Hydrogen Generation

A Ruthenium-Based Biomimetic Hydrogen Cluster for Efficient Photocatalytic Hydrogen Generation from Formic Acid

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Abstract: A ruthenium-based biomimetic hydrogen cluster, [$Ru_2(CO)_6(\mu$ -SCH₂CH₂CH₂S)] (1), has been synthesized and, in the presence of the P ligand tri(*o*-tolyl)phosphine, demonstrated efficient photocatalytic hydrogen generation from formic acid decomposition. Turnover frequencies (TOFs) of 5500 h⁻¹ and turnover numbers (TONs) over 24700 were obtained with less than 50 ppm of the catalyst, thus representing the highest TOFs for ruthenium complexes as well as the best efficiency for photocatalytic hydrogen production from formic acid. Moreover, **1** showed high stability with no significant degradation of the photocatalyst observed after prolonged photoirradiation at 90 °C.

Introduction

The development of clean and sustainable energy, such as hydrogen production driven by water splitting, has been a worldwide goal and challenge for scientists for more than four decades.^[1] To date, more than 95% of generated hydrogen is from steam reformation and coal gasification, which originates from limited fossil resources such as coal and oil. Nevertheless, safe and reversible hydrogen generation and storage is a significant obstacle for the utilization of hydrogen as transportation fuel. Alternatively, formic acid, one of the main products formed in biomass processes such as pyrolysis, fermentation, and supercritical reactions, is a liquid at ambient conditions. The ease of storing, transporting, and handling makes formic acid a highly competitive and low-cost source for hydrogen generation. Although greenhouse gas carbon dioxide is produced during hydrogen production from formic acid, recycling is possible through natural photosynthesis or industrial technologies such as carbon capture.^[2]

Notably, the natural iron-based hydrogenase (H_2 ase) family of proteins produces hydrogen or utilizes it as an energy source under ambient conditions. The dinuclear iron–iron catalytic site, referred to as the hydrogen cluster, is responsible for reversible reduction of protons to hydrogen, with a remarkable efficiency of 6000–9000 molecules of hydrogen per site under optimal conditions.^[3] In spite of the high efficiency of hydrogen generation, the low availability and stability of the iron– iron hydrogen cluster during light-driven hydrogen production

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201406381. has prompted the synthesis of model complexes that mimic the hydrogen cluster in structure, function, and reactivity.^[4] In the past several years, significant effort has been put forth to design and synthesize [FeFe]-based biomimetic hydrogen clusters and to study the mechanism of proton reduction.^[5] In comparison to the highly efficient hydrogen cluster present in nature, however, none or a small amount of H₂ was produced upon photoirradiation, and ultimately they complete their photochemical H₂ production in organic solutions or a mixture of organic solvents and water. More strikingly, these synthetic hydrogen-cluster mimics were not stable and would decompose generally within one hour of irradiation. Thus the creation of an artificial hydrogen-cluster system that can produce H₂ with high catalytic activity and stability in an aqueous or organic solution remains a significant scientific challenge and an important objective that is pursued to this day.

Various approaches, including homogeneous and heterogeneous systems to generate hydrogen from formic acid with heat treatment, have been reported in recent years. For example, Puddephatt et al. reported a binuclear ruthenium-phosphine complex capable of selective H₂ production from formic acid with a turnover frequency (TOF) of approximately 500 h^{-1} at ambient temperature.^[6] Fukuzumi et al. reported a heteronuclear iridium-ruthenium complex capable of producing hydrogen with a TOF of approximately 426 h^{-1.[7]} Similarly, Boddien et al. showed that hydrogen is generated from formic acid and a ruthenium-phosphine catalyst system under mild conditions and visible light.^[8] Recently, Himeda investigated an iridiumazole-containing complex for H_2 generation from formic acid in water, thereby obtaining a TOF of 34000 h⁻¹ at high temperature.^[9] In contrast to ruthenium–polypyridine complexes, photocatalytic hydrogen-generation catalysts based on a diruthenium-based biomimetic hydrogen cluster have rarely been studied.^[10]

