catalyzed by Thiolate-Bridged Diruthenium Complexes

Scheme 1. Preparation of Thiolate-Bridged Diruthenium Complexes Bearing Various Alkane Substituents
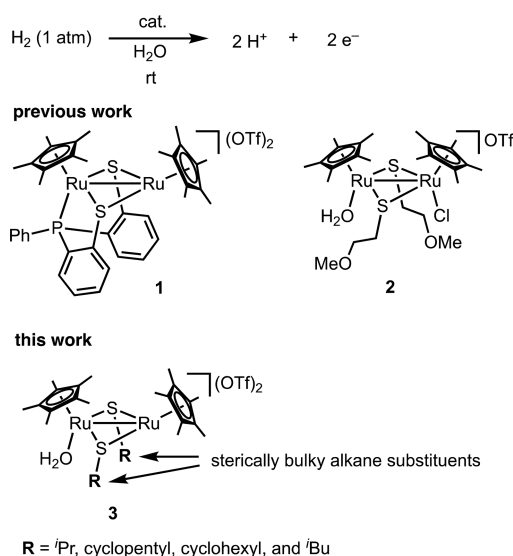
was used as a catalyst. In these cases, however, stepwise processes and preliminary syntheses of thiols involving functional groups such as phosphine and ether moieties are necessary to prepare these thiolate-bridged diruthenium complexes. This research background prompted us to investigate the use of more simple and convenient thiolate-bridged diruthenium complexes by readily preparative methods. After a detailed study, we have found that dicationic thiolate-bridged diruthenium complexes bearing sterically bulky alkane substituents on the thiolate ligands $[Cp*Ru(\mu-SR)_2Ru(OH_2)-Cp*](OTf)_2$ (3; R = ^iPr, cyclopentyl, cyclohexyl; $Cp*$ = η^5-C_5Me_5) have catalytic activity toward the oxidation of molecular dihydrogen into protons and electrons in protic solvents such as water and methanol. Here, we describe the results of oxidation of molecular dihydrogen catalyzed by dicationic thiolate-bridged diruthenium complexes bearing various alkane substituents on the thiolate ligands together with a theoretical study on the proposed reaction pathway.

■ RESULTS AND DISCUSSION

Preparation of Dicationic Thiolate-Bridged Diruthenium Complexes. According to a similar procedure of the preparation of $[Cp*Ru(\mu-SMe)_2Ru(OH_2)Cp*](OTf)_2$ (3a),[23] dicationic thiolate-bridged diruthenium complexes bearing various alkane substituents on the thiolate ligands $[Cp*Ru(\mu-SR)_2Ru(OH_2)Cp*](OTf)_2$ (3b, R = ^iPr;[23] 3c, R = cyclopentyl; 3d, R = cyclohexyl; 3e, R = ^iBu ($(CH_3)_2CHCH_2-$); 3f, R = Et; 3g, R = ^nPr) were prepared in good to high yields from reactions of $[Cp*RuCl]_4$ with the corresponding disulfide in THF followed by treatment with 2 equiv of AgOTf in CH_2Cl_2 at room temperature for 20 h (Scheme 1). A detailed molecular structure of 3c was determined by X-ray analysis. An ORTEP drawing of 3c is shown in Figure 1, which clearly shows that an OTf anion and water are coordinated to the ruthenium atoms, respectively. This molecular structure of 3c is quite different from that of 3a. As previously reported by our group,[23] no coordination of a OTf anion to the ruthenium atoms in the complex was observed in the structure of 3a. In sharp contrast to the molecular structures of 3a,c in the solid state, the behavior in the solution state is almost the same in both cases.
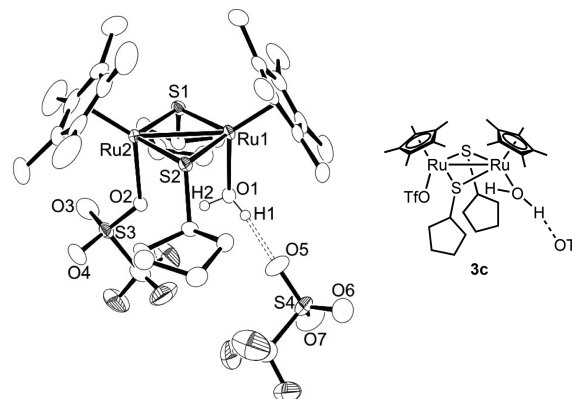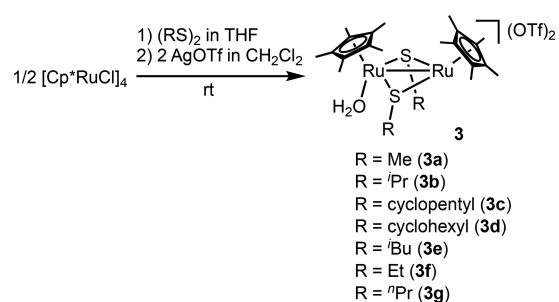
Figure 1. ORTEP drawing of $[Cp*Ru(\mu-S-cyclo-C_5H_9)_2Ru(OH_2)-Cp*](OTf)_2$ (3c). Selected interatomic distances (Å): Ru1−Ru2 2.8076(3), Ru1−S1 2.3262(6), Ru1−S2 2.3110(6), Ru2−S1 2.3173(6), Ru2−S2 2.3159(6), Ru1−O1 2.1926(18), Ru2−O2 2.2545(16).

