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Photochemical Hydrogenation of π -Conjugated Bridging Ligands in Photofunctional Multinuclear Complexes

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Supporting Information



ABSTRACT: Vinylene or ethynylene linkers in the bridging ligands of photofunctional multinuclear complexes synthesized by various coupling reactions, such as the Mizoroki–Heck reaction, olefin metathesis, and Sonogashira coupling, were successfully converted to their corresponding saturated carbon chains using photochemical hydrogenation, which proceeded in an MeCN– pyridine–CF₃COOH (3:1:0.1 v/v/v) mixed solution containing the starting metal complexes and 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[*d*]imidazole (BIH) as a sacrificial electron donor under visible light irradiation in high yields. Hydrogenation of linkers in a Ru₂–Re trinuclear complex improved the photocatalytic ability for CO₂ reduction.

INTRODUCTION

Photofunctional multinuclear complexes have attracted great interest owing to their useful and unique photofunctional properties that cannot be obtained in mixed systems of the corresponding mononuclear complexes, e.g., improvement of photophysical properties, electronic interaction among each of the complex units, and rapid intramolecular energy and electron transfer even on the heterogeneous surface. Therefore, multinuclear metal complexes have been used as efficient photosensitizers,¹ photocatalysts,² and light harvesting systems.³ In particular, the use of these complexes for photocatalytic CO₂ reduction reactions often results in more efficient and durable photocatalytic systems compared with a mixed system of the corresponding mononuclear complexes.⁴

Most of these complexes have been synthesized using preconnected bridging ligands and stepwise coordination of metal complexes that can react with the bridging ligands under relatively mild reaction conditions.⁵ Although this synthetic method is useful for connecting two metal complexes, its application for connecting more than three metal complexes, including more than two kinds of different metals, is problematic since multiple isomers with different ratios and positions of metals can form. In recent times, some coupling reactions,⁶ e.g., the Mizoroki-Heck reaction,⁷ Sonogashira coupling,⁸ olefin metathesis,⁹ Suzuki-Miyaura coupling,¹⁰ and homocoupling,¹¹ have been used for connecting metal complexes possessing functional groups on their ligands, such as bromo groups, vinyl groups, ethynyl groups, and boronic acid substituents, for use as active spots for coupling reactions. These coupling methods can supply integration between or among metal complexes without drastic changes in the structures of each complex unit. In addition, by introducing plural functional groups into one metal complex, the complex can be connected to several metal complexes in a single step. Therefore, the variety of multinuclear complexes has been enlarged with the development of these coupling methods.

Most complexes synthesized by these coupling methods have an unsaturated bond or bonds, i.e., double bonds, triple bonds, and phenylene groups, for use as a linker or linkers. Such unsaturated linkages between the ligands in multinuclear complexes usually extend the π -conjugation in the bridging ligands.^{2e,7a,12} A larger π -conjugation causes positive shifts in the reduction potentials of the multinuclear metal complexes. This leads to a decrease in the reduction power of the reduced multinuclear metal complexes, which induces a serious problem, i.e., a drastic decrease in their photocatalytic abilities when the complexes are used as catalysts or photocatalysts, such as for CO₂ reduction.^{2e,4,12,13} Therefore, synthetic methods for converting the unsaturated linkages to the corresponding saturated carbon chains are desired for applying the C–C coupling reactions to construct various photofunctional multinuclear metal complexes.

In this context, we report new photochemical hydrogenation methods of vinylene or ethynylene chains in the bridging ligands of various photofunctional multinuclear metal complexes synthesized by Mizoroki–Heck reactions, olefin metathesis, and Sonogashira-coupling reactions. The $Ru(II)_2$ –Re(I)

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trinuclear complex, which was made by a combination of the Mizoroki–Heck reaction and photochemical hydrogenation, showed a higher photocatalytic ability for CO_2 reduction than the trinuclear complex without hydrogenation.

RESULTS AND DISCUSSION

Chemical hydrogenation reactions of unsaturated bonds using Pd/C or homogeneous catalysts, such as Wilkinson's¹⁴ and Crabtree's catalysts,¹⁵ are candidates for converting unsaturated linkers in the bridging ligands of multinuclear complexes. Therefore, we first examined chemical hydrogenation reactions of a Ru₂–Re trinuclear complex synthesized by the Mizoroki–Heck reaction^{7a} using either Pd/C or Crabtree's catalysts¹⁵ under a 1 atm H₂ atmosphere (eq 1). Unfortunately, the reactions did not proceed at ambient temperature, likely due to high steric hindrance in the bulky metal complex units, preventing the catalysts from approaching the olefin moieties. Therefore, we sought to develop a new photochemical hydrogenation method via a photochemical electron transfer reaction, applicable for various multinuclear complexes synthesized by C–C coupling reactions.

In order to investigate suitable reaction conditions for photochemical hydrogenation, a Ru(II)–Re(I) dinuclear complex (Ru(C=C)Re³⁺), synthesized by the Mizoroki–Heck reaction (eq 2) containing two kinds of metal-complex units linked through a vinylene chain, was chosen as a starting material for the photochemical hydrogenation reaction (eq 3). Figure 1a shows the absorption spectral change of an acetonitrile-pyridine-CF₃COOH mixed solution (3:1:0.1 v/v/v, 4 mL) containing Ru(C=C)Re³⁺ (0.03 mM) and 1,3-dimethyl-2-phenyl-2,3dihydro-1*H*-benzo[*d*]imidazole (BIH, 10 mM) as a reductant during irradiation at $\lambda_{ex} = 600$ nm under Ar (optical pass



Figure 1. (a) Absorption spectral changes of the MeCN–pyridine– CF₃COOH (3:1:0.1 v/v/v) mixed solution containing Ru(C=C)Re³⁺ (0.03 mM) and BIH (10 mM) during irradiation with 600 nm excitation light (0–160 min). (b) Time course of the absorbance at 550 nm.

length, 1 cm; light intensity, 4.3×10^{-8} einstein s⁻¹). During the reaction, the singlet metal-to-ligand charge transfer (¹MLCT) absorption band from the Ru(II) unit of the binuclear complex

was blue-shifted, and a decrease in the molar extinction coefficient was observed. The spectral change was accomplished within approximately 2 h (Figure 1b), and the shape of the spectrum became similar to that of $[Ru(bpy)_2(dmb)]^{2+}$ (bpy = 2,2'-bipyridine, dmb = 4,4'-dimethyl-bpy, Figure S1 in the Supporting Information). Further irradiation did not cause any spectral changes to the solution. This is reasonable since the product could not absorb the irradiating light at a wavelength of 600 nm. These results strongly suggest that the vinylene moiety of the bridging ligand in $Ru(C=C)Re^{3+}$ was converted to a single bond.

The main product was successfully isolated using ion exchange chromatography with CM Sephadex as an absorbent and an MeCN–water mixed solution (v/v = 1:1) containing NH₄PF₆ (0–8 mM) as an eluent. In the size exclusion chromatograms (SEC),¹⁶ the retention time of the product was similar to that of Ru(C=C)Re³⁺ (product RT = 34.7 min; Ru(C=C)Re³⁺ RT = 34.4 min), which clearly indicates that the product has a similar molecular size to Ru(C=C)Re³⁺. Figure 2a shows the main peaks of the product obtained via electron spray ionization time-of-flight mass spectros-copy (ESI–TOF-MS), where m/z values (511.11 ([M]³⁺), 839.16 ([M + PF₆⁻]²⁺)) were shifted by 2/3 and 2/2 compared



Figure 2. Main peaks in the ESI–TOF-mass spectra: (a) Ru(CH–CH)Re³⁺ and (c) Ru(C=C)Re³⁺. The calculated spectrum of Ru(CH–CH)Re³⁺ is illustrated in b.

to those of Ru(C=C)Re³⁺ (510.44 and 838.14, Figure 2c), respectively. The isotope distributions in the peaks were identical with those calculated for Ru(CH–CH)Re³⁺ (Figure 2b). These results clearly indicate that the photochemical hydrogenation reaction of Ru(C=C)Re³⁺ giving Ru(CH–CH)Re³⁺ was achieved (eq 3). The isolated yield of Ru(CH–CH)Re³⁺ was 72%. The quantum yield of the conversion of Ru(C=C)Re³⁺ to Ru(CH–CH)Re³⁺ was about 3% under these reaction conditions (Figure S2 in the Supporting Information).