The higher hydrogen-generation efficiency of rutheniumbased complexes relative to that of [FeFe]-based hydrogen

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clusters and the increasing demand for efficient hydrogen-generation techniques prompted our investigation of the photocatalytic decomposition of formic acid by an [RuRu]-based biomimetic hydrogen cluster. Herein, two [RuRu]-based biomimetic hydrogen clusters, [Ru₂(CO)₆(μ -SCH₂CH₂CJ₂S)] (1) and [{(μ -H)Ru₃(CO)₁₀}₂(μ -SCH₂CH₂CH₂S)] (2), were synthesized and characterized by spectroscopic techniques and X-ray diffraction.^[11] Furthermore, the optical characteristics and electrochemical properties of these ruthenium-based hydrogen clusters were analyzed by UV/Vis spectroscopy and cyclic voltammetry. The photocatalytic hydrogen-generation activity of 1 was evaluated in the organic phase with various phosphine ligands (Scheme 1).



Scheme 1. Hydrogen-generation reaction catalyzed by the ruthenium-based biomimetic hydrogen cluster and P ligands.

Results and Discussion

Reflux treatment of [Ru₃(CO)₁₂] with 1,3-propanedithiol in toluene gave two [RuRu]-based biomimetic hydrogen clusters: a major product $[Ru_2(CO)_6(\mu-SCH_2CH_2CH_2S)]$ (1) and a minor product $[{(\mu-H)Ru_3(CO)_{10}}_2(\mu-SCH_2CH_2CH_2S)]$ (2). The two compounds were characterized by mass spectrometry (MS), infrared (IR) spectroscopy, ¹H and ¹³C NMR spectroscopy, and single-crystal X-ray crystallography (Figures S1-S3 and Tables S1–S4 in the Supporting Information). $^{[11,12]}$ Compounds 1 and 2 formed light yellow and yellow-orange crystals, respectively, from hexane and dichloromethane at -20 °C. The crystallographic data and select bond lengths and angles for 1 and 2 are summarized in Tables S1 to S3 of the Supporting Information. The molecular structures of 1 and 2 are depicted in Figure 1. Compound 1 exhibited a butterfly-like geometry of the Ru₂S₂ moiety, and each Ru atom was coordinated with three linear carbonyl groups and two bridging sulfur ligands to form a "sawhorse" arrangement. The Ru-Ru distance of 1 (2.6592(6) Å) is longer than the Fe-Fe distance of $[Fe_2(CO)_6(\mu-SCH_2CH_2CH_2S)]$ (2.5103(11) Å), but shorter than the Ru-Ru distance of [Ru₃(CO)₁₂] (2.854 Å).^[13] The structure of 2 shows that two [Ru₃(CO)₁₂] groups were connected by a propanedithiolate ligand with the loss of two carbonyl groups. The average Ru-Ru distances of 2 (2.8315 Å) is slightly shorter than that of [Ru₃(CO)₁₂] (2.854 Å) but is longer than that of 1 (2.6592(6) Å). This result indicates that the Ru–Ru distance in 1 is affected by the nature of the terminal ligand. The bridging Ru-S distance of 1, which ranges from 2.3569(13) to 2.3650(14) Å, is also longer than the bridging Fe-S distance of $[Fe_2(CO)_6(\mu$ -SCH₂CH₂CH₂S)] (2.2491(10) to 2.2542(10) Å). The bridging Ru–S distance of 2 (range from 2.384(4) to 2.398(4) Å) is also longer than that of 1 (2.3569(13) to 2.3650(14) Å).



Figure 1. Solid-state structure of: A) [Ru₂(CO)₆(μ -SCH₂CH₂CH₂SI] (1), and B) [{(μ -H)Ru₃(CO)₁₀}₂(μ -SCH₂CH₂CH₂SI] (2) shown by a thermal ellipsoid plot. Hydrogen atoms are omitted for clarity.

