Thiolate-Bridged Dinuclear Ruthenium and Iron Complexes as Robust and Efficient Catalysts toward Oxidation of Molecular Dihydrogen in Protic Solvents

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(S) *Supporting Information*

ABSTRACT: Thiolate-bridged dinuclear ruthenium and iron complexes are found to work as efficient catalysts toward oxidation of molecular dihydrogen in protic solvents such as water and methanol under ambient reaction conditions. Heterolytic cleavage of the coordinated molecular dihydrogen at the dinuclear complexes and the sequential oxidation of the produced hydride complexes are involved as key steps to promote the present catalytic reaction. The catalytic activity of the dinuclear complexes toward the chemical oxidation of molecular dihydrogen achieves up to 10000 TON (turnover number), and electrooxidation of molecular dihydrogen proceeds quite rapidly. The result of the density functional theory (DFT) calculation on the reaction pathway indicates that a synergistic effect between the two ruthenium atoms plays an important role to realize the catalytic oxidation of molecular dihydrogen efficiently. The present dinuclear ruthenium complex is found to work as an efficient organometallic anode catalyst for the fuel cell. It is noteworthy that the present dinuclear complex worked not only as an effective catalyst toward chemical and electrochemical oxidation of molecular dihydrogen but also as a good anode catalyst for the fuel cell. We consider that the result described in this paper provides useful and valuable information to develop highly efficient and low-cost transition metal complexes as anode catalysts in the fuel cell.
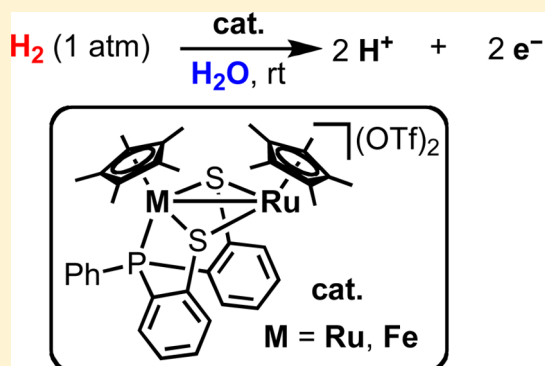
■ INTRODUCTION

Molecular dihydrogen is one of the leading candidates as a fuel source for the future of green chemistry. The best catalyst for the electrochemical production in oxidation of molecular dihydrogen is platinum metal. In fact, platinum is currently used as the catalyst in fuel cells for automotive transportation. However, the high cost of platinum provides a strong motivation for development of less expensive alternatives. Toward the goal of the achievement of efficient catalysts for the production and oxidation of molecular dihydrogen, many trials have already been investigated by using a variety of transition metal complexes as catalysts. For the production of molecular dihydrogen, there are a number of reports on the catalytic reduction of proton into molecular dihydrogen, including photoelectrochemical systems.[1,2] On the other hand, successful examples of oxidation of molecular dihydrogen under ambient reaction conditions are still limited to selected reaction systems.[1,3−9]

In biochemical sciences, hydrogenases reversibly catalyze both the oxidation of molecular dihydrogen into proton and electron and the formation of molecular dihydrogen from proton and electron under ambient reaction conditions.[10−12] Crystal structural studies of hydrogenases have provided useful information on the active sites of the enzyme.[10−12] Based on information on structures of hydrogenases, the construction of model complexes mimicking the enzymes structurally and functionally has been one of the challenging topics for chemists. Ogo and co-workers designed and prepared model complexes of [NiFe] hydrogenases such as [NiRu] and [NiFe] dinuclear complexes, where the [NiRu] dinuclear complexes worked as catalysts toward the oxidation of molecular dihydrogen (up to 17 TON at 50 °C under 8 atm of H₂).[5] Thiolate-bridged dinuclear iron complexes bearing either a ferrocenylphosphine as a redox-active unit or the second coordination sphere pendent amine moiety were reported as mimicking the core of [FeFe] hydrogenases, where only low catalytic activity was observed under ambient reaction conditions (up to 6 TON).[8]

A series of mononuclear nickel-diphosphine complexes bearing the second coordination sphere pendent amine moiety were designed and prepared as mononuclear mimicking compounds, where the presence of the amine moiety significantly improved the reaction rate of electrocatalysis.[4]

Scheme 1. Catalytic Oxidation of Molecular Dihydrogen
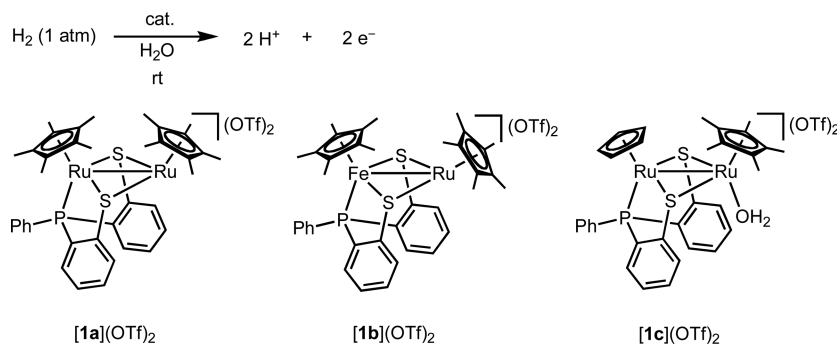
Interestingly, the incorporation of glycine[4e] or arginine[4h] as an amino group to the diphosphine ligand realized catalytic oxidation of molecular dihydrogen in water. More recently, Bullock and co-workers reported mononuclear iron- and ruthenium-diphosphine complexes bearing the pendent amine moiety in electrocatalysis, where the presence of the amine moiety also plays a critical role to promote the catalytic oxidation of molecular dihydrogen under ambient conditions (up to 25 TON).[9] In these reaction systems by use of mononuclear metal complexes in electrocatalysis, the amine moiety proximal to the metal center was considered to accelerate the heterolytic cleavage of the coordinated molecular dihydrogen and also plays an important role as a proton relay.