Scheme 1 illustrates the expected reaction mechanism for the photochemical hydrogenation reaction. Under these reaction conditions, the Ru unit in $Ru(C=C)Re^{3+}$ was selectively excited with the irradiating light (λ_{ex} = 600 nm). Then, its excited state was reductively quenched by BIH, owing to its strong reducing power $(E_{0x}^{P} = 0.33 \text{ V vs SCE in MeCN})^{2d}$ The reaction solution did not show any emission; thus the quenching process should proceed quantitatively. The rate constant for the quenching process (k_q) was determined as $1.6 \times 10^9 [M^{-1} s^{-1}]$ by the Stern–Volmer constant and the emission lifetime ($K_{SV} = 2700$, $\tau = 1700$ ns, Figure S3 in the Supporting Information). It is noteworthy that BIH has no absorption in the visible region. BIH can be widely used as an electron donor for the various photochemical reactions because of these properties. The oneelectron-reduced species $Ru(C=C^{\bullet-})Re^{2+}$ that was produced was expected to be protonated by CF₃COOH and/or BIH^{•+}, giving $Ru(CH-C^{\bullet})Re^{3+}$. This process was confirmed by the cyclic voltammogram of $Ru(C=C)Re^{3+}$, which showed that the first reduction wave was reversible in the absence of CF₂COOH and became irreversible with the addition of CF₃COOH (Figure S4 in the Supporting Information). The redox-photosensitized hydrogenation reactions of various olefins with $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) as a photosensitizer and a sacrificial electron donor have been reported,¹⁷ and the reactions proceeded via reduction of the olefins by the photochemically reduced Ru(II) photosensitizer, followed by protonation with MeOH as a solvent. For conversion of the produced radical intermediate Ru(CH-C•)Re3+ to the final Ru(CH-CH)Re³⁺ product, the intermediate needs to accept both one more electron and one more proton. Although the details of this reaction mechanism are not clear, another electron can be supplied by another reductive quenching process following photoexcitation of the intermediate or from the strong reductant BI[•] ($E_{ox}^{P} = -2.06$ V vs SCE), which is produced by deprotonation of the one-electron-oxidized species (OEOS) of BIH

Scheme 1. Reaction Mechanism of the Photochemical Hydrogenation Reaction of Ru(C=C)Re³⁺



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(BIH^{•+}; eq 4).^{2d} Pyridine could assist this deprotonation process as a base and suppress back electron transfer from Ru(C= $C^{\bullet-}$)Re²⁺ to BIH^{•+}. Since the first electron can be supplied through intramolecular electron transfer from the photochemically produced one-electron-reduced species (OERS) of the metal complex unit to the double bond in the bridging ligand, and the following processes were also not retarded by the bulky Ru and Re units, this photochemical hydrogenation reaction should be useful for the reduction of multiple bonds with bulky substituents, such as metal complexes.

The absorption spectral changes of the reaction solution during irradiation at λ_{ex} = 480 nm, which is close to the absorption maximum of Ru(C=C)Re³⁺ (Figure S5 in the Supporting Information), was different from those using $\lambda_{ex} =$ 600 nm (Figure 1a). Similarly shaped but more rapid spectral changes, i.e., the blue shift of the ¹MLCT absorption band and decrease in the absorbance attributed to the conversion of $Ru(C=C)Re^{3+}$ to $Ru(CH-CH)Re^{3+}$, were observed in the first stage of the reaction (<10 min irradiation). Although the reaction rate was accelerated compared to the case using 600 nm irradiation light, owing to the stronger absorption of $Ru(C=C)Re^{3+}$ at 480 nm, further irradiation caused a decrease and broadening in the ¹MLCT absorption band, which is attributable to ligand substitution of the Ru(II) trisdiimine complex unit of $\tilde{Ru}(CH-CH)Re^{3+}$ with solvent molecules (S) producing the corresponding Ru(II) bis-diimine complexes, i.e., $[Ru^{II}(N^N)_2(S)_2]^{n+}$. As previously reported, such photochemical ligand substitution reactions of Ru(II) trisdiimine complexes proceed efficiently in the presence of acid.¹⁸ Note that Ru(CH-CH)Re³⁺ can absorb irradiating light of 480 nm, and excitation of Ru(CH-CH)Re3+ should induce further decomposition. Therefore, the 480 nm excitation light is useful for increasing the reaction rate of the hydrogenation reaction, but the reaction should be stopped before ligand substitution takes place.

Photochemical hydrogenation reactions were also conducted in other organic solvents, i.e., *N,N*-dimethylformamide (DMF) and MeOH, instead of MeCN. Although similar absorption spectral changes were observed during irradiation in DMF– pyridine–CF₃COOH, the ESI–mass spectrum of the main product was quite different from that of MeCN (Figure 3); i.e., the main peaks were attributed to DMF-incorporated complexes. DMF should have reacted with the OERS of Ru(C=C)Re³⁺ or



Figure 3. ESI-mass spectra of the product produced by the hydrogenation reaction of $Ru(C=C)Re^{3+}$ using (a) MeCN-pyridine-CF₃COOH or (b) DMF-pyridine-CF₃COOH as the solvent.

its protonated form. Although the use of MeOH instead of MeCN gave Ru(CH–CH)Re³⁺ as the main product, irradiation longer than 12 h was required to finalize the reaction, likely the result of suppression of deprotonation from the OEOS of BIH and accelerated back electron transfer from Ru(C=C^{•-})Re²⁺ to BIH^{•+}, and small amounts of MeOH-incorporated complexes were also observed in the ESI–mass spectrum. Therefore, MeCN is a suitable organic solvent for this photochemical hydrogenation reaction.

As mentioned above, photochemical hydrogenation can be achieved selectively in an MeCN–pyridine mixed solution in the presence of BIH as an electron donor and CF₃COOH as a proton source with irradiation at $\lambda_{ex} = 600$ nm. These reaction conditions were applied in hydrogenating other photofunctional dinuclear complexes that could be synthesized using other C–C coupling reactions with high yields. A Ru(II) dinuclear complex





 $(Ru(C=C)Ru^{4+})$ synthesized by olefin metathesis (eq 5) and a Ru–Ir dinuclear complex $(Ru(C\equiv C)Ir^{3+})$ synthesized by Sonogashira coupling (eq 6) were also hydrogenated under the same reaction conditions in relatively high isolated yields (eqs 7 and 8, Table 1). It should be emphasized that the photochemical hydrogenation method can be used for not only double bonds but also triple bonds in the bridging ligands.

When using an Ir–Re dinuclear complex $(Ir(C=C)Re^{2+})$ as a substrate, a shorter irradiation wavelength should be used

since only small absorbance occurs at 600 nm. Irradiation at $\lambda_{ex} = 510$ nm caused absorption spectral changes in the reaction solution for 5 h, and the isolated yield of Ir(CH–CH)Re²⁺ was 66% (eq 9).

In the case of a Re(I) dinuclear complex with different phosphorus ligands on each Re unit ((EtO)Re(C=C)Re(Et)²⁺), similar absorption spectra changes, i.e., a blue-shift and decrease in the absorption bands, were observed during irradiation at $\lambda_{ex} = 600$ nm; however, the reaction took place over more than

Entry	Substrate	Reaction Time / h ^b	Product	Isolation Yield / %
1	Ph ₃ P _b , N OC CO PPh ₃ CO CO PPh ₃ Ru(C=C)Re ³⁺	15 (6)	PhyPe Phy OC ^C CO ^{PPhy} Ru(CH-CH)Re ³⁺	72
2	$(EtO)Re(C=C)Re(Et)^{2+}$	37 (21)	$(EtO)P^{CO}_{P(OEI)_3} \xrightarrow{(EtO)P^{CO}_{P(OEI)_3}} \downarrow^{2+}$	36
3 ^c	(pFC ₆ H ₄) ₂ P ₄ oc ⁺ C ₀ ⁻ P(pFC ₆ H ₄) ₃ Ir(C=C)Re ²⁺	8 (5)	(pFCqHq)p oc ⁺ (pFCqHq)p (pFCqHq)s Ir(CH-CH)Re ²⁺	66
4	H H H H H H H H H H H H H H	15 (1)	Ru(CH-CH)Ru ⁴⁺	62
5	Ru(C=C)lr ³⁺	14 (5)	(N, N) (N, N) (N) (N, N) (N) (N) (N) (N) (N) (N) (N) (N) (N) (78
6	(p+Fc ₄ H ₄)p, where the second seco	15 (7)	(p-FC _e H _d) ₂ P _c -Re _p H _c -C _e H _d) ₃ C Ru(CH-CH)Re(CH-CH)Ru ⁵⁺	55

Table 1. Photochemical Hydrogenation Reactions of Various Multinuclear Complexes^a

^{*a*}The reactions were conducted in an acetonitrile-pyridine-CF₃COOH mixed solution (3:1:0.1 v/v/v) containing BIH (10 or 50 mM) and substrates under irradiation with 600 nm excitation light. ^{*b*}The values shown in parentheses indicate the irradiation time when the photochemical hydrogenation reaction was almost completed. ^{*c*}The irradiation wavelength was 510 nm.