The UV/Vis absorption spectra of solutions of [Ru₃(CO)₁₂], 1, and 2 were analyzed in ethyl acetate (EA) at room temperature. As shown in Figure 2, [Ru₃(CO)₁₂] (black line), 1 (dashed line), and 2 (dotted line) exhibited characteristic absorption bands at 254/393, 275/347, and 253/282/352/421 nm, respectively. The electronic absorption bands of [Ru₃(CO)₁₂], 1, and 2 observed in the UV region could be designated as $\pi \rightarrow \pi^*$ transitions and attributed to a metal-to-ligand charge-transfer (MLCT) transition.^[14] Similarly, the broad and low-energy bands at 393, 347, and 352/421 nm observed for [Ru₃(CO)₁₂], 1, and 2, respectively, could be assigned to $\sigma \rightarrow \sigma^*$ transitions in metalmetal d orbitals.^[14b,c] The electrochemical properties of 1 and 2 were analyzed by cyclic voltammetry (CV) and differential pulse voltammetry (DPV; Figure S4 in the Supporting Information). The redox potentials were measured with an Ag/AgNO₃ electrode. Compound 1 displayed two reversible oxidation potentials and one reversible reduction potential at +0.772, +1.676, and -1.856 V, attributed to Ru^IRu^I to Ru^IRu^{II}, Ru^IRu^{II} to Ru^{II}Ru^{II}, and Ru^IRu^I to Ru^IRu⁰, respectively. Because the standard potential of Ag/AgNO₃ relative to the normal hydrogen electrode (NHE) is +0.56 V, the oxidation and reduction potentials were recalculated to be +1.282, +2.236, and -1.296 V, respectively. Compound 2 displayed two reversible oxidation potentials and one reversible reduction potential at +0.716, +1.312, and -1.55 V, respectively. The oxidation and reduction potentials relative to NHE were recalculated to be +1.276, +1.872, and -0.992 V, respectively. The oxidation and reduction potentials could be attributed to the loss of two electrons and reduction in the triruthenium catalytic center, respectively.

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Figure 2. UV/Vis absorption spectrum of $[Ru_3(CO)_{12}]$ (black line), 1 (dashed line), and 2 (dotted line).

We started our photocatalytic hydrogen-generation studies with 1 in combination with different phosphorous-containing ligands. Compound 2 was omitted from photocatalytic hydrogen-generation experiments owing to insufficient amounts of compound. The preliminary reactions were performed with catalyst (20 µmol) in dimethylformamide (DMF; 1 mL) and formic acid/triethylamine (FA/TEA, 5:2; 4 mL) under a 500 W Xe lamp and kept at 40 °C for six hours. Subsequently, a number of P ligands with different electronic or steric properties, including triphenylphosphine (PPh₃, 3), tri(o-tolyl)phosphine (P(otol)₃, **4**), tri(*m*-tolyl)phosphine (P(*m*-tol)₃, **5**), tri(*p*-tolyl)phosphine $P(p-tol)_3$, (6), tris(2-methoxyphenyl)phosphine (P(o-7), tris(4-methoxyphenyl)phosphine (P(p- $C_6H_4OCH_3)_3$, $C_6H_4OCH_3)_3$, **8**), tris(4-fluorophenyl)phosphine (P(p-C_6H_4F)_3, **9**), and tris(4-trifluoromethylphenyl)phosphine (P(p-C₆H₄CF₃)₃, 10), were investigated for their ability to increase hydrogen-generation efficiency. Figure 3 shows H₂ production at 40 °C over time using 1 as the catalyst with the addition of different P ligands. As expected, only gas mixtures that contained H₂/CO₂ and not CO were detected in cases of significant gas production. Control experiments in the absence of catalysts showed no detectable production of H₂, thus verifying that the catalyst is essential for the photocatalytic generation of H₂. Reaction with 1 in the absence of the P ligand gave very slight activity. The addition of electron-donating P ligands provided higher activity than addition of electron-withdrawing P ligands. Among the P