As an extension of our study on the development of novel catalytic reactivity of thiolate-bridged dinuclear ruthenium and iron complexes $[Cp*Ru\{PhP(C_6H_4\text{-}o\text{-}S)_2\}RuCp*](OTf)_2$ ($[1a](OTf)_2$; $Cp* = \eta^5\text{-}C_5Me_5$; $OTf = OSO_2CF_3$), $[Cp*Fe\{PhP(C_6H_4\text{-}o\text{-}S)_2\}RuCp*](OTf)_2$ ($[1b](OTf)_2$), and $[CpRu\{PhP(C_6H_4\text{-}o\text{-}S)_2\}RuCp*(H_2O)](OTf)_2$ ($[1c](OTf)_2$; $Cp = \eta^5\text{-}C_5H_5$),[13] we have now found that these dinuclear complexes work as robust and efficient catalysts toward oxidation of molecular dihydrogen under ambient reaction conditions (Scheme 1). In the chemical oxidation, an outstanding catalytic performance (up to 10000 TON) has been achieved especially in protic solvents such as water and methanol. We also performed a DFT (density functional theory) study on the reaction pathway based on the stoichiometric and catalytic reactions. The combined experimental and theoretical studies revealed that the thiolate-bridged dinuclear core structure plays a critical role in promoting the catalytic oxidation. The present dinuclear ruthenium complex **1a** is found to work as an efficient organometallic anode catalyst for the fuel cell. It is noteworthy that the present dinuclear complex worked not only as an effective catalyst toward chemical and electrochemical oxidation of molecular dihydrogen but also as a good anode catalyst for the fuel cell. Herein, we describe the results of oxidation of molecular dihydrogen catalyzed by the thiolate-bridged dinuclear ruthenium and iron complexes together with a theoretical study on the proposed reaction pathway by DFT calculations and the electrochemical properties of these dinuclear complexes including the use of the dinuclear ruthenium complex as anode catalyst in the fuel cell.

■ RESULTS AND DISCUSSION

Stoichiometric Reactions of Dinuclear Complexes with Molecular Dihydrogen. Treatment of $[1a](OTf)_2$ in water at room temperature for 10 min under 1 atm of molecular dihydrogen gave the corresponding diruthenium-hydride complex $[Cp*Ru\{PhP(C_6H_4\text{-}o\text{-}S)_2\}RuHCp*](OTf)$

($[2a]OTf$) in 96% isolated yield (Scheme 2). The formation of a stoichiometric amount of trifluoromethanesulfonic acid

Scheme 2. Stoichiometric Reaction of Dinuclear Ruthenium Complex with Molecular Dihydrogen
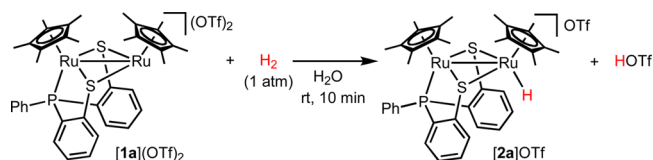

(HOTf) was observed in an aqueous phase after the reaction. The amount of acid was determined by titration with KOH aqueous solution. This result indicated that the heterolytic cleavage of molecular dihydrogen at the diruthenium core should occur to form a hydride complex ($[2a]OTf$) and proton, respectively, where water worked as a base to deprotonate the molecular dihydrogen coordinated to Ru[14] (Scheme 3). ^{1}H NMR spectrum of $[2a]OTf$ in dichloromethane-d_2 exhibited a doublet signal at -16.44 ppm ($J_{PH} = 3$ Hz) assignable to the hydride on the ruthenium center, together with other signals involving two Cp* ligands and the $\{PhP(C_6H_4\text{-}o\text{-}S)_2\}$ moiety.

When $[1a](OTf)_2$ in dichloromethane-d_2 was exposed to an atmosphere of molecular dihydrogen at room temperature in the presence of a stoichiometric amount of base such as 2,6-lutidine and $P(o\text{-}MeC_6H_4)_3$, the solution color of the reaction mixture immediately turned from green to orange-brown. The ^{1}H NMR spectrum of the reaction mixture indicated the formation of $[2a]OTf$. On the other hand, the reaction of $[2a]OTf$ with a stoichiometric amount of HOTf in dichloromethane-d_2 at room temperature under 1 atm of argon (Ar) gave $[1a](OTf)_2$ in 99% NMR yield together with the formation of molecular dihydrogen (97% GC yield). These results clearly indicated the reversibility between $[1a]^{2+}$ and $[2a]^+$ as shown in Scheme 3.

Next, we have investigated the reactivity of $[2a]OTf$ toward the oxidant. The chemical oxidation of $[2a]OTf$ with 1 equiv of $[Cp_2Fe]OTf$ in dichloromethane at room temperature for 5 min under 1 atm of N_2 gave $[1a](OTf)_2$ and ferrocene (Cp_2Fe) in 91% and 61% NMR yields, respectively, together with molecular dihydrogen in 94% GC yield (Scheme 4). The slightly lower yields of Cp_2Fe and molecular dihydrogen are considered to be due to unidentified side reactions. In order to obtain more information on the reaction pathway for the formation of molecular dihydrogen, we investigated the electrochemistry of both $[1a](OTf)_2$ and $[2a]OTf$. The cyclic voltammogram of $[1a](OTf)_2$ in dichloromethane displayed two reversible one-electron reduction waves at -0.62 and -1.31 V vs $Cp_2Fe^{+/0}$ corresponding to $[1a]^{2+/1+}$ and $[1a]^{1+/0}$ redox couples. On the