Figure 4. ¹H NMR spectra of (a) (EtO)Re(C=C)Re(Et)²⁺ and (b) (EtO)Re(CH-CH)Re(Et)²⁺ in acetone- d_{6^*}

20 h due to the low absorbance at 600 nm. Purification of the target molecule (EtO)Re(CH-CH)Re(Et)²⁺ required both ion exchange chromatography and silica-gel column chromatography. Figure 4 shows ¹H NMR spectra of (EtO)Re(C=C)Re(Et)²⁺ and (EtO)Re(CH-CH)Re(Et)²⁺. The peak attributed to the olefinic protons in the bridging ligand of (EtO)Re(C=C)Re(Et)²⁺

at 8.07 ppm disappeared, and new peaks derived from ethylene chains of (EtO)Re(CH–CH)Re(Et)²⁺ were observed at 3.42 ppm. Byproducts derived from a coupling reaction between the photochemically reduced species of (EtO)Re(C=C)Re(Et)²⁺ and the oxidation product(s) of BIH were observed in a fraction of the ion exchange chromatography (Figure S6 in the Supporting Information). The BIH adduct(s), which had different charges than (EtO)Re(CH–CH)Re(Et)²⁺, were obtained in about a 30% isolation yield (eq 10). This likely occurred since (EtO)Re(C=C)Re(Et)²⁺ has relatively low steric hindrance around the vinylene linker compared to the other dinuclear complexes mentioned above, allowing the oxidized product(s) of BIH to approach the bridging ligand.¹⁹

The trinuclear Ru(C=C)Re(C=C)Ru⁵⁺ complex was also successfully hydrogenated under similar reaction conditions with 7 h of irradiation at $\lambda_{ex} = 600$ nm giving Ru(CH–CH)-Re(CH–CH)Ru⁵⁺, where both vinylene chains were converted to ethylene chains (eq 11). Purification was achieved by ion exchange chromatography with an isolation yield of 55%. It might



be noteworthy that we chose 4,4'-dimethylbipyridine (dmb) as peripheral ligands on the Ru units because of application of the hydrogenated complex as a photocatalyst for CO₂ reduction,² but this trinuclear complex has a very similar structure to the Ru₂-Re trinuclear complex with the bpy ligands on the Ru units, which could not be hydrogenated by the chemical hydrogenation. This suggests that various trinuclear complexes connected through ethylene chains can also be synthesized using the combination of C-C coupling and photochemical hydrogenation reactions. In the trinuclear Ru(CH-CH)Re(CH-CH)Ru⁵⁺ complex, two photosensitizer moieties were connected with one Re(I) catalyst moiety in the center position, which cannot be selectively produced by ordinary synthetic methods using preconnected bridging ligands. The reaction of a bridging ligand with three diimine moieties and two kinds of precursor metal complexes should give a mixture of various trinuclear complexes with different numbers of Ru units and/or a different order of Ru and Re units. This is likely one reason why most reported supramolecular photocatalysts containing an Re(I) complex with a diimine ligand as the catalyst had only one photosensitizer unit. The combination of C-C coupling reactions and the photochemical hydrogenation of multiple bonds in the bridging ligands can supply synthetic routes to new multinuclear complexes with different metal complexes connected through saturated alkyl chains. The isolated yields and required irradiation time of the complexes synthesized in this work are summarized in Table 1.

As previously reported, some dinuclear complexes with a Ru(II) trisdiimine photosensitizer unit and an Re(I) diiminecarbonyl catalyst unit connected by an alkyl chain are efficient and durable photocatalysts for CO₂ reduction.^{2a,c-f} Accordingly, we used the newly synthesized trinuclear Ru(CH-CH)Re-(CH-CH)Ru⁵⁺ complex for photocatalytic CO₂ reduction and $Ru(C=C)Re(C=C)Ru^{5+}$ as a reference where the complex units are connected by vinylene chains. A DMF-triethanolamine (5:1 v/v) solution containing 0.05 mM of the complex and 0.1 M 1-benzyl-1,4-dihydronicotinamide (BNAH) as a reductant was irradiated at λ_{ex} > 500 nm using a high-pressure mercury lamp (Figure 5a and Table 2). Triethanolamine was added as a base in order to remove a proton from OEOS of BNAH and suppress back electron transfer (eq 12). Note that TEOA did not work as a reductant because it could not reductively quench emission from Ru(CH-CH)Re(CH-CH)Ru^{5+, 2e} Under these conditions, the Ru units were selectively or mainly excited, and their excited states were reductively quenched by BNAH (Figure S7 in the Supporting Information), followed by electron transfer from the reduced Ru unit to the Re catalyst unit. Both photocatalytic reactions using either complex produced CO as the main product and HCOOH and H₂ as minor products $(Ru(CH-CH)Re(CH-CH)Ru^{5+}: TON_{CO} = 313,$ $TON_{HCOOH} = 85$, $TON_{H2} = 22$; $Ru(C=C)Re(C=C)Ru^{5+}$: $TON_{CO} = 283$, $TON_{HCOOH} = 100$, $TON_{H2} = 26$). The TON_{CO} of Ru(CH-CH)Re(CH-CH)Ru⁵⁺ was higher than that of Ru(C=C)Re(C=C)Ru⁵⁺, and the TON_{CO} was the highest value reported for photocatalytic systems using Re complexes as



Figure 5. (a) Time courses for the TON of reduction products, i.e., CO (solid line), HCOOH (dotted line), and H₂ (dashed line) during photocatalytic reaction (20 h, $\lambda_{ex} > 500$ nm) using a DMF and triethanolamine (5:1 v/v) solution containing 0.1 M of BNAH and 0.05 mM of Ru(C=C)Re(C=C)Ru⁵⁺ (red) or Ru(CH-CH)Re(CH-CH)Ru⁵⁺ (blue). The enlarged views of the time courses for production of CO and HCOOH within 1 h (the green square in a) are illustrated in b and c, respectively.

(photo)catalysts under similar reaction conditions using BNAH as the reductant.^{2f} The main reason for the decrease in the efficiency of the reaction after 5 h of irradiation was accumulation of the oxidation products of BNAH, i.e., BNA_2 (eq 12), which are known as inhibitors of photocatalytic reactions.^{2b-d} The trinuclear complexes were detected as major compounds in

Table 2. Photocatalytic Ability of the Trinuclear Complexes^a

complex	TON _{CO} ^b	TON _{HCOOH}	TON _{H2} ^b	TOF_{CO}/h^{-1c}	$k_{ m q} au^d$	$\eta_q^{\ e}/\%$
$Ru(C=C)Re(C=C)Ru^{5+}$	283	100	26	137	94	90
Ru(CH-CH)Re(CH-CH)Ru ⁵⁺	313	85	22	166	24	71

^{*a*}A DMF and triethanolamine (5:1 v/v) solution containing 0.05 mM of Ru(C=C)Re(C=C)Ru⁵⁺ or Ru(CH-CH)Re(CH-CH)Ru⁵⁺ and 0.1 M of BNAH under a CO₂ atmosphere was irradiated at $\lambda_{ex} > 500$ nm using a high-pressure mercury lamp. ^{*b*}The turnover number (TON) of each reduction product is calculated by the following equation: TON = (the amount of the products after 20-h irradiation [mol])/(the amount of the metal complex [mol]). ^{*c*}Determined by the slope of the fitting curves (within 1 h). ^{*d*}Determined by Stern–Volmer plots (Figure S7 in the Supporting Information). ^{*e*}Quenching fractions for emission from the Ru units by 0.1 M of BNAH calculated using the following equation: $0.1k_q\tau/(1 + 0.1k_q\tau)$.



the reaction solution on the SEC charts, even after a 5-h irradiation time (Figure 6).