Figure 3. Photocatalytic hydrogen-generation efficiency of 1 as catalyst in the absence and presence of various P ligands including PPh₃ (**3**), P(o-tol)₃ (**4**), P(*m*-tol)₃ (**5**), P(*p*-tol)₃ (**6**), P(o-C₆H₄OCH₃)₃ (**7**), P(*p*-C₆H₄OCH₃)₃ (**8**), P(*p*-C₆H₄F)₃ (**9**), and P(*p*-C₆H₄CF₃)₃ (**10**).

ligands tested, the electron-withdrawing P ligand such as 10 showed a low activity comparable to that of reactions performed in the absence of P ligand. The addition of a P ligand such as 4 provided the highest activity, with the efficiency of P ligands decreasing in the order of $4 > 7 > 8 \approx 6 > 5 > 3 > 9 > 10$.

We next evaluated the influence of light, catalyst-to-substrate ratio, and temperature on H₂-generation efficiency (Table 1). When compound **1** was heated at 40 or 60 °C in the presence of P ligand **4** without photoirradiation for six hours, a slight amount of hydrogen was generated and detected at a turnover number (TON) of 47.4 and 61.7 and a TOF of 8.0 and 10.3 h⁻¹, respectively. Interestingly, when compound **1** was photoirradiated without temperature control in the presence of P ligand **4**, a higher TON of 2149.4 and TOF of 358.2 h⁻¹ was detected, thus indicating that light has a strong enhancing effect on the H₂-generation efficiency.

To determine the optimal catalyst-to-substrate ratio, the catalyst was photoirradiated under a 500 W Xe lamp and kept at 60 °C for six hours at concentrations of 40, 20, 10, 5, or 2 μ mol in DMF (1 mL) and FA/TEA (5:2; 4 mL). Interestingly, the system with 20 μ mol of catalyst generated a higher total amount of

Table 1. Influence of light, catalyst-to-substrate ratio, and temperature of the ruthenium complex 1 and P ligand 4 on hydrogen-generation efficiency.									
Entry	Amount [µmol]	<i>Т</i> [°С]	TON 1 h (TOF [h ⁻¹])	TON 2 h (TOF [h ⁻¹])	TON 3 h (TOF [h ⁻¹])	TON 4 h (TOF [h ⁻¹])	TON 5 h (TOF [h ⁻¹])	TON 6 h (TOF [h ⁻¹])	Conversion [%]
1 ^[a]	40	60	42 (42)	150 (75)	280 (93)	449 (112)	552 (110)	625 (104)	50 (6 h)
2 ^[a]	20	60	227 (227)	584 (292)	957 (319)	1189 (297)	1469 (294)	1748 (291)	70 (6 h)
3 ^[a]	10	60	184 (184)	1035 (518)	1894 (631)	2431 (608)	2810 (562)	3276 (546)	66 (6 h)
4 ^[a]	5	60	522 (522)	1848 (924)	2910 (970)	4074 (1019)	5105 (1021)	5626 (938)	56 (6 h)
5 ^[a]	2	60	308 (308)	2075 (1038)	3248 (1083)	4654 (1164)	6142 (1228)	7492 (1249)	28 (6 h)
6 ^[a]	2	40	242 (242)	845 (422)	1330 (443)	1879 (470)	2128 (426)	2563 (427)	10 (6 h)
7 ^[a]	2	80	3655 (3655)	8212 (4106)	13194 (4398)	16117 (4029)	19328 (3866)	22428 (3738)	90 (6 h)
8 ^[a]	2	90	4705 (4705)	10672 (5336)	16595 (5532)	21004 (5251)	24700 (4940)		98 (5 h)
[a] For entries 1–8, the reaction mixtures were photoirradiated in 4 mL of 5 HCO ₂ H·2 NEt ₃ and 1 mL of DMF by using a 500 W xenon lamp.									