Scheme 3. Reversibility of Dinuclear Ruthenium Complex via Ruthenium-Dihydrogen Complex
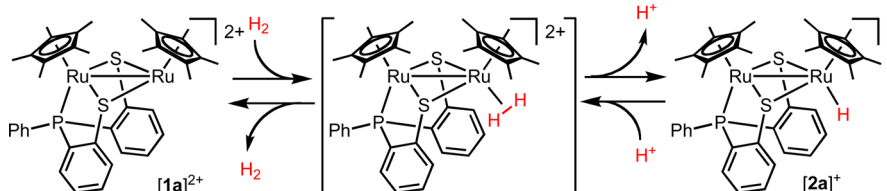
Scheme 4. Chemical Oxidation of [2a]OTf
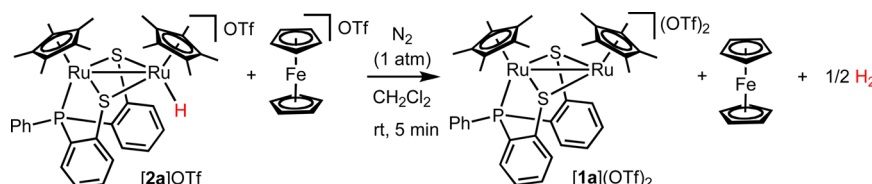
other hand, the voltammogram of [2a]OTf showed a reversible one-electron reduction wave at −1.68 V of [2a]$^{1+/0}$ and an irreversible oxidation wave at +0.22 V, respectively. The irreversible wave of [2a]OTf was assigned to ECE (electrochemical−chemical−electrochemical) reaction shown in Figure 1. The ECE reaction was initiated by one-electron oxidation of
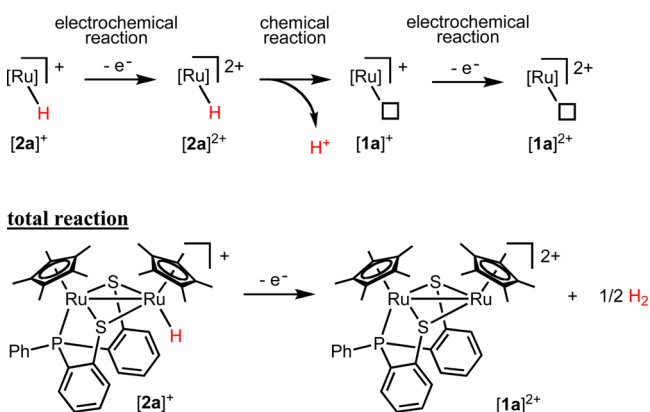

**Figure 1.** Electrochemical−chemical−electrochemical reaction.

the diruthenium-hydride complex 2a$^+$ followed by the formation of monocationic complex together with proton. Subsequent one-electron oxidation of the monocationic complex afforded dicationic complex 1a^{2+}. The liberated proton reacted with diruthenium-hydride complex 2a$^+$ to afford another 1a^{2+} together with a stoichiometric amount of molecular dihydrogen (Scheme 3). As a whole, 2a$^+$ was oxidatively converted into 1a^{2+}

together with 0.5 equiv of molecular dihydrogen (total reaction in Figure 1).

The result of the ECE reaction shown in Figure 1 prompted us to investigate the chemical oxidation of [2a]OTf in the presence of a stoichiometric amount of base. In this reaction system, the base may trap the liberated proton, and the generation of molecular dihydrogen may be inhibited. Actually, the reaction of [2a]OTf with 2 equiv of [Cp$_2$Fe]OTf and 1 equiv of P(o-MeC$_6$H$_4$)$_3$ at room temperature for 5 min under 1 atm of N$_2$ gave [1a](OTf)$_2$ and Cp$_2$Fe in 91% and 64% NMR yields, respectively, together with [HP(o-MeC$_6$H$_4$)$_3$]OTf in 66% NMR yield (Scheme 5), and no formation of molecular dihydrogen was observed. This result indicated that the conversion of hydride in [2a]OTf into proton occurred during the oxidation of [2a]OTf. Based on the result of stoichiometric reaction of [1a](OTf)$_2$ with molecular dihydrogen (Scheme 2) and that of [2a]OTf with oxidant (Scheme 4), we have envisaged that [1a](OTf)$_2$ may promote the catalytic conversion of molecular dihydrogen into 2 equiv of proton and 2 equiv of electron under ambient reaction conditions (Scheme 1). The detailed results are shown in the next section.

Catalytic Behavior of Dinuclear Complexes toward Molecular Dihydrogen. The catalytic oxidation of molecular dihydrogen using [1a](OTf)$_2$ as a catalyst was carried out according to the following procedure. A dichloromethane solution (5 mL) of [Cp$_2$Fe]OTf (0.40 mmol) as an oxidant and P(o-MeC$_6$H$_4$)$_3$ (0.40 mmol) as a base in the presence of a catalytic amount of [1a](OTf)$_2$ (0.002 mmol) was stirred at room temperature for 9 h under 1 atm of molecular dihydrogen. After the reaction, the formation of [HP(o-MeC$_6$H$_4$)$_3$]OTf and

Scheme 5. Chemical Oxidation of [2a](OTf) in the Presence of Base
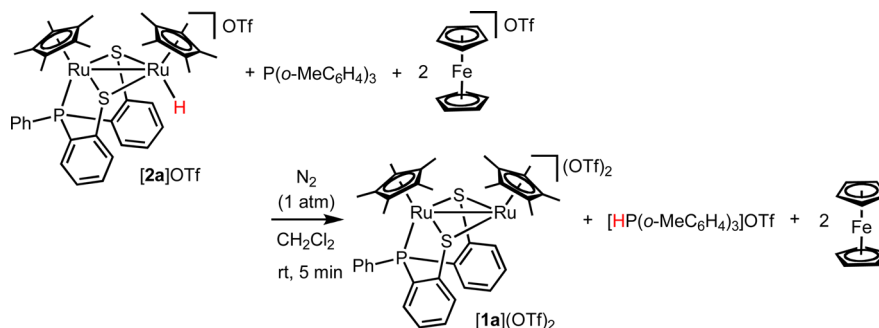
Scheme 6. Catalytic Oxidation of Molecular Dihydrogen in the Presence of [1a](OTf)₂