A difference in photocatalytic ability between Ru(C=C)Re-(C=C)Ru⁵⁺ and Ru(CH-CH)Re(CH-CH)Ru⁵⁺ was clearly observed, especially in the initial stages of the photocatalytic reaction (Figure 5b). In the case of $Ru(C=C)Re(C=C)Ru^{5+}$ an induction period of about 5 min was observed for CO formation but was not clearly seen in the case of Ru(CH-CH)Re(CH-CH)Ru⁵⁺. In addition, the turnover frequency (TOF) of CO formation using Ru(CH-CH)Re(CH-CH)- Ru^{5+} (TOF_{CO} = 166 h⁻¹) was larger than that when using $Ru(C=C)Re(C=C)Ru^{5+}$ (TOF_{CO} = 137 h⁻¹). It should be noted that absorbance at $\lambda > 500$ nm (Figure 7) and the quenching fraction⁴ of the excited state of $Ru(C=C)Re(C=C)Ru^{5+}$ by BNAH ($\eta_q = 90\%$) were larger than those of Ru(CH-CH)Re(CH-CH)Ru⁵⁺ (71%). On the other hand, induction periods for HCOOH formation were observed in both cases; the induction period for Ru(CH-CH)Re(CH-CH)Ru⁵⁺ was longer than that of $Ru(C=C)Re(C=C)Ru^{5+}$ (Figure 5c), and the TON_{HCOOH} of Ru(CH-CH)Re(CH-CH)Ru⁵⁺ was smaller than that of $Ru(C=C)Re(C=C)Ru^{5+}$. Since Re(I) complexes have been reported as catalysts and/or photocatalysts for selective CO production in organic solutions,²⁰ as well as in photocatalytic systems using a Ru(II) trisdiimine complex as the photosensitizer (unit) and a Re(I) complex as the catalyst (unit),^{2a,c-h,k,l} formation of HCOOH should be induced by the catalytic ability of ligand-substitution products of the Ru(II) complex, i.e., Ru(II) bisdiimine bissolvento complexes, 2b,21 which were produced by the decomposition reaction of the Ru(II) photosensitizer units.^{18a,b,22} These results indicate that hydrogenation of the vinylene chains of Ru(C=C)Re(C=C)Ru⁵⁺ improved both the efficiency and durability of the trinuclear complex in photocatalytic CO formation.



Figure 6. SEC charts of the photocatalytic reaction solutions containing (a) $Ru(CH-CH)Re(CH-CH)Ru^{5+}$ and (b) $Ru(C=C)Re(C=C)Ru^{5+}$ measured after irradiation for 10 (red), 30 (orange), 60 (green), and 300 min (blue). The black dotted lines show SEC charts before the photocatalytic reaction. Detection wavelength was 420 nm.

For investigating the difference in the photocatalytic ability between Ru(CH-CH)Re(CH-CH)Ru⁵⁺ and Ru(C=C)Re- $(C=C)Ru^{5+}$ in detail, the reaction solutions after the photocatalytic reactions were analyzed using SEC. Figure 6a shows the SEC charts of the reaction solution using Ru(CH-CH)Re(CH-CH)Ru⁵⁺, where two main peaks were detected at retention times (RT) = 33 and 34 min after 10 min of irradiation. The former was attributed to the starting material, Ru(CH-CH)Re(CH-CH)Ru⁵⁺. The latter could be attributed to the trinuclear Ru(CH-CH)Re'(CH-CH)Ru complex (Scheme 2), where the Re(I) moiety was converted to the tricarbonyl form, i.e., $[\text{Re}^{I}(\text{BL}) (\text{CO})_{3}(\text{S})]^{n+}$ (BL = bridging ligand, S = solvent) from the ESI-MS results (Figure S9 in the Supporting Information). Similar phenomena were reported in photocatalytic systems using binuclear complexes with Ru(II) trisdiimine and Re(I) biscarbonyl units (eq 13), where the converted binuclear complex with the Re tricarbonyl unit worked as a photocatalyst and the starting complex with the Re biscarbonyl unit assisted



Figure 7. Absorption spectra of $Ru(C=C)Re(C=C)Ru^{5+}$ (red) and $Ru(CH-CH)Re(CH-CH)Ru^{5+}$ (blue) measured in MeCN.

photocatalytic CO₂ reduction as a redox photosensitizer.^{26,23} The starting trinuclear Ru(CH–CH)Re(CH–CH)Ru⁵⁺ complexes were partially converted to Ru(CH–CH)Re'(CH– CH)Ru with the Re(I) tricarbonyl unit during the early stages of the photocatalytic reaction (<5 min). After this partial conversion, photocatalytic CO₂ reduction actively proceeded to give CO selectively, where the trinuclear complex with the Re(I) tricarbonyl unit worked as a photocatalyst, and the residual trinuclear complex with the Re(I) biscarbonyl unit assisted the photocatalytic reaction as a redox photosensitizer since the ratio of the peaks between Ru(CH–CH)Re(CH–CH)Ru⁵⁺ and Ru(CH–CH)Re'(CH–CH)Ru in the SEC charts did not drastically change during 20 min of irradiation. Longer irradiation (>1 h) caused a slow decrease of both peaks and appearance of a new broad peak at a RT = 35-37 min. In this stage, the decomposition processes of both Ru(CH–CH)Re(CH–CH)-Ru⁵⁺ and Ru(CH–CH)Re'(CH–CH)Ru, which include ligand substitution reactions of the Ru units, partially proceeded to give Ru(II) bisdiimine bissolvento complexes (Scheme 2). The Ru(II) bisdiimine bissolvento complexes worked as catalysts for CO₂ reduction, giving HCOOH, as described above, due to the fact that formation of HCOOH required a relatively long induction period (Figure 5c). The small amount of hydrogen should also be produced by photocatalyses of the Ru(II) bisdiimine bissolvento complexes due to the fact that formation are should also be produced by photocatalyses of the Ru(II) bisdiimine bissolvento complexes because a similar induction period was observed.

In the case of $Ru(C=C)Re(C=C)Ru^{5+}$, two similar peaks attributed to two kinds of trinuclear complexes were detected at RT = 33-34 min, as well as in the case using Ru(CH-CH)Re(CH-CH)Ru⁵⁺ (Figure 6b). Interestingly, the UV-vis absorption spectrum of an eluent at RT = 33 min in the SEC of the photocatalytic reaction solution irradiated for 10 min was identical to Ru(CH-CH)Re(CH-CH)Ru⁵⁺, but not $Ru(C=C)Re(C=C)Ru^{5+}$ (Figure 8). This strongly suggests that the vinylene chains in the bridging ligands of $Ru(C=C)Re(C=C)Ru^{5+}$ were converted to the corresponding trinuclear complexes with saturated chains in the early stages of the photocatalytic reaction. The peak at RT = 34 min was attributed to Ru(CH-CH)Re'(CH-CH)Ru from ESI-MS results; therefore, CO should be catalytically produced by the mixed system of the two kinds of trinuclear complexes, one having the Re(I) tricarbonyl unit and another having the Re(I)biscarbonyl unit, of which vinylene chains in the bridging ligands have been already reduced (Scheme 3). The decrease in the intensity of these peaks was slightly faster than in the case of $Ru(CH-CH)Re(CH-CH)Ru^{5+}$. In addition, the peak observed at RT = 35-37 min increased much faster in this system. This peak was attributed to the decomposition compounds where

Scheme 2. Photochemical Processes in the Reaction Solution Containing Ru(CH-CH)Re(CH-CH)Ru⁵⁺







Figure 8. UV-vis absorption spectra of eluents at RT = 33 min in SEC of the photocatalytic reaction solution of Ru(C=C) $Re(C=C)Ru^{5+}$ before (red) and after irradiation for 10 min irradiation (orange). The blue line shows that of an eluent at RT = 33 in the SEC of the solution containing $Ru(CH-CH)Re(CH-CH)Ru^{5+}$.

one of the Ru(II) moieties was converted to a Ru(II) bisdiimine bissolvento complex (Figure S10 in the Supporting Information). Note that the induction period of HCOOH formation was longer when using Ru(CH–CH)Re(CH–CH)Ru⁵⁺ (1 h) compared to that of Ru(C=C)Re(C=C)Ru⁵⁺ (~20 min; Figure 5c). The lower TON_{CO} using Ru(C=C)Re(C=C)Ru⁵⁺

compared to Ru(CH–CH)Re(CH–CH)Ru⁵⁺ was likely caused by this faster decomposition process. The higher yield of the Ru(II) bisdiimine bissolvento complexes in the system using Ru(C=C)Re(C=C)Ru⁵⁺ also induced higher formation of HCOOH with a shorter induction period, as mentioned above.