In fact, ^1H NMR spectra of 3a,c in $CDCl_3$ indicate that only one peak derived from two $Cp*$ moieties in the complexes was observed in both complexes. These results suggest that the ligand exchange of OTf anion and water on the ruthenium atoms readily occurs even at room temperature. Taking into consideration the dissociative ability of the OTf anion, we have expressed dicationic thiolate-bridged diruthenium complexes in the present paper as the general formula $[Cp*Ru(\mu-SR)_2Ru-(OH_2)Cp*](OTf)_2$.

Catalytic Oxidation of Molecular Dihydrogen. At first, we carried out the catalytic oxidation of molecular dihydrogen in the presence of a catalytic amount of dicationic methanethiolate-bridged diruthenium complex 3a according to the same experimental procedure shown in our previous paper.[22] In this case, the reaction did not proceed smoothly, where a long reaction time such as 12 h is necessary to complete the catalytic oxidation (Table 1, run 1). The catalytic activity of 3a is quite similar to that of the monocationic methanethiolate-bridged diruthenium complex $[Cp*RuCl(\mu-SMe)_2Ru(OH_2)Cp*]OTf$ (4), whose catalytic activity was previously investigated by our group.[22] On the other hand, the use of the dicationic thiolate-bridged diruthenium complex bearing sterically bulky ^iPr groups on the thiolate ligands $[Cp*Ru(\mu-S^iPr)_2Ru(OH_2)Cp*](OTf)_2$ (3b) as a catalyst promoted oxidation of molecular dihydrogen rapidly under the same reaction conditions. A typical experimental procedure using 3b as a catalyst is as follows. A water solution (5 mL) of $[Cp_2Fe]OTf$ (0.40 mmol) as an oxidant and 3b (0.002 mmol) as a catalyst was stirred at room temperature under 1 atm of

Table 1. Catalytic Oxidation of Molecular Dihydrogen in the Presence of Catalyst in Water[a]
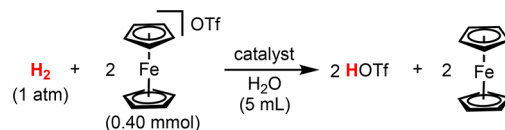
| run | catalyst (amt (mmol)) | reacn temp (°C) | reacn time (h) | amt (mmol) | | amt of consumed H_2 (mmol) | TON[d] | TOF[e] (h^{-1}) |
				HOTf[b] (mmol)	ferrocene[c] (mmol)			
1	**3a** (0.002)	room temp	12	>0.39	0.39		98	8
2	**3b** (0.002)	room temp	0.9	>0.39	0.37	0.19	93	103
3	**3b** (0.0001)	70	0.9	0.39	0.39		1950	2167
4	**3c** (0.0001)	70	2.5	0.38	0.38		1900	760
5	**3d** (0.0001)	70	3.5	0.39	0.39		1950	557
6	**3e** (0.0001)	70	3.0	0.39	0.39		1950	650
7	**3f** (0.0001)	70	8.0	0.39	0.39		1950	244
8	**3g** (0.0001)	70	4.5	0.39	0.40		2000	444
9	**3a** (0.0001)	70	48	0.38	0.39		1950	41
10[f]	**3b** (0.0002)	room temp	0.12	0.39	0.36		900	7500
11[f]	**3b** (0.00004)	room temp	1.4	0.39	0.40		5000	3571
12	**5** (0.002)	room temp	1.0	>0.39	0.39	0.19	98	98