TON 98, TOF 11 h⁻¹
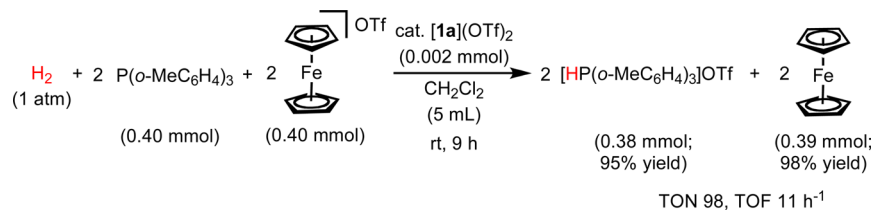
Table 1. Catalytic Oxidation of Molecular Dihydrogen in the Presence of Catalyst in Water[a]
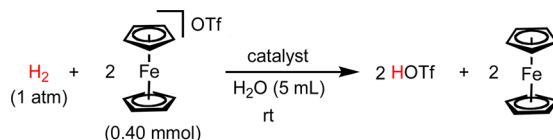
entry	catalyst (mmol)	reaction time (h)	amount of HOTf[b] (mmol)	amount of ferrocene[c] (mmol)	amount of consumed H₂ (mmol)	TON[d]	TOF[e] (h⁻¹)
1	[1a](OTf)₂ (0.002)	1.5	>0.39	0.37	>0.19	93	62
2	[2a](OTf) (0.002)	1.5	>0.39	0.39	>0.19	98	65
3	[1a](OTf)₂ (0.0002)	15	>0.39	0.39		975	65
4	[1a](OTf)₂ (0.00004)	72	>0.39	0.38		4700	65
5[f]	[1a](OTf)₂ (0.00004)	6	>0.39	0.38		4775	796
6[f]	[1a](OTf)₂ (0.00002)	12	>0.39	0.39		9900	825
7[g]	[1a](OTf)₂ (0.002)	1.5			>0.19	100[h]	67
8[i]	[1a](OTf)₂ (0.002)	5			0	0	
9[j]	[1a](OTf)₂ (0.002)	0.05	>0.39	0.38	>0.19	95	1900
10	[1b](OTf)₂ (0.002)	1.5	>0.39	0.40	>0.19	100	67
11	[1c](OTf)₂ (0.002)	3	>0.39	0.38	>0.19	95	32

[a]Reactions of [Cp₂Fe]OTf (0.40 mmol) under 1 atm of H₂ in the presence of catalyst in water (5 mL) at room temperature. [b]The amount of acid was estimated by titration with KOH aqueous solution. [c]The amount of ferrocene was determined by ¹H NMR with an internal standard. [d]TON = [(amount of ferrocene (mmol))/(amount of catalyst (mmol))/2]. [e]TOF = TON/(reaction time (h)). [f]At 70 °C. [g][Fe(NO₃)₃] (0.40 mmol) was used in place of [Cp₂Fe]OTf. [h]The value of TON was estimated on the amount of consumed H₂. [i][CuSO₄·5H₂O] (0.20 mmol) was used in place of [Cp₂Fe]OTf. [j]MeOH (5 mL) was used in place of H₂O as solvent.

Cp₂Fe in 95% and 98% yields, respectively, was observed by NMR (Scheme 6). The consumption of molecular dihydrogen was monitored to check the state of progress. In the absence of [1a](OTf)₂, no reaction occurred under the same reaction conditions. It was also confirmed that no reaction took place under 1 atm of N₂, in place of H₂. These results clearly indicated that molecular dihydrogen was catalytically converted into 2 equiv of proton and 2 equiv of electron under ambient reaction conditions.

When the reaction was carried out in water as solvent, it proceeded quite smoothly even in the absence of P(o-MeC₆H₄)₃ as a base. Typical results are shown in Table 1. In this reaction system, the reaction was complete within 1.5 h, where turnover frequency (TOF) was 62 h⁻¹ (Table 1, entry 1). Under aqueous conditions, water worked as a base to form HOTf, and actually the quantitative formation of HOTf was confirmed after the reaction. A similar catalytic activity of [2a]OTf was also achieved under the same reaction conditions (Table 1, entry 2), showing that [2a](OTf) was involved as a key reactive intermediate toward the catalytic reaction. When a smaller amount of [1a](OTf)₂ (0.0002 and 0.00004 mmol) was used as a catalyst, the complete conversion of molecular dihydrogen was achieved after 15 and 72 h, respectively (Table 1, entries 3 and 4). In these cases, turnover numbers (TONs) were 975 and 4700, respectively, where the catalytic activity of [1a](OTf)₂ (ca. 65 h⁻¹) was maintained for over 72 h. At higher reaction temperature (70 °C), the reaction using [1a](OTf)₂ (0.00004 mmol) was dramatically accelerated and completed within 6 h,

where the catalytic activity was increased (ca. 800 h⁻¹) (Table 1, entry 5). Even in the presence of 0.00002 mmol of [1a](OTf)₂ as a catalyst, the reaction at 70 °C proceeded smoothly without the loss of the catalytic activity (Table 1, entry 6). Separately, no consumption of molecular dihydrogen was observed at all in the absence of [1a](OTf)₂ as a catalyst under the same reaction conditions. This result indicates that the catalytic use of the dinuclear complexes promoted the oxidation of molecular dihydrogen. The utility of [Cp₂Fe]OTf as an oxidant in water is discussed in the Supporting Information.