CONCLUSIONS

We successfully developed a photochemical method for the hydrogenation of the vinylene and ethynylene linker(s) in the bridging ligand(s) of photofunctional multinuclear complexes synthesized using various C–C coupling reactions in relatively high isolated yields by irradiating the reaction solution in the presence of proton and electron sources. The hydrogenation reaction proceeded well when the unsaturated linkers possessed bulky metal complex units. The hydrogenated Ru₂–Re trinuclear complex worked as an efficient photocatalyst for CO₂ reduction. Application of this hydrogenation reaction will supply new tuning methods for photophysical, photochemical, and electrochemical properties of various photofunctional multinuclear complexes with multiple bonds as linkers, and improvement in the photocatalytic ability is an important example.

EXPERIMENTAL SECTION

General Procedures. ¹H NMR and ³¹P NMR spectra were measured using acetone- d_6 and a JEOL ECA400-II (400 MHz) system. IR spectra were measured by a JASCO FT/IR-610 spectrometer at 1 cm⁻¹ resolution with a solvent of dichloromethane. Electrospray ionization–mass spectrometry (ESI–MS) was performed using a

Scheme 3. Photochemical Changes in the Structures of the Trinuclear Complexes $Ru(C=C)Re(C=C)Ru^{5+}$ during the Photocatalytic Reactions



Shimadzu LC-MS-2010A system with acetonitrile as a mobile phase. Electrospray ionization time-of-flight mass spectrometry (ESI-TOFMS) was undertaken with a Waters LCT Premier using acetonitrile as a mobile phase. For analysis by size exclusion chromatography (SEC), a pair of Shodex PROTEIN KW-402J (300 mm × 8.0 mm i.d.) with a KW-LG guard column (50 mm × 6.0 mm i.d.), a JASCO 880-51 degasser, an 880-PU pump, an MD-2010 Plus UV-vis photodiode-array detector, and a Rheodyne 7125 injector was used. The column temperature was maintained at 40 °C using a JASCO 860-CO oven. The eluent was a 1:1 (v/v) mixture of methanol and acetonitrile with 0.5 M CH₃COONH₄, and the flow rate was 0.2 mL/min. Separation of multinuclear complexes was achieved by SEC using a pair of Shodex PROTEIN KW-2002.5 columns (300 mm × 20.0 mm i.d.) with a KW-LG guard column (50 mm × 8.0 mm i.d.) and a recycling preparative HPLC apparatus with a JASCO 870-UV detector. The eluent was a 1:1 (v/v) mixture of methanol and acetonitrile with 0.15 M CH₃COONH₄, and the flow rate was 6.0 mL/min. UV-vis absorption spectra were measured with a JASCO V-670. The irradiation light for photochemical hydrogenation reactions was 600 or 510 nm light derived from a Xe lamp in a Max 303 system equipped with band-pass filters (fwhm =10 nm), purchased from Asahi Spectra Co. UV-vis absorption spectra changes during the photochemical hydrogenation reactions and absorbed photon number were recorded by a Shimadzu QYM-01 system. The cyclic voltammograms of Ru(C=C)Re³⁺ (0.01 mM) are measured in MeCN solutions or MeCN-pyridine-CF₃COOH mixed solutions (3:1:0.1 v/v/v) containing Et₄NBF₄ (0.1 M) as a supporting electrolyte using an ALS/CHI CHI-720Dx electrochemical analyzer with a glassy-carbon disk working electrode (3 mm diameter), Ag/AgNO3 (0.01 M) reference electrode, and Pt counter electrode.

Materials. All reagents were reagent-grade quality and were used without further purification. $[\text{Re}(4\text{-bromo-bpy})(\text{CO})_2\{P(p_{\text{C}_6}\text{H}_4\text{F})_3\}_2](\text{PF}_6),^{7a}$ $[\text{Re}(4\text{-bromo-bpy})(\text{CO})_2(\text{PPh}_3)_2](\text{PF}_6),^{7a}$ $[\text{Ir}(\text{ppy})_2(\text{vbpy})](\text{PF}_6)$ (ppy = 2-phenylpyridine, vbpy = 4-methyl-4'-vinyl-bpy),^{7a} $[\text{Ru}(\text{bpy})_2(\text{vbpy})](\text{PF}_6)_2,^{7a}$ $[\text{Ru}(\text{dmb})_2(4\text{-bromo-bpy})]-(\text{PF}_6)_2,^{24}$ (EtO)Re(C=C)Re(Et)^{2+,7a} Ru(C=C)Re(C=C)Ru^{5+,7a} 4-ethynyl-bpy,^{24} BNAH,^{25} and 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole (BIH)^{2d} were prepared according to the reported methods with some modifications. $[\text{Ir}(\text{ppy})_2(4\text{-ethynyl-bpy})](\text{PF}_6)$ was synthesized with similar synthetic methods for $[\text{Ir}(\text{ppy})_2(\text{bpy})](\text{PF}_6)$ using 4-ethynyl-bpy instead of bpy.²⁶ DMF was dried over 4A molecular sieves and then distilled under reduced pressure (10–20 mm Hg). TEOA was distilled under reduced pressure (<1 mmHg). DMF and TEOA were stored under an Ar atmosphere prior to use.

Photocatalytic Reactions. Photocatalytic reactions were performed in 11 mL test tubes (i.d. = 8 mm) containing 2 mL of DMF–triethanolamine (TEOA; 5:1 v/v) solutions of Ru(CH–CH)Re(CH–CH)Ru⁵⁺ (0.05 mM) and BNAH (0.1 M) after purging with CO₂ for more than 20 min. The solutions were irradiated using a merry-goround irradiation apparatus at λ_{ex} > 500 nm with a high-pressure Hg lamp combined with a Pyrex water jacket and a K₂CrO₄ (30%, w/w, d = 1 cm) solution filter. During irradiation, the tubes were cooled with a thermostatic bath (25 °C). The gaseous reaction products (CO and H₂) were analyzed using a GC-TCD instrument (GL Science GC323). HCOOH was analyzed using a capillary electrophoresis system (Otsuka Electronics Co. CAPI-3300I).