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hydrogen than that with 40 µmol of catalyst. In addition, the TOF activity is reversely proportional to the concentration of catalyst (Table 1), whereby a higher TOF is observed in $2 \mu mol > 5 \mu mol > 10 \mu mol > 20 \mu mol > 40 \mu mol$. In the subsequent evaluation of the temperature effect, 2 µmol of compound 1 (50 ppm) and P ligand 4 in DMF (1 mL) and 4 mL of FA/TEA (5:2) was photoirradiated under a 500 W Xe lamp for five or six hours at 40, 60, 80, and 90 °C. The hydrogen-generation efficiency was observed to be proportional to the temperature increase with the highest efficiency observed at 90 °C. As shown in Table 1, the highest TON and TOF of 24700 and 5500 h^{-1} , fourfold relative to that measured at 60 °C, was observed for the system photoirradiated at 90 °C for 5 h (Table 1, entries 5 and 8). In lieu with this finding, the hydrogen yield calculated for formic acid dehydrogenation by 1 was close to 98%. These results indicate that H₂-generation efficiency is dependent on both light and temperature. Furthermore, approximately 0.4 L of H₂ per hour was generated from the system, thus suggesting the feasibility of the direct application of the system for H₂ generation. This is the highest catalyst productivity known to date for any homogeneous hydrogen generation from formic acid with an [RuRu]-based biomimetic hydrogen cluster.

To investigate the stability of the catalyst, the system was photoirradiated and kept at 90 °C for 24 h (Figure 4). During the reaction, 0.8 mL of FA/TEA (5:2) per hour was added to the reaction vessel to maintain the substrate concentration. Hydrogen-generation efficiency remained linear for approximately ten hours before a deceleration occurred. A total turnover number of 44102 in 24 h and an averaged turnover frequency of 1838 h⁻¹ was achieved. To the best of our knowledge, this represents the highest stability of the catalyst and the TON ever reported for photocatalytic formic acid decomposition.

The photoinduced and photoassisted effects were investigated by performing a series of experiments in which the temperature was kept at 60 °C and the light was turned on and off at a constant time interval. As shown in Figure 5, only a slight increase in hydrogen production was observed during the first hour in the absence of light. Then, an apparent hydrogen-gen-



Figure 4. Stability of ruthenium complex 1 and P ligand 4 for continuous hydrogen generation.

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eration increase was observed during the irradiation period but not between two irradiation periods. Consistent with this observation is that when different wavelengths ((280 nm cutoff, 280–397 nm (T=346 nm), 301–384 nm (T=352 nm), 355–469 nm (T=397 nm)) were tested for hydrogen-generation efficiency, the percentage of formic acid consumed in six hours was 100, 92, 60, 9% for the 280, 280–397, 301–384, and 355–469 nm wavelengths of light cutoffs, respectively. Furthermore, by calculating the total number of moles of photon absorbed at 355 nm and the net number of moles of hydrogen generated by photoirradiation, the measured quantum yield is about 0.331. These results indicate the photoinduced and photoassisted effects on hydrogen generation.



Figure 5. The photoinduced and photoassisted effect of hydrogen generation was investigated with 1 (2 µmol)+4 (2 µmol) in DMF (1 mL)+FA/TEA (4 mL, 5:2). The solution was heated at 60 °C for 1 h before the light was switched on and off every 1 h. Gas (500 µL) was harvested for every 15 min by a gas-tight syringe and analyzed by means of GC-TCD.