In order to investigate the catalytic performance under an aqueous solution, the use of stronger oxidant [Fe(NO₃)₃] ($E°(Fe^{3+/2+}(aq)) = +0.77$ V vs SHE)[15] in place of [Cp₂Fe]OTf ($E°(aq) = +0.40$ V vs SHE)[15] gave a similar result under the same reaction conditions (Table 1, entry 7). In contrast, no reaction occurred at all when weaker oxidant [CuSO₄] ($E°(Cu^{2+/+}(aq)) = +0.15$ V vs SHE, $E°(Cu^{2+/0}(aq)) = +0.34$ V vs SHE)[15] was used in place of [Cp₂Fe]OTf (Table 1, entry 8). The nature of oxidants is considered to be one of the important factors to promote the catalytic transformation. On the other hand, oxidation of molecular dihydrogen proceeded quite rapidly when methanol was used as solvent. In the presence of a catalytic amount of [1a](OTf)₂ (0.002 mmol), the reaction in methanol was complete within 0.05 h, where the highest TOF (ca. 2000 h⁻¹) was observed (Table 1, entry 9). Although the exact role of methanol is not yet clear in this catalytic oxidation of molecular dihydrogen, methanol may work as a stronger nucleophile than

water and it may dramatically accelerate the deprotonation step of the coordinated dihydrogen.[16]

Other thiolate-bridged dinuclear ruthenium and iron complexes, [1b](OTf)$_2$ and [1c](OTf)$_2$, have been found to work as effective catalysts as well toward oxidation of molecular dihydrogen in water (Table 1, entries 10 and 11). Here, the reaction using [1c](OTf)$_2$ as a catalyst proceeded slightly slower, probably because of a less bulky Cp moiety of [1c](OTf)$_2$ allowing water solvent to be coordinated to the active ruthenium center.

To obtain more information on the reaction pathway, we monitored the consumption of molecular dihydrogen in the reaction with [Cp$_2$Fe]OTf in the presence of a catalytic amount of [1a](OTf)$_2$. The time profile is shown in Figure 2 and typical
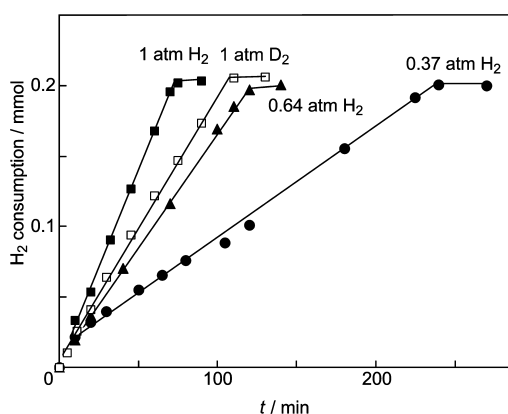
Figure 2. Time course of the consumption of molecular dihydrogen in the oxidation of molecular dihydrogen with [Cp$_2$Fe]OTf (0.40 mmol) in the presence of [1a](OTf)$_2$ (0.002 mmol) in water (5 mL) at room temperature.

results are shown in Table 2. The consumption of molecular dihydrogen was observed with the constant rate of 0.13 mmol h^{-1} until the end of the reaction when the reaction with [Cp$_2$Fe]OTf (0.40 mmol) was carried out in the presence of [1a](OTf)$_2$ (0.002 mmol) under 1 atm of molecular dihydrogen. The linearity of the consumption of molecular dihydrogen indicated that the reaction rate was independent of both the concentration of the oxidant and the pH value of the reaction mixture. The decrease in the rate of the consumption of molecular dihydrogen was observed under a lower partial

pressure of molecular dihydrogen (Table 2, entries 2 and 3). Furthermore, 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, entry 4). These results indicated that both the heterolytic cleavage of molecular dihydrogen on the ruthenium complex and the deprotonation from the produced hydride complex may be involved as rate-determining steps of the catalytic reaction.

Reaction Pathway for Catalytic Oxidation of Molecular Dihydrogen. Based on the stoichiometric and catalytic reactions, we have proposed a reaction pathway shown in Scheme 7. At first, the formation of dicationic ruthenium-

Scheme 7. Proposed Reaction Pathway of Oxidation of Molecular Dihydrogen Catalyzed by [1a](OTf)$_2$
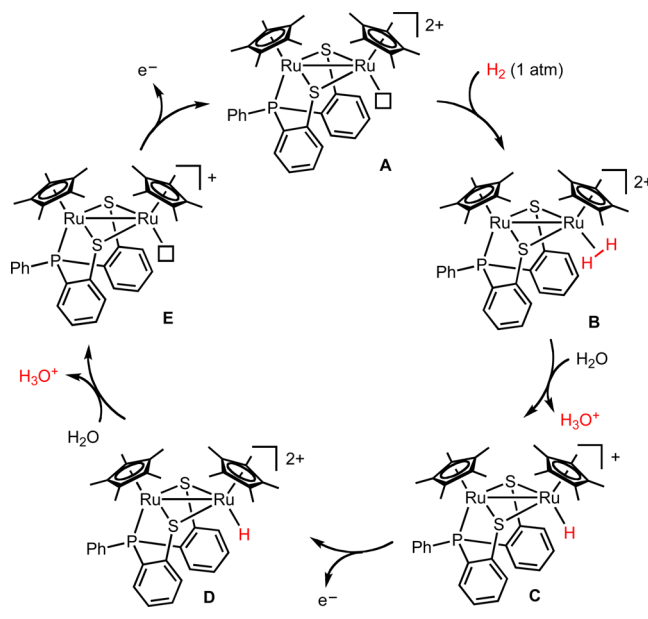
dihydrogen complex **B** by the coordination of molecular dihydrogen to dicationic ruthenium complex **A** occurs, and then the nucleophilic attack of water to the coordinated dihydrogen gives the corresponding monocationic ruthenium-hydride complex **C** together with an acid. One-electron oxidation of the complex **C** gives the corresponding dicationic ruthenium-hydride complex **D** and further deprotonation from **D** with water leads to the formation of monocationic ruthenium complex **E**.