Synthesis. $Ru(C=C)Re^{3+}$. [Re(4-bromo-bpy)(CO)₂(PPh₃)₂](PF₆) (100 mg, 88 µmol), [Ru(bpy)₂(vbpy)](PF₆)₂ (160 mg, 180 µmol), Pd(OAc)₂ (20 mg, 88 µmol), and AcONa (37 mg, 450 µmol) were dissolved in acetonitrile (20 mL, bubbled by N₂). The solution was heated at 65 °C under Ar for 3 days. Additional Pd(OAc)₂ (5.9 mg, 26 µmol) was added to the solution, and the solution was heated for another 3 days. The product was isolated by ion-exchange chromatography (CM Sephadex C-25, eluent: acetonitrile–water (1:1 v/v) containing NH₄PF₆ (0–8 mM)). Acetonitrile was evaporated under reduced pressure. The red precipitate was filtered off and washed with water and then with ether. Yield: 74 mg (42%). ¹H NMR (400 MHz, acetone- d_6): δ 8.98 (s, 1H), 8.83 (s, 1H), 8.82 (s, 1H), 8.81 (s, 1H), 8.80 (s, 1H), 8.74 (s, 1H), 8.51 (s, 1H), 8.39 (d, J = 8.4 Hz, 1H), 8.24–8.18 (m, 5H), 8.16 (d, J = 5.6 Hz, 1H, bpy-3), 8.11–8.05 (m, 4H), 7.91–7.88 (m, 2H), 7.87 (d, J = 6.0 Hz, 1H), 7.79 (m, 2H,
$$\begin{split} -C\underline{H} =& C\underline{H} -), 7.69 \text{ (d, } J = 6.0 \text{ Hz}, 1\text{ H}), 7.62 - 7.55 \text{ (m, 4H)}, 7.43 \text{ (d, } J = 6.0 \text{ Hz}, 1\text{ H}), 7.36 - 7.23 \text{ (m, 30H, } 6P\underline{Ph}_3), 7.07 \text{ (d, } J = 7.4 \text{ Hz}, 1\text{ H}), 7.02 \text{ (dd, } J = 6.6, 6.6 \text{ Hz}, 1\text{ H}), 2.61 \text{ (s, } 3\text{ H}, -C\underline{H}_3). ^{31}\text{P} \text{ NMR (400 MHz, acetone-}d_6): \delta 22.1 \text{ (s, } 2\text{ P}, -\underline{P}\text{Ph}_3), -143.5 \text{ (sep, } 3\text{ P}, 3\underline{P}\text{ F}_6^{-}). \\ \text{FT-IR (in CH}_2\text{Cl}_2) \nu_{\text{CO}}/\text{cm}^{-1}: 1938, 1869. \text{ ESI}-\text{MS (in acetonitrile): } m/z \text{ 510 ([M-3PF}_6^{-}]^{3+}), 838 \text{ ([M-2PF}_6^{-}]^{2+}). \text{ HRMS (ESI-TOF): } m/z \text{ [M-3PF}_6^{-}]^{3+} \text{ Anal. Calcd for } C_{81}\text{H}_{64}\text{N}_8\text{O}_2\text{P}_2\text{ReRu: } \text{ $10.4416. Found: $10.4395. [M-2PF}_6^{-}]^{2+} \text{ Anal. Calcd for } C_{81}\text{H}_{64}\text{F}_6\text{N}_8\text{O}_2\text{P}_3\text{ReRu: } \text{$38.1445. Found: $838.1412.} \end{split}$$

 $Ru(CH-CH)Re^{3+}$. Ru(C=C)Re³⁺ (10.0 mg, 5.09 μ mol) and BIH (45.0 mg, 201 μ mol) were dissolved in an acetonitrile-pyridine-CF₃COOH mixed solution (4 mL, 3:1:0.1 v/v/v). After bubbling with Ar for 30 min, the solution was irradiated with a Xe lamp equipped with a band-pass filter (600 \pm 10 nm) for 15 h. The crude was purified by ion-exchange chromatography (CM Sephadex C-25, eluent: acetonitrile-water (1:1 v/v) containing NH_4PF_6 (0-8 mM)). Some portion of acetonitrile was evaporated under reduced pressure. The red precipitate was filtered off and washed with water and ether. Yield: 7.2 mg (72%). ¹H NMR (400 MHz, acetone- d_6): δ 8.84 (s, 1H), 8.82 (s, 2H), 8.80 (s, 2H), 8.71 (s, 1H), 8.34 (d, J = 8.8 Hz, 1H), 8.33 (s, 1H), 8.23-8.17 (m, 4H), 8.14 (d, J = 5.2 Hz, 1H), 8.08 (d, J = 5.2 Hz, 1H), 8.06-8.03 (m, 3H), 7.94 (d, J = 6.0 Hz, 1H), 7.89 (dd, J = 8.0, 8.0 Hz, 1H), 7.85 (d, J = 6.0 Hz, 1H), 7.76 (d, J = 5.6 Hz, 1H), 7.60-7.54 (m, 5H), 7.41 (d, J = 5.6 Hz, 1H), 7.36–7.27 (m, 30H, 6PPh₃), 7.00 (dd, J = 7.6, 7.6 Hz, 1H), 6.89 (dd, J = 1.2, 6.8 Hz, 1H), 3.21-3.08 (m, 4H, $-C\underline{H}_2-C\underline{H}_2-$), 2.59 (s, 3H, $-C\underline{H}_3$). ³¹P NMR (400 MHz, acetone- d_6): δ 22.6 (s, 2P, -<u>PPh_3</u>), -143.5 (sep, 3P, 3<u>PF_6</u>). FT-IR (in CH₂Cl₂) ν_{CO}/cm^{-1} : 1937, 1867. ESI–MS (in acetonitrile): m/z 511 ([M-3PF₆⁻]³⁺), 839 ([M-2PF₆⁻]²⁺). HRMS (ESI-TOF): m/z $[M-3PF_6^-]^{3+}$ Anal. Calcd for $C_{81}H_{66}N_8O_2P_2ReRu$: 511.1135. Found: 511.1123. $[M-2PF_6^-]^{2+}$ Anal. Calcd for $C_{81}H_{66}F_6N_8O_2P_3ReRu$: 839.1523. Found: 839.1550.



 $(EtO)Re(CH-CH)Re(Et)^{2+}$. (EtO)Re(C=C)Re(Et)^{2+} (9.25 mg, 5.46 μ mol) and BIH (45.0 mg, 201 μ mol) were dissolved in an acetonitrile-pyridine-CF₃COOH mixed solution (4 mL, 3:1:0.1 v/v/v). After bubbling with Ar for 30 min, the solution was irradiated with a Xe lamp equipped with a band-pass filter (600 ± 10 nm) for 37 h. The crude was purified by ion-exchange chromatography (CM Sephadex C-25, eluent: acetonitrile-water (1:1 v/v) containing NH_4PF_6 (0-8 mM)) and silica-gel chromatography (eluent: CH2Cl2/MeOH (100:1 v/v)). Obtained yellow solid was recrystallized with acetone/ether. The yellow precipitate was filtered off and washed with ether. Yield: 3.3 mg (36%). ¹H NMR (400 MHz, acetone- d_6): δ 9.28 (d, J = 6.7 Hz, 1H, γ py-6), 9.17 $(d, J = 5.4 \text{ Hz}, 1\text{H}, \beta \text{py-6}), 9.00 (d, J = 6.2 \text{ Hz}, 1\text{H}, \delta \text{py-6}), 8.92 (d, J = 6.2 \text{ Hz}, 1\text{Hz}, 1\text{Hz}, \delta \text{py-6}), 8.92 (d, J = 6.2 \text{ Hz}, 1\text{Hz}, \delta \text{py-6}), 8.92 (d, J = 6.2 \text{ Hz}, 1\text{Hz}, \delta \text{py-6}), 8.92 (d, J = 6.2 \text{ Hz}, 1\text{Hz}, \delta \text{py-6}), 8.92 (d, J = 6.2 \text{ Hz}, 1\text{Hz}, \delta \text{py-6})), 8.92 (d, J = 6.2 \text{ Hz}, 1\text{Hz}, \delta \text{py-6})), 8.92 (d, J = 6.2 \text{ Hz}, 1\text{Hz}, \delta \text{py-6})), 8.92 (d, J = 6.2 \text{ Hz}, 1\text{Hz}, \delta \text{py-6})), 8.92 (d, J = 6.2 \text{ Hz}, 1\text{Hz}, \delta \text{py-6})), 8.92 (d, J = 6.2 \text{ Hz}, 1\text{Hz}, \delta \text{py-6})), 8.92 (d, J = 6.2 \text{ Hz}, 1\text{Hz}, 1\text{Hz}, 1\text{H$ 5.6 Hz, 1H, α py-6), 8.85 (s, 1H, γ py-3), 8.81 (d, J = 8.2 Hz, 1H, δ py-3), 8.76 (s, 1H, β py-3), 8.61 (s, 1H, α py-3), 8.34 (dd, J = 7.4, 8.2 Hz, 1H, δ py-4), 7.84 (dd, J = 6.2, 7.4 Hz, 1H, δ py-5), 7.83 (d, J = 5.4 Hz, 1H, β py-5), 7.80 (d, J = 6.7 Hz, 1H, γ py-5), 7.65 (d, J = 5.6 Hz, 1H, α py-5), 3.91-3.84 (m, 12H, P(OCH₂CH₃)₃), 3.42 (m, 4H, $-CH_2-CH_2-$), 2.64(s, 3H, α py-C<u>H</u>₃), 1.58–1.51 (m, 12H, 2P(C<u>H</u>₂CH₃)₃), 1.04 (t, J = 6.8 Hz, 18H, 2P(OCH₂CH₃)₃), 0.94–0.83 (m, 18H, 2P(CH₂CH₃)₃). ³¹P NMR (400 MHz, acetone-*d*₆): δ/ppm, 117.5 (s, 2P, -<u>P</u>(OEt)₃), -1.80 (s, 2P, $-\underline{P}Et_3$), -143.5 (sep, 2P, $2\underline{P}F_6^-$). FT-IR (in CH_2Cl_2) $\nu_{\rm CO}/{\rm cm}^{-1}$: 1953, 1929, 1879, 1857. ESI–MS (in acetonitrile): m/z 703 $([M-2PF_6^{-}]^{2+})$. HRMS (ESI-TOF): m/z $[M-2PF_6^{-}]^{2+}$ Calcd for C₅₁H₈₀N₄O₁₀P₄Re₂: 702.1957. Found: 702.1934.