[a]Reactions of [Cp$_2$Fe]OTf (0.40 mmol) were carried out under 1 atm of H_2 in the presence of catalyst in water (5 mL). [b]The amount of acid was estimated by titration with KOH aqueous solution. [c]The amount of ferrocene was determined by ^{1}H NMR with an internal standard. [d]TON = (amount of ferrocene (mmol))/(amount of catalyst (mmol))/2. [e]TOF = TON/(reaction time (h)). [f]MeOH (5 mL) was used in place of H_2O as solvent.

molecular dihydrogen. After 0.9 h, the complete consumption of [Cp$_2$Fe]OTf was confirmed by the disappearance of its blue color and the formation of ferrocene (Cp$_2$Fe) was observed as a yellow precipitate. The TON and turnover frequency (TOF) were estimated on the basis of the yield of ferrocene (93% yield), where the TON and TOF were 93 and 103 h^{-1}, respectively (Table 1, run 2). The amounts of the consumed molecular dihydrogen (ca. 0.20 mmol) and the produced HOTf (ca. 0.40 mmol) are also consistent with the stoichiometry of the present catalytic oxidation.

As described in the previous paragraph, the dicationic thiolate-bridged diruthenium complex bearing sterically bulky ^{i}Pr groups on the thiolate ligands has been found to work as an effective catalyst toward the oxidation of molecular dihydrogen under ambient reaction conditions. As the next step, we investigated the catalytic activity of a series of dicationic thiolate-bridged diruthenium complexes bearing sterically bulky alkane substituents on the thiolate ligands (**3b–e**) at higher reaction temperature. The catalytic reaction in the presence of a smaller amount of **3b** (0.0001 mmol) as a catalyst at 70 °C proceeded rapidly without loss of the catalytic activity, the TON and TOF being 1950 and 2167 h^{-1}, respectively (Table 1, run 3). When other dicationic thiolate-bridged diruthenium complexes **3c–e** were used as catalysts at 70 °C, the catalytic oxidation of molecular dihydrogen did not proceed smoothly, and a longer reaction time was necessary to complete the catalytic reaction. Their TOFs are 760, 557, and 650 h^{-1}, respectively (Table 1, runs 4–6). These results indicate that **3b** worked as the most effective catalyst in a series of dicationic thiolate-bridged diruthenium complexes bearing sterically bulky alkane substituents on the thiolate ligands. We also carried out the catalytic reaction at 70 °C in the presence of a catalytic amount of dicationic thiolate-bridged diruthenium complexes bearing n-alkane substituents on the thiolate ligands such as **3f**, **3g**, and **3a**, where these complexes worked as less effective catalysts in comparison to **3b** (Table 1, runs 7–9).

Next, we carried out the catalytic reaction using **3b** as a catalyst in methanol. Reactions in the presence of 0.0002 and 0.00004 mol of **3b** in methanol proceeded quite rapidly, where excellent TONs and TOFs were observed (up to 5000 and 7500 h^{-1}, respectively) (Table 1, runs 10 and 11). This TOF (7500 h^{-1}) is the highest value in the ruthenium-catalyzed reaction systems reported by our group, although the TON is lower than the previous value.[21,22] These results suggest that the catalytic oxidation of molecular dihydrogen proceeded more smoothly in methanol than in water.