To identify active catalyst species, we performed time-dependent ³¹P NMR spectroscopic analyses of 1+4+FA/TEA+hv(1 h; Figure 6). The ³¹P NMR spectroscopic signal observed at $\delta = -30.1$ ppm corresponds to the P ligand **4** before photoirradiation. In the absence of FA/TEA and before photoirradiation, one small singlet at $\delta = 39.8$ ppm, which corresponds to the P ligand coordinated to the metal center to form a complex, was detected. After photoirradiation for 30 min, two singlets at $\delta =$ 37.2 and -21.1 ppm were observed in the ³¹P NMR spectrum, with concordant diminishing of the singlet at $\delta = 39.8$ ppm and decrease in the free P ligand **4** at $\delta = -30.1$ ppm. The singlet at $\delta = 37.2$ ppm corresponds to protonated tri(o-tolyl)phosphine oxide, which was also observed after photoirradiation of 4+FA/TEA (data not shown). After one hour of photoirradiation, the signal at $\delta = -21.1$ ppm increased and a new singlet at $\delta = -26.1$ ppm appeared. The intensity of the signal at $\delta =$ 37.2 ppm remained unchanged, whereas the signals at $\delta =$ -21.1 and -26.1 ppm increased with prolonged photoirradiation, thus indicating an increase in P ligands coordinated to the metal center and subsequently treated with FA. Consistent with this observation is the acceleration of hydrogen generation after one hour of photoirradiation. These results also sug-

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Figure 6. ³¹P NMR spectra of the time courses of the $1+4+FA/TEA+h\nu$ (0 min, 30 min, 1 h) catalyst solution.

gest that in the presence of FA/TEA the binding of P ligands to the ruthenium complex is preferred over the photo-oxidation.

In parallel, after photoirradiation for six hours and completion of the reaction, the reaction solution was subjected to column chromatography for product characterization. The isolated product was characterized by both ³¹P NMR spectroscopy and X-ray crystallography. The only isolated product is the [Ru₂(CO)₅(μ -SCH₂CH₂CH₂CH₂S)(P(o-tol)₃)] complex, which has been characterized by X-ray crystallography previously in our laboratory (data not shown). In addition, when the isolated product was subjected to photocatalytic hydrogen generation, both TON and TOF similar to those of **1**+**4** were obtained (Figure S5 in the Supporting Information). These results showed that no decomposition product could be detected after six hours of photoirradiation, which indicates that all the formic acid was completely decomposed to H₂ and CO₂.

On the basis of the results described above and the catalytic

cycle described for the [FeFe]based hydrogen cluster, a proposed mechanism for the photogeneration of H₂ by an [RuRu]based biomimetic hydrogen cluster and P ligands can be put forth, as in Scheme 2.^[15] In the absence of FA/TEA and before photoirradiation, the addition of the P ligand to the [RuRu]-based hydrogen cluster generated a small amount of ruthenium/Pligand complex (I). Upon photoirradiation and in the presence of FA/TEA, a minor amount of free P ligand was initially oxidized to form inactive tri(o-tolyl)phosphine oxide and the subsequent protonated product, which showed a singlet at $\delta =$ 37.2 ppm. Simultaneously, the carbonyl group of the ruthenium/P-ligand complex (I) was activated to generate a new species (II). The carbonyl group was then replaced with a formate (III) or a hydride (IV) to result in the shift of the singlet at δ =39.8 to -21.1 ppm and the newly generated singlet signal at δ =-26.1 ppm. Protonation by FA resulted in generation of H₂, the release of CO₂, and the regeneration of the active species III and IV, which was supported by the detection of the ³¹P NMR spectroscopic signals from prolonged photoirradiation reactions.

Conclusion

In conclusion, we have utilized a novel ruthenium-based biomimetic hydrogen cluster for efficient photocatalytic H₂ generation from formic acid decomposition. The addition of electron-donating P ligands provides higher activity than electronwithdrawing P ligands, from which the tri(o-tolyl)phosphine exhibits the highest activity. Remarkably, the highest TON and TOF of 24700 and 5500 h^{-1} , respectively, and up to 0.4 L of H_2 per hour could be generated from a 5 mL reaction solution that contained 50 ppm of catalyst-to-substrate ratio. In addition, the catalyst is highly stable and shows constant catalytic activity under prolonged photoirradiation at 90°C; it is putatively feasible that the system could be directly applied for hydrogen generation. Accompanying light on and off experiments and ³¹P NMR spectroscopic studies suggest that the H₂ generation reaction is photoinduced and photoassisted, and in the presence of FA/TEA the binding of the P ligand to 1 is preferred over its own photo-oxidation. Finally, the overall activity of the [RuRu]-based biomimetic hydrogen cluster is more than 20-fold higher than that of [FeFe]-based hydrogen clusters.^[15] In further studies we will focus on improving the activity of covalent incorporation of P ligands to the metal center.