 $Ir(C = C)Re^{2+}$. [Re(4-bromo-bpy) (CO)₂{P(p-C₆H₄F)₃}₂](PF₆) (39.9 mg, 31.8 μ mol), [Ir(ppy)₂(vbpy)](PF₆) (53.5 mg, 63.6 μ mol), Pd(OAc)₂ (4.3 mg, 19.2 μ mol) and AcONa (13.0 mg, 158 μ mol) were dissolved in acetonitrile (4 mL, bubbled by N₂). The solution was heated at 65 °C under Ar for 3 days. The solution was cooled to room temperature and was purified by ion-exchange chromatography (SP Sephadex C-25, eluent: acetonitrile–water (1:1 v/v) containing NH₄PF₆ (0–2 mM)). Some portion of acetonitrile was evaporated under reduced pressure. The orange precipitate was filtered off and washed with water and ether. Obtained products were used in the next reaction without further purification. Yield: 37.0 mg (58%). FT-IR (in CH₂Cl₂) ν_{CO} /cm⁻¹: 1941, 1872. ESI–MS (in acetonitrile): m/z 863 ([M-2PF₆⁻]²⁺). HRMS (ESI–TOF): m/z [M-2PF₆⁻]²⁺ Anal. Calcd for C₈₃H₅₈F₆IrN₆O₂P₂Re: 863.1601. Found: 863.1643.

 $Ir(CH-CH)Re^{2+}$. $Ir(C=C)Re^{2+}$ (10.0 mg, 4.96 μ mol) and BIH (45.0 mg, 201 µmol) were dissolved in an acetonitrile-pyridine-CF₃COOH mixed solution (4 mL, 3:1:0.1 v/v/v). After bubbling with Ar for 30 min, the solution was irradiated with a Xe lamp equipped with a band-pass filter $(510 \pm 10 \text{ nm})$ for 8 h. The crude was purified by ion-exchange chromatography (CM Sephadex C-25, eluent: acetonitrile-water (1:1 v/v) containing NH4PF6 (0-8 mM)) and silica-gel chromatography (eluent: CH₂Cl₂-MeOH (100:1 v/v)). Obtained yellow solid was recrystallized with acetone/ether. The yellow precipitate was filtered off and washed with ether. Yield: 6.6 mg (66%). ¹H NMR (400 MHz, acetone- d_6): δ 8.86 (s, 1H), 8.70 (s, 1H), 8.41 (s, 1H), 8.40 (d, J = 7.6 Hz, 1H), 8.23 (d, J = 8.0 Hz, 2H), 8.19 (dd, J = 3.2, 6.0 Hz, 2H), 8.00-7.83 (m, 11H), 7.81 (dd, J = 3.2, 6.4 Hz, 2H), 7.60 (d, J = 5.6 Hz, 1H), 7.53 (d, J = 5.6 Hz, 1H), 7.35-7.32 (m, 12H), 7.10 (m, 12H), 7.02 (dd, J = 7.2, 7.2 Hz, 2H), 6.90 (dd, J = 7.2, 7.2 Hz, 2H), 6.34 (dd, J = 7.2, 7.2 Hz, 2H), 3.19 (m, 4H, $-CH_2$ - CH_2 -), 2.60 (s, 3H, $-CH_3$). ³¹P NMR (400 MHz, acetone- d_6): δ 20.9 (s, 2P, -<u>P</u>Ph₃), -143.6 (sep, 2P, 2<u>P</u>F₆⁻). FT-IR (in CH₂Cl₂) $\nu_{\rm CO}/{\rm cm}^{-1}$: 1940, 1870. ESI-MS (in acetonitrile): m/z 864 $([M-2PF_6^{-}]^{2+})$. HRMS (ESI-TOF): m/z $[M-2PF_6^{-}]^{2+}$ Anal. Calcd

for $C_{83}H_{60}F_6IrN_6O_2P_2Re: 864.1679$. Found: 864.1676. $Ru(C=C)Ru^{4+}$. [Ru(dmb)₂(vbpy)](PF₆)₂ (22 mg, 23 μ mol) and Grubbs catalyst II (2.5 mg, 2.9 μ mol) were dissolved in CH₂Cl₂ (ca. 10 mL degassed by N_2). The solution was refluxed with N_2 bubbling for 16 h (in dim light). Then Grubbs catalyst II (1.95 mg, 2.3 μ mol) and CH₂Cl₂ (ca. 10 mL degassed under N₂) were added as the second charge and refluxed 17 h. Another Grubbs catalyst II (2.5 mg, 2.9 μ mol) and CH₂Cl₂ (ca. 10 mL degassed under N₂) were added as the third charge and refluxed for 6 h. The solvent was removed in vacuo, and the black-red solid was collected. The solid was purified by size exclusion chromatography, and the obtained red solution was evaporated. The residue was dissolved in CH2Cl2 and washed with water (containing NH₄PF₆) twice. After evaporating, the obtained red solid was dissolved in MeOH, and a concentrated methanol solution of NH₄PF₆ was added. Some water was added to the solution, and the MeOH evaporated under reduced pressure. After filtration, red solid was collected and washed with water and Et₂O and dried in a vacuum. Yield: 7.8 mg (38%). ¹H NMR (400 MHz, acetone- d_6): δ 8.94 (s, 2H), 8.70 (s, 2H), 8.67 (s, 2H), 8.66 (s, 6H), 8.02 (d, J = 6.0 Hz, 2H), 7.90 (d, J = 6.8 Hz, 2H), 7.89 (s, 2H), 7.84-7.81 (m, 8H), 7.67 (d, J = 6.0 Hz, 2H), 7.40-7.37 (m, 10H), 2.58 (s, 6H), 2.56 (s, 6H), 2.55 (s, 6H), 2.54 (s, 12H). ESI–MS (in acetonitrile): m/z 326 ([M-4PF₆⁻]⁴⁺), 483 ([M-3PF₆⁻]³⁺), 797 $([M-2PF_6^{-}]^{2+})$. HRMS (ESI-TOF): m/z [M-4PF₆⁻]⁴⁺ Anal. Calcd for C72H68N12Ru2: 326.0952. Found: 326.0920.

Ru(*CH*-*CH*)*Ru*⁴⁺. Ru(*C*=*C*)Ru⁴⁺ (2.6 mg, 1.4 μ mol) and BIH (9.0 mg, 40 μ mol) were dissolved in an acetonitrile-pyridine-*CF*₃COOH mixed solution (4 mL, 3:1:0.1 v/v/v). After bubbling with Ar for 30 min, the solution was irradiated with a Xe lamp equipped with band-pass filter (600 ± 10 nm) for 15 h. The crude was purified by ion-exchange chromatography (CM Sephadex C-25, eluent: acetonitrile-water (1:1 v/v) containing NH₄PF₆ (0–16 mM)). Some portion of acetonitrile was evaporated under reduced pressure. The red precipitate was filtered off and washed with water and ether. Yield: 1.6 mg (62%). ¹H NMR (400 MHz, acetone-*d*₆): δ 8.78 (s, 1H), 8.75 (s, 1H), 8.65 (s, 10H), 7.89 (d, *J* = 5.6 Hz, 2H), 7.84–7.80 (m, 8H), 7.79 (d, *J* = 6.0 Hz, 1H), 7.74 (d, *J* = 5.2 Hz, 1H), 7.51 (d, *J* = 6.0 Hz, 1H), 7.37 (d, *J* = 5.6 Hz, 8H), 7.33 (d, *J* = 5.6 Hz, 1H), 7.20 (d, *J* = 4.8 Hz, 1H), 3.20 (s, 4H, -C<u>H₂-CH₂-),</u> 2.55 (s, 24H), 2.50 (s, 6H). ESI–MS (in acetonitrile): m/z 327 ([M-4PF₆⁻]⁴⁺), 484 ([M-3PF₆⁻]³⁺), 798 ([M-2PF₆⁻]²⁺). HRMS (ESI–TOF): m/z [M-4PF₆⁻]⁴⁺ Anal. Calcd for C₇₂H₇₀N₁₂Ru₂: 326.5992. Found: 326.5984.