To get more information on the reaction pathway, we carried out the following stoichiometric and catalytic reactions. The reaction of **3b** under 1 atm of molecular dihydrogen in dichloromethane–water at room temperature for 1 h gave the corresponding hydride complex [Cp*Ru(μ-S^{i}Pr)$_2$RuHCp*]-OTf[24] (**5**) in 98% isolated yield together with an equimolar amount of HOTf (Scheme 2). We confirmed that the catalytic

Scheme 2. Stoichiometric Reaction of 3b with Molecular Dihydrogen
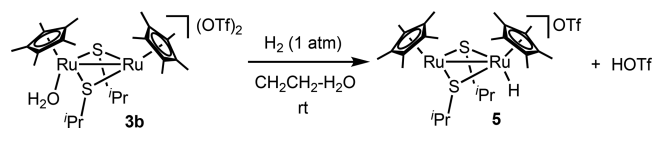
activity of **5** was almost the same with that of **3b** under the same reaction conditions (Table 1, run 12). These results suggest that **5** may be involved as a key reactive intermediate of the catalytic reaction.[25]

The consumption of molecular dihydrogen was monitored in the reaction of [Cp$_2$Fe]OTf in the presence of a catalytic amount of **3b** under molecular dihydrogen in water. The time profile is shown in Figure 2, and typical results are shown in Table 2. In all cases, the reaction rate did not decrease until the end of the catalytic reaction. These results indicate that the reaction rate does not depend on the concentration of
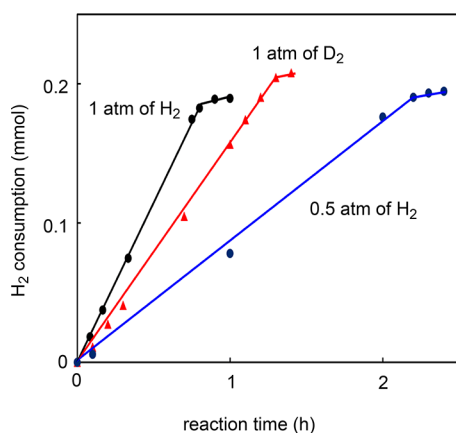
Figure 2. Time profile of H_2 consumption in the oxidation of H_2 with $[Cp_2Fe]OTf$ catalyzed by **3b** in water at room temperature.

$[Cp_2Fe]OTf$ but on the pressure of molecular dihydrogen (Table 2, runs 1 and 2). Separately, we observed the reaction rate with different concentrations of $[Cp_2Fe]OTf$ and under more acidic conditions (Table 2, runs 3 and 4). Interestingly, a substantial isotope effect ($k_{H_2}/k_{D_2} = 1.4$) was observed when D_2 was used in place of H_2 (Table 2, runs 1 and 5). This result suggests that the heterolytic cleavage of molecular dihydrogen on the ruthenium complex may be the rate-determining step of the catalytic reaction.

On the basis of results of the catalytic and stoichiometric reactions, we have proposed the reaction pathway shown in Scheme 3. The dicationic diruthenium complex **A** reacts with molecular dihydrogen to give the monocationic diruthenium–hydrogen complex **C** and an acid via nucleophilic attack of water to the coordinated dihydrogen on the ruthenium atom of the dicationic diruthenium dihydrogen complex **B**. Then, oxidation of **C** affords the dicationic diruthenium hydride complex **D**. Deprotonation of **D** with water and sequential oxidation leads to the formation of the starting **A** via the monocationic diruthenium complex **E**. When methanol is used as a solvent for the catalytic reaction, the deprotonation step of the coordinated dihydrogen on the ruthenium atom with methanol may be accelerated by nucleophilic attack of methanol as a stronger base to the coordinated dihydrogen on the ruthenium atom of **B**. As acceleration of the rate-