Scheme 2. Proposed hydrogen-generation reaction catalyzed by 1 and P ligand 4.

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Experimental Section

Synthesis and spectroscopic characterization of $[Ru_2(CO)_6(\mu-SCH_2CH_2CH_2S)]$ and $[{(\mu-H)Ru_3(CO)_{10}}_2(\mu-SCH_2CH_2CH_2S)]$

A suspension of $[Ru_3(CO)_{12}]$ (0.32 mmol, 204 mg) in toluene (80 mL) was treated with 1,3-propanedithiol (2 equiv) under argon. The reaction mixture was stirred at 80 °C until its color changed from yellow-orange to deep orange. The solvent and an excess amount of 1,3-propanedithiol were removed under vacuum, and the residue was purified through a silica gel column eluting with 100% hexane and hexane/CH₂Cl₂ (98:2 v/v) to develop two bands. The two compounds were characterized by spectroscopic data and X-ray diffraction and compared to previously published literature reports.⁽¹⁰⁻¹²⁾

Spectroscopic and crystal structure determination of $[Ru_2(CO)_6(\mu\text{-SCH}_2CH_2CH_2S)]$ and $[\{(\mu\text{-H})Ru_3(CO)_{10}\}_2(\mu\text{-SCH}_2CH_2CH_2S)]$

 $[Ru_2(CO)_6(\mu-SCH_2CH_2CH_2S)] \text{ was crystallized as yellow crystals from hexane and CH_2Cl_2 at -20 °C, and <math display="inline">[\{(\mu-H)Ru_3(CO)_{10}\}_2(\mu-SCH_2CH_2CH_2S)]$ was crystallized as yellow-orange crystals also with hexane and CH_2Cl_2 at -20 °C. Each crystal was formed onto the end of a thin glass tube and was measured by using single-crystal X-ray determination. The crystal structures were analyzed and confirmed by the instrumentation at the National Taiwan Normal University. Crystallographic data were recorded at 200 K using a Bruker Nonius Kappa CCD X-ray diffraction.

Photocatalytic hydrogen generation

Formic acid was used as a proton source. A quartz Schlenk tube that contained the photocatalyst/ruthenium-based hydrogen-cluster/[Ru₃(CO)₁₂] (20 µmol), phosphine ligands (20 µmol) in DMF (1 mL), and proton source (4 mL) aliquot of $5 \text{HCO}_2\text{H}\cdot2 \text{NEt}_3$ (FA/TEA) was degassed under pure Ar atmosphere. The reaction solution was stirred and irradiated at 60 °C using a Xe lamp (500 W) without a filter. For each hour, 500 µL of the gas in the headspace of the sample tube was harvested by means of a gas-tight syringe and analyzed using a Bruker 450 GC gas chromatograph instrument equipped with a Carboxen 1010 PLOT-fused silica capillary column (Supelco, 30 m×0.53 mm) in 40 °C oven temperature, a thermal conductivity detector (TCD), and with Ar as carrying gas to measure the volume of H₂. In addition, the amount of hydrogen was determined and calculated by an external standard method.

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FULL PAPER

Chemical copycat: A diruthenium complex with efficient photocatalytic hydrogen evolution from formic acid decomposition was developed by mimicking an [FeFe]-based hydrogen cluster (see figure). The catalytic activities obtained with less than 50 ppm of the catalyst amount represented the highest turnover frequency for ruthenium complexes as well as the best efficiency for photocatalytic hydrogen production from formic acid.



Hydrogen Generation

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A Ruthenium-Based Biomimetic Hydrogen Cluster for Efficient Photocatalytic Hydrogen Generation from Formic Acid