Table 2. Catalytic Oxidation of Molecular Dihydrogen in the Presence of [1a](OTf)$_2$ in Water[a]

entry	pressure of H$_2$ (atm)	reaction time (h)	amount of HOTf[b] (mmol)	amount of ferrocene[c] (mmol)	amount of consumed H$_2$ (mmol)	TON[d]	TOF[e] (h^{-1})
1	1	1.5	>0.39	0.37	>0.19	93	62
2	0.64	3	>0.39	0.37	>0.19	93	31
3	0.37	4	>0.39	0.39	>0.19	98	25
4[f]	1	2.1	>0.39	0.40	>0.19	100	48

[a]Reactions of [Cp$_2$Fe]OTf (0.40 mmol) under H$_2$ in the presence of [1a](OTf)$_2$ (0.002 mmol) in water (5 mL) at room temperature. [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]D$_2$ (1 atm) was used in place of H$_2$ (1 atm).
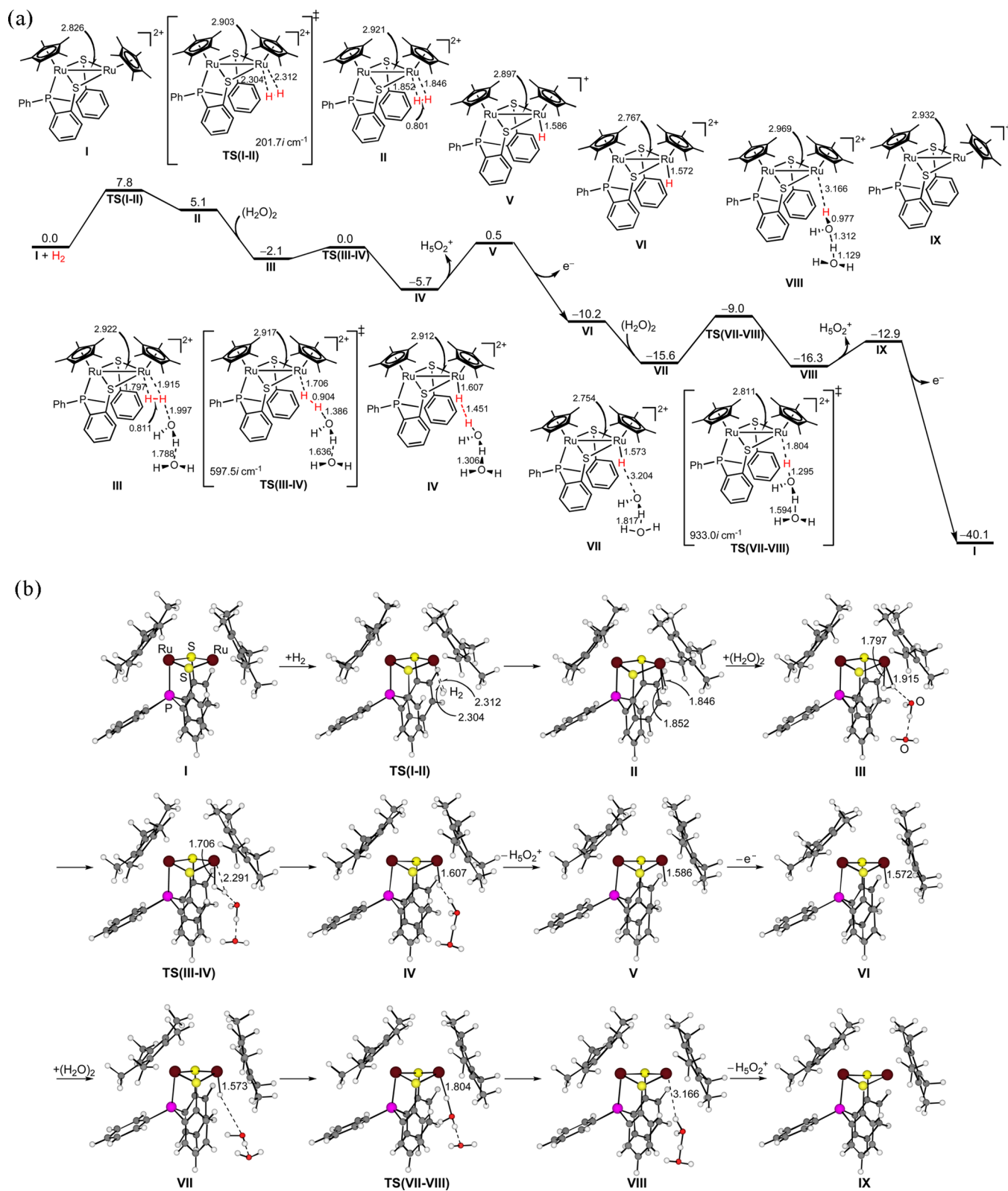
Figure 3. (a) Relative energy diagram (kcal/mol). Electrons are trapped by ferrocenium ion Cp$_2$Fe$^+$. Bond lengths in structures are in angstroms. (b) Optimized structures of stationary points for the oxidation of molecular dihydrogen catalyzed by [**1a**]$^{2+}$. Bond lengths in structures are in angstroms.

Further one-electron oxidation of the complex **E** affords the starting complex **A**.

The proposed reaction pathway is supported by DFT calculations using the B3LYP functional (LANL2DZ for Ru atom and 6-31G* for other atoms).[17−20] The polarizable

continuum model (PCM) was utilized for the solvent effects of water.[21] We investigated the model oxidation reaction of hydrogen molecule catalyzed by the dicationic thiolate-bridged dinuclear ruthenium complex [**1a**]$^{2+}$ (**I**) (Figure 3), where the deprotonation from the hydrogen-coordinated complex and the

one-electron oxidation of the produced hydride complex proceed alternately (eq1):