Scheme 3. Proposed Reaction Pathway of Oxidation of Molecular Dihydrogen Catalyzed by 3b[a]
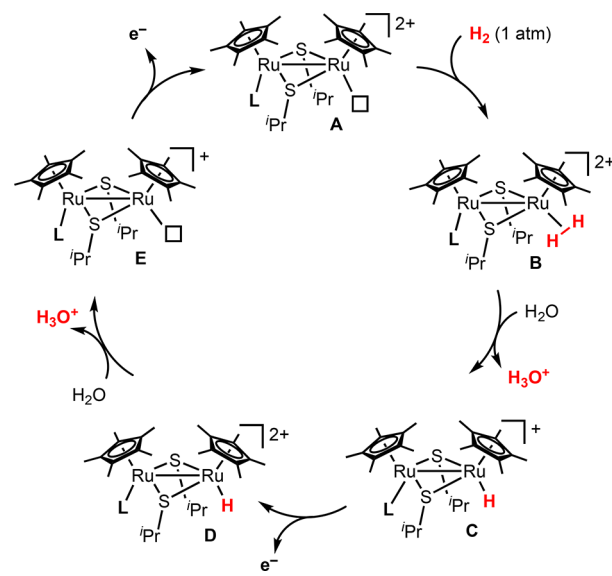

[a]L = H_2O or vacant site.

determining step of the catalytic reaction, the catalytic reaction in methanol proceeded quite rapidly (vide supra).

DFT Calculations of Reaction Pathway. To clarify the effect of sterically bulky ^iPr groups on the thiolate ligands in the diruthenium complex $[Cp*Ru(\mu\text{-}S^iPr)_2Ru(OH_2)Cp*](OTf)_2$ (**3b**) on the catalytic activity, B3LYP-D3//B3LYP level DFT calculations[26−28] were performed for the model reaction system (Figure 3) (SDD for Ru atom[29] and 6-311G** for other atoms[30] were used for basis sets, and the IEF-PCM model[31] was employed for solvent effects of water). The Gibbs free energy ($\Delta G^{298\,K}$) diagram based on the proposed catalytic cycle is shown in Figure 3. The transition state for the dihydrogen coordination to the ruthenium atom at the initial dicationic complex **I** is **TS(I-II)**. In the case of $[Cp*Ru(\mu\text{-}SMe)_2Ru(OH_2)Cp*]^{2+}$ (**3a′**), the activation energy is 13.1 kcal/mol and the reaction energy is endergonic by 4.7 kcal/mol. In the subsequent deprotonation step, the water tetramer $(H_2O)_4$ abstracts one of the coordinated hydrogen atoms (**III** → **TS(III-IV)** → **IV**). The activation energy from **III** to **TS(III-**

Table 2. Catalytic Oxidation of Molecular Dihydrogen in the Presence of Catalyst in Water[a]
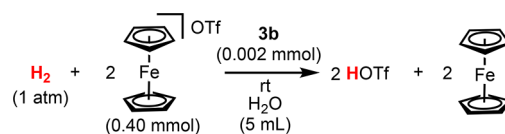
| run | pressure of H_2 (atm) | reacn time (h) | amt (mmol) | | amt of consumed H_2 (mmol) | TON[d] | TOF[e] (h^{-1}) |
			HOTf[b] (mmol)	ferrocene[c] (mmol)			
1	1	0.9	>0.39	0.37	0.19	93	103
2	0.5	2.3	>0.39	0.40	>0.19	100	43
3[f]	1	0.5	>0.19	0.19	0.10	48	95
4[g]	1	0.8	>0.39	0.39	0.19	98	122
5[h]	1	1.3	0.39	0.39	>0.19	98	75