 $Ru(C \equiv C) lr^{3+}$. [Ru(dmb)₂(Brbpy)](PF₆)₂ (11 mg, 11 μ mol), $[Ir(ppy)_2(4-ethynyl-bpy)](PF_6)$ (8.8 mg, 11 μ mol), PdCl₂(PPh)₂ (0.23 mg, 0.33 μ mol), CuI (0.20 mg, 1.1 μ mol), and diisopropylamine (40 μ L, 300 μ mol) were dissolved in DMF (5 mL, bubbled by N₂). The solution was heated at 50 °C under Ar for 3 h. Additional $[Ir(ppy)_2(4-ethynyl-bpy)](PF_6)$ (8.8 mg, 11 µmol) was added to the solution, and the solution was heated for another 3 h. After adding $[Ir(ppy)_2(4-ethynyl-bpy)](PF_6)$ (8.8 mg, 11 µmol), the solution was heated overnight. The solution was cooled to room temperature and was purified by ion-exchange chromatography (CM Sephadex C-25, eluent: acetonitrile-water (1:1 v/v) containing NH_4PF_6 (0-8 mM)). Some portion of acetonitrile was evaporated under reduced pressure. The red precipitate was filtered off and washed with water and ether. Yield: 7.4 mg (40%). ¹H NMR (400 MHz, acetone- d_6): δ 8.98 (s, 1H), 8.93 (s, 1H), 8.87 (d, J = 8.4 Hz, 1H), 8.83 (d, J = 8.4 Hz, 1H), 8.68 (s, 1H), 8.67 (s, 3H), 8.30-8.23 (m, 3H), 8.19-8.14 (m, 3H), 8.11 (d, I = 5.6 Hz, 1H), 8.06 (d, I = 6.4 Hz, 1H), 7.99–7.88 (m, 6H), 7.85– 7.78 (m, 5H), 7.74 (dd, J = 5.6, 5.6 Hz, 1H), 7.63 (dd, J = 2.0, 6.0 Hz, 1H), 7.59 (dd, J = 6.0, 6.0 Hz, 1H), 7.41 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.18–7.12 (m, 2H), 7.03 (dd, J = 7.6, 7.6 Hz, 2H), 6.91 (dd, J = 7.2, 7.2 Hz, 2H), 6.33 (dd, J = 7.6, 7.6 Hz, 2H), 2.57 (s, 3H), 2.56 (s, 6H), 2.55 (s, 3H). ESI-MS (in acetonitrile): m/z435 ($[M-3PF_6^{-}]^{3+}$), 725 ($[M-2PF_6^{-}]^{2+}$). HRMS (ESI-TOF): m/z $[M-3PF_6^{-}]^{3+}$ Anal. Calcd for $C_{68}H_{54}IrN_{10}Ru$: 435.1074. Found: 435.1057. $[M-2PF_6^{-}]^{2+}$ Anal. Calcd for $C_{68}H_{54}F_6IrN_{10}PRu$: 725.1432. Found: 725.1426.

 $Ru(CH_2 - CH_2)Ir^{3+}$. Ru(C=C)Ir³⁺ (5.8 mg, 3.3 µmol) and BIH (45 mg, 200 μ mol) were dissolved in an acetonitrile-pyridine-CF₃COOH mixed solution (4 mL, 3:1:0.1 v/v/v). After bubbling with Ar for 30 min, the solution was irradiated with a Xe lamp equipped with a band-pass filter (600 \pm 10 nm) for 14 h. The crude was purified by ionexchange chromatography (CM Sephadex C-25, eluent: acetonitrilewater (1:1 v/v) containing NH_4PF_6 (0-8 mM)). Some portion of acetonitrile was evaporated under reduced pressure. The red precipitate was filtered off and washed with water and ether. Yield: 4.5 mg (78%). ¹H NMR (400 MHz, acetone- d_6): δ 8.81 (s, 1H), 8.79 (s, 1H), 8.76– 72 (m, 2H), 8.66 (s, 4H), 8.27-8.22 (m, 3H), 8.13 (dd, J = 8.0, 8.0 Hz, 1H), 8.08 (d, J = 5.2 Hz, 1H), 8.01 (d, J = 5.2 Hz, 1H), 7.98-7.87 (m, 6H), 7.83–7.74 (m, 6H), 7.69 (d, J = 6.4, 6.4 Hz, 1H), 7.61–7.48 (m, 3H), 7.40–7.34 (m, 2H), 7.29 (d, J = 7.2 Hz, 1H), 7.23 (d, J = 4.8 Hz, 1H), 7.17-7.08 (m, 2H), 7.02 (m, J = 7.2 Hz, 2H), 6.92-6.88 (m, 2H), 6.32 (d, J = 7.6 Hz, 2H), 3.29 (m, 4H, $-CH_2-CH_2-$), 2.56 (s, 6H), 2.54 (s, 3H), 2.52 (s, 3H). ESI–MS (in acetonitrile): m/z436 ([M-3PF₆⁻]³⁺), 726 ([M-2PF₆⁻]²⁺). HRMS (ESI–TOF): m/z $[M-3PF_6^{-}]^{3+}$ Anal. Calcd for $C_{68}H_{58}IrN_{10}Ru$: 436.4512. Found: 436.4529. [M-2PF₆⁻]²⁺ Anal. Calcd for C₆₈H₅₈F₆IrN₁₀PRu: 727.1589. Found: 727.1597.



 $Ru(CH-CH)Re(CH-CH)Ru^{5+}$. Ru(C=C)Re(C=C)Ru^{5+} (10.2 mg, 3.31 μ mol) and BIH (45.0 mg, 201 μ mol) were dissolved in an

acetonitrile-pyridine-CF₃COOH mixed solution (4 mL, 3:1:0.1 v/v/v). After bubbling with Ar for 30 min, the solution was irradiated with a Xe lamp equipped with a band-pass filter $(600 \pm 10 \text{ nm})$ for 15 h. The crude was purified by ion-exchange chromatography (CM Sephadex C-25, eluent: acetonitrile-water (1:1 v/v) containing NH₄PF₆ (0-8 mM)). Some portion of acetonitrile was evaporated under reduced pressure. The red precipitate was filtered off and washed with water and ether. Yield: 5.5 mg (55%). ¹H NMR (400 MHz, acetone- d_6): δ 8.83 (s, 2H, β py-3), 8.68 (s, 2H, α py-3), 8.66 (s, 8H, dmb-3,3'), 8.46 (s, 2H, γ py-3), 7.99 (d, J = 5.6 Hz, 2H, β py-6), 7.95 (d, J = 5.6 Hz, 2H, α py-6), 7.84 (d, J = 5.6 Hz, 8H, dmb-6,6'), 7.82 (d, J = 5.6 Hz, 2H, γ py-6), 7.55 (d, J = 5.6 Hz, 2H, β py-5), 7.39–7.32 (m, 22H, dmb-5,5', Ph-m, α py-5), 7.13-7.08 (m, 14H, Ph-o, γ py-5), 3.18-3.10 (m, 8H, $-C\underline{H}_2-C\underline{H}_2-)$, 2.56 (s, 12H, dmb-C<u>H₃</u>), 2.55 (s, 6H, α py-C<u>H₃</u>), 2.54 (s, 12H, dmb-C<u>H₃</u>), ³¹P NMR (400 MHz, acetone- d_6): δ 20.9 (s, 2P, 2<u>P</u>(C₆H₄F)₃), -143.6 (sep, 5P, 5<u>P</u>F₆⁻). FT-IR (in CH₂Cl₂) ν_{CO} /cm⁻¹