$$H_2 + 2\,(H_2O)_2 + 2\,\underset{Fe}{\bigg|}^+ \xrightarrow{\text{cat. }[\mathbf{1a}]^{2+}} 2\,H_5O_2^+ + 2\,\underset{Fe}{\bigg|} \qquad (1)$$
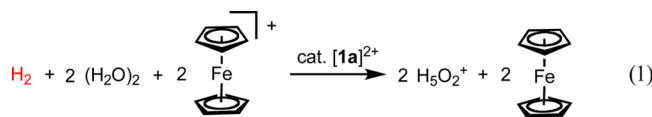
A molecular dihydrogen coordinates to the dicationic complex **I** in a side-on fashion via the transition state **TS(I−II)** to afford dicationic ruthenium-dihydrogen complex **II**. The barrier height of **TS(I−II)** from the initial state is 7.8 kcal/mol, and the relative energy of **II**, ΔE, is +5.1 kcal/mol. The coordinated hydrogen atoms in **II** have the same positive atomic charge (+0.16 in the natural population analysis (NPA)[22]), which is likely to be attacked by nucleophiles such as solvent water molecules and OTf$^-$ ion. We examined the proton abstraction from **II** by water dimer $(H_2O)_2$ (**II → V**). The nucleophilic attack of the oxygen atom in the water dimer gives the complex **IV** ($\Delta E = −5.7$ kcal/mol), which consists of the monocationic ruthenium-hydride complex and Zundel cation $H_5O_2^+$, through the reactant complex **III** ($\Delta E = −2.1$ kcal/mol) and the transition state **TS(III−IV)** ($\Delta E = 0.0$ kcal/mol). The barrier height of **TS(III−IV)** from **III** is quite small (2.1 kcal/mol), so this deprotonation step can occur smoothly. Then, one-electron oxidation of the isolated monocationic ruthenium-hydride complex **V** leads to the corresponding dicationic hydride complex **VI**. If we consider that an electron is trapped by Cp_2Fe^+ ion, the complex **VI** ($\Delta E = −10.2$ kcal/mol) is calculated to be more stable than monocationic complex **V** ($\Delta E = +0.5$ kcal/mol) by 10.7 kcal/mol in energy. The subsequent deprotonation from **VI** caused by $(H_2O)_2$ was examined. The barrier height of **TS(VII−VIII)** from the reactant complex **VII** is 6.6 kcal/mol, and the deprotonation process from **VII** to **VIII** is slightly exothermic by 0.7 kcal/mol. Although the reaction barrier is slightly higher than that of the first deprotonation step, this deprotonation step can also occur smoothly. Finally, the oxidation of the isolated monocationic complex $[\mathbf{1a}]^+$ (**IX**) reproduces the starting dicationic complex **I**, and this step gives great stability in energy. As a whole, the present results achieved by the DFT calculations support the proposed reaction pathway shown in Scheme 7.

In the propargylic substitution reaction catalyzed by thiolate-bridged diruthenium complex, it has been proposed that the flexible Ru−Ru structure plays a crucial role for the catalytic cycle.[23] As shown in Figure 3, the bond distance between two ruthenium atoms alters along the reaction pathway. This result indicates the importance of similar dimetallic effect in the present oxidation reaction system. In fact, we have examined the changes in electron population through two deprotonation steps (**II → V** and **VI → IX**) as shown in Figure 4. In the first deprotonation step (**II → V**), the atomic charge of the coordinated hydrogen atom in **II** is +0.16, which means that the hydrogen that is to be lost in the deprotonation possesses an electron population of 0.84e$^-$. By elimination of the proton nuclei from **II**, the electron population of the hydrogen atom in **II** is distributed not only to the coordinated Ru site (0.38e$^-$) but also to the thiolate-bridge site (0.22e$^-$) and to the other Ru site (0.24e$^-$) in **V**. This result shows that both the other Ru site and the thiolate-bridge site play roles in electron storage. In the second deprotonation step (**VI → IX**), the electron population of the hydrogen atom in **VI** (0.78e$^-$) is distributed to the thiolate-bridge site (0.54e$^-$) and to the other Ru site (0.28e$^-$) in **IX**, and the electron population at the coordinated Ru site decreases slightly in an opposite manner.
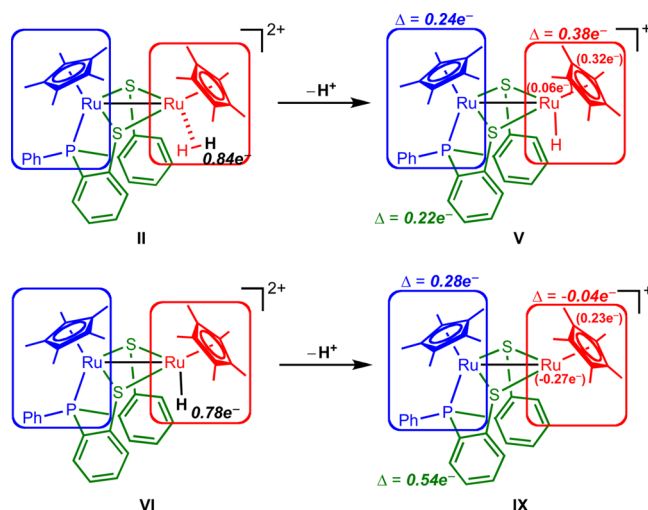

Figure 4. Changes in electron population (e$^-$) estimated by NPA through two deprotonation steps (**II → V** and **VI → IX**).

Thus, the synergistic effect between two ruthenium atoms supported by the thiolate ligands plays an important role also in the present reaction system.

Electrocatalysis of Dinuclear Complex toward Molecular Dihydrogen. We investigated the electrocatalysis of $[\mathbf{1a}](OTf)_2$ toward the oxidation of molecular dihydrogen. The cyclic voltammogram of $[\mathbf{1a}](OTf)_2$ in methanol under 1 atm of N_2 showed an irreversible oxidation wave at +0.08 V vs $Cp_2Fe^{+/0}$ (Figure 5, black trace). In contrast, the cyclic
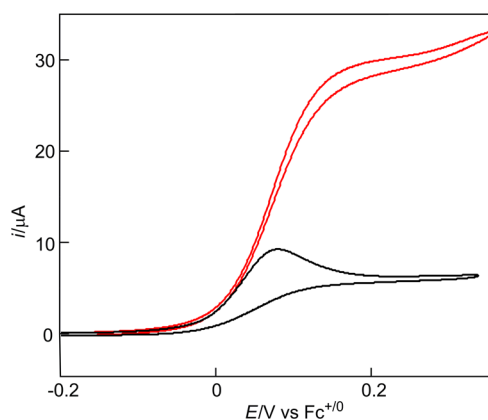