[a]Reactions of $[Cp_2Fe]OTf$ (0.40 mmol) were carried out under 1 atm of H_2 in the presence of **3b** (0.002 mmol) in water (5 mL). [b]The amount of acid was estimated by titration with KOH aqueous solution. [c]The amount of ferrocene was determined by ^{1}H NMR with an internal standard. [d]TON = (amount of ferrocene (mmol))/(amount of catalyst (mmol))/2. [e]TOF = TON/(reaction time (h)). [f]$[Cp_2Fe]OTf$ (0.20 mmol) was used. [g]A dilute H_2SO_4 solution (pH 1) was used as a solvent. [h]D_2 (1 atm) was used in place of H_2
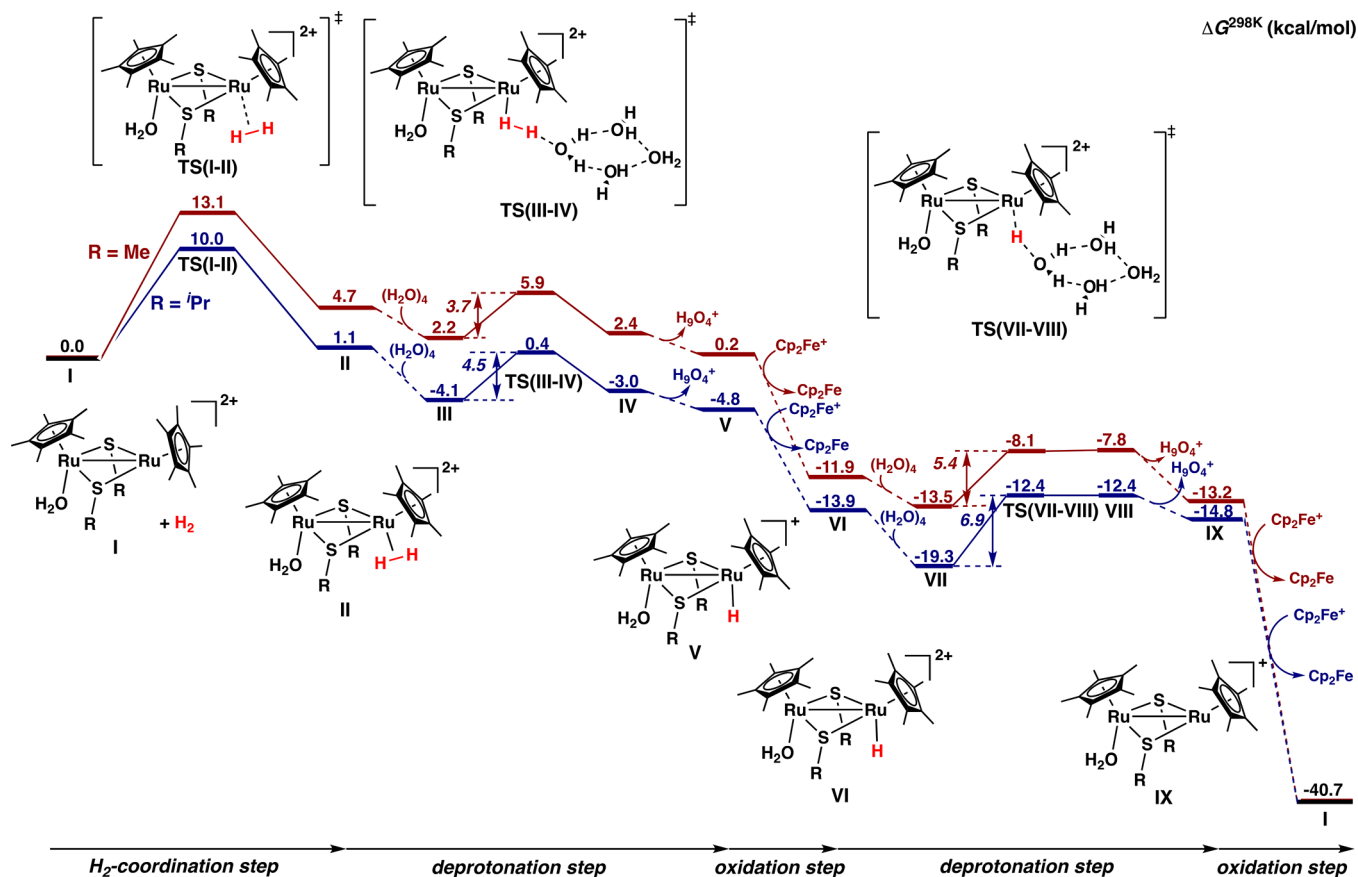
Figure 3. Relative energy diagram (ΔE, kcal/mol) for the model reaction system.
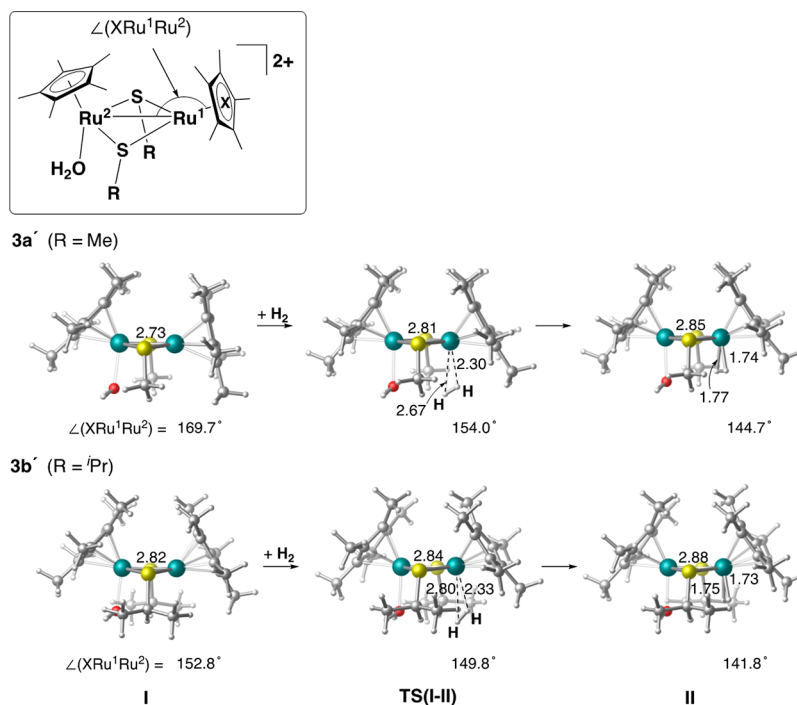
Figure 4. Structural changes along the dihydrogen coordination step. The bond lengths are given in Å. The coordinate of X is the average of the coordinates for five carbon atoms in the Cp* ring which is coordinated to the Ru^1 atom.

IV) is 3.7 kcal/mol. Then, the one-electron oxidation of the monocationic diruthenium hydride complex **V**, in which the $H_9O_4^+$ complex is eliminated from **IV**, is invoked by ferrocenium cation Cp_2Fe^+. This gives a stabilization in energy of 12.1 kcal/mol. In the second deprotonation step (**VII** → **TS(VII-VIII)** → **VIII**), the other hydrogen atom at the

Chart 2. Comparison of Thiolate-Bridged Diruthenium Complexes toward Catalytic Oxidation of Molecular Dihydrogen

$$H_2 \ (1 \ atm) \xrightarrow[\text{rt}]{\text{cat.}} 2 \ H^+ + 2 \ e^-$$

	previous work	previous work	this work
	1	**2**	**3b**
TON	9900	1860	5000
TOF (h⁻¹)	1900	993	7500
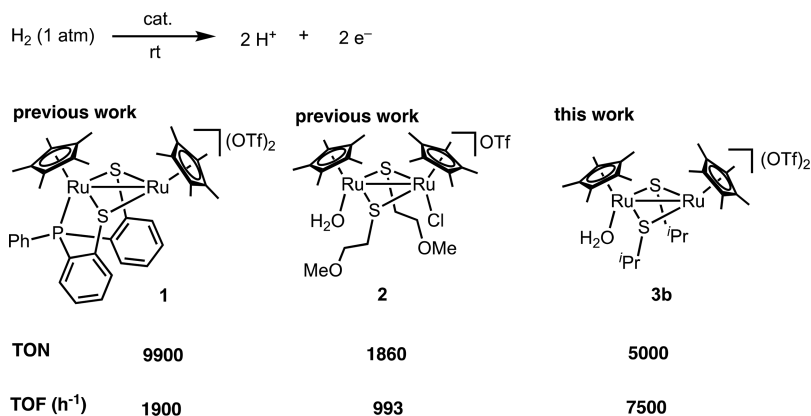
dicationic diruthenium hydride complex **VI** is abstracted by $(H_2O)_4$. The activation energy is 5.4 kcal/mol, which is higher than that of the first deprotonation step. The one-electron oxidation of monocationic complex **IX** regenerates the initial complex **I**. The second oxidation step gives a large stabilization in energy, and the model reaction (Figure 3) is exergonic by 40.7 kcal/mol. The obtained energy diagram is similar to that for previous results.[21,22] In the case of $[Cp*Ru(\mu\text{-}S^iPr)_2Ru\text{-}(OH_2)Cp*]^{2+}$ (**3b′**), the activation energy for the H_2 coordination, 10.0 kcal/mol, is smaller than that for **3a′** (13.1 kcal/mol). Although the activation energies of the first and second deprotonations, 4.5 and 6.9 kcal/mol, are slightly higher than those for **3a′**, the differences (0.8 and 1.5 kcal/mol) are smaller than that in the dihydrogen coordination step (3.1 kcal/mol). Thus, it is indicated that the dihydrogen coordination step affects the catalytic activity.