Figure 5. Cyclic voltammogram of a solution of $[\mathbf{1a}](OTf)_2$ in methanol (1.0 mM) under 1 atm of molecular dinitrogen (black) and molecular dihydrogen (red) ($v = 10$ mV/s, 20 °C, glassy carbon working electrode, 0.1 M $^nBu_4NClO_4$ as supporting electlyte).

voltammogram of $[\mathbf{1a}](OTf)_2$ in methanol under 1 atm of H_2 showed a plateau shaped oxidation wave with the increased current, corresponding to the catalytic current of oxidation of molecular dihydrogen (Figure 5, red trace). The rate constant, k_{obs}, of the electrooxidation of molecular dihydrogen catalyzed by $[\mathbf{1a}](OTf)_2$ was roughly estimated to be 1.6 s^{-1} by eq 2 (see the Supporting Information for details).[24] For the electrochemical oxidation, the value of the rate constant k_{obs} of $[\mathbf{1a}](OTf)_2$ is lower than that of the most effective homogeneous nickel catalyst (210 s^{-1}; under 1 atm of H_2)[4] as well as heterogeneous platinum catalyst (15 s^{-1}).[10] However, the use of $[\mathbf{1a}](OTf)_2$ as a catalyst led to ca. 10000 TON in the chemical oxidation of molecular dihydrogen with oxidant, and the catalytic activity was

maintained for over a few days (vide supra). This means that $[\mathbf{1a}](OTf)_2$ works as the one of the most robust and efficient catalysts toward the chemical oxidation of molecular dihydrogen under ambient reaction conditions.

$$i_{cat} = nFAC\sqrt{Dk_{obs}} \qquad (2)$$

Ability of Dinuclear Complex to Function as an Anode Catalyst in the Fuel Cell. Finally, we evaluated the ability of $[\mathbf{1a}](OTf)_2$ to function as an anode catalyst under carbon supported conditions for the fuel cell system. A preliminary result of the polarization curve showed the open circuit voltage (OCV) of 1.04 V and maximum power density of 8.3 mW/cm^2 at 0.38 V at 40 °C (Figure 6; see the Supporting Information for details).
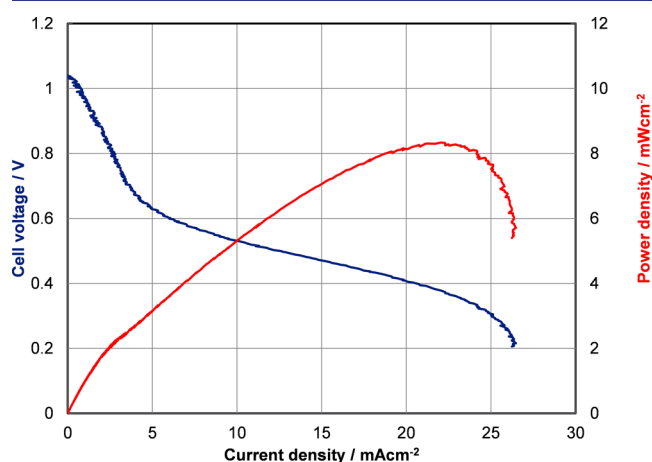

Figure 6. I−V curve and power density curve for the fuel cell using $[\mathbf{1a}](OTf)_2$ as an anode catalyst and Pt as a cathode catalyst. The cell was operated at 40 °C with constant flow (500 mL/min each) of hydrogen and oxygen gases into anode and cathode, respectively. The polarization curve was recorded at the current sweep rate of 0.5 mA/s.

This result indicates that $[\mathbf{1a}](OTf)_2$ can work as an efficient organometallic anode catalyst of the fuel cell although the present ability of $[\mathbf{1a}](OTf)_2$ as an anode catalyst is lower than that of Pt catalyst in the fuel cell. Previously, Ogo and co-workers reported the use of the $[NiRu]$ dinuclear complexes as organometallic anode catalysts in the fuel cell.[5c,e] For comparison, the use of the $[\mathbf{1a}](OTf)_2$ as an organometallic anode catalyst has significantly improved the function of the fuel cell. To the best of our knowledge, the thiolate-bridged dinuclear ruthenium complex has the highest performance in an organometallic fuel cell.[25]

CONCLUSION

We have found that thiolate-bridged dinuclear ruthenium and iron complexes work as robust and efficient catalysts toward oxidation of molecular dihydrogen in protic solvent such as water and methanol under ambient reaction conditions. The catalytic activity of the complexes toward the chemical oxidation of molecular dihydrogen achieves up to 10000 TON, and electrooxidation of molecular dihydrogen proceeds quite rapidly. The high proton conductivity by the Grotthus mechanism[26] in protic solvents seems to play a crucial role for the high performance of the catalysis. The experimental results and the DFT calculations indicate that heterolytic cleavage of the coordinated molecular dihydrogen at the dinuclear complexes and the sequential oxidation of the hydride complexes are key steps to promote the present catalytic reaction.[27] Synergistic

effect between the two ruthenium atoms is observed during the catalytic transformation of molecular dihydrogen. We have confirmed the ability of the thiolate-bridged dinuclear ruthenium complex to function as a good anode catalyst for the fuel cell although the present ability of the dinuclear ruthenium complex as an anode catalyst is lower than that of Pt catalyst in the fuel cell. We believe that the thiolate-bridged dinuclear ruthenium complex has the highest performance in an organometallic fuel cell. It is noteworthy that the present dinuclear complex worked not only as an effective catalyst toward chemical and electrochemical oxidation of molecular dihydrogen but also as a good anode catalyst for the fuel cell. We consider that the result described in this paper provides useful and valuable information to develop highly efficient and low-cost transition metal complexes, instead of Pt, as anode catalysts in fuel cells.[28,29]

ASSOCIATED CONTENT

Ⓢ Supporting Information

Full preparative, analytical, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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