The difference in the activation energy for the dihydrogen coordination is attributed to the structure of initial complex **I**.[32] As shown in Figure 4, the Cp* ring which is coordinated to the unsaturated ruthenium atom, Ru¹, moves toward the opposite direction to the other ruthenium atom, Ru² $(\angle(Ru^2Ru^1X) = 169.7°)$ in the case of **3a′**, because a large vacant space exists around the Ru¹ unsaturation site. As the dihydrogen molecule coordinates to Ru¹, the Cp* ring gets away from the dihydrogen $(\angle(Ru^2Ru^1X) = 154.0$ and 144.7° for **TS(I-II)** and **II**, respectively). Moreover, the distance between two ruthenium atoms (2.73 Å in **I**) becomes longer (2.81 and 2.85 Å in **TS(I-II)** and **II**, respectively). On the other hand, in the case of **3b′**, the Cp* ring is not able to move toward the opposite direction to Ru² because of the bulkiness of isopropyl groups. Therefore, the structural change caused by dihydrogen coordination is small $(\angle(Ru^2Ru^1X) = 152.8, 149.8,$ and 141.8° for **I**, **TS(I-II)**, and **II**, respectively). The change in the Ru¹−Ru² distance is also small (2.82 Å (**I**) → 2.84 Å (**TS(I-II)**) → 2.88 Å (**II**)). Thus, the larger structural deformation and the repulsion between the Cp* ring and the dihydrogen molecule increase the activation energy for **3a′** (see Table S2 in the Supporting Information for the fragment analysis).[33] At present, we consider that easy incorporation of molecular dihydrogen on the ruthenium center provides one of the important factors to achieve a high catalytic performance because of the low solubility of molecular dihydrogen in water (only a few milligrams per liter in water under 1 atm).[34]

In summary, we have found that dicationic thiolate-bridged diruthenium complexes bearing sterically bulky alkane substituents on the thiolate ligands such as $[Cp*Ru(\mu\text{-}S^iPr)_2Ru\text{-}(OH_2)Cp*](OTf)_2$ (**3b**) worked as effective catalysts toward the oxidation of molecular dihydrogen into protons and electrons in protic solvents such as water and methanol. An excellent TOF has been achieved (7500 h⁻¹) in methanol at room temperature (Chart 2). The DFT calculations indicate that the steric congestion between sterically bulky thiolate ligands such as 2-propanethiolate moieties and a Cp* ligand resulted in the distortion of the coordination geometry around the ruthenium center. As a result, the coordination of molecular dihydrogen in the diruthenium complex **3b** is preferred in comparison to that in **3a**. Further study in the development of cheaper and more effective catalysts is currently in progress by our group.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00764.

> Experimental and computational details (PDF)
> Cartesian coordinates (XYZ)

Accession Codes

CCDC 1569910 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail for K.S.: sakata@hoshi.ac.jp.
*E-mail for Y.N.: ynishiba@sys.t.u-tokyo.ac.jp.

ORCID ⓘ

Masahiro Yuki: 0000-0002-6940-9627
Ken Sakata: 0000-0002-6920-0735
Kazunari Nakajima: 0000-0001-9892-5877
Yoshiaki Nishibayashi: 0000-0001-9739-9588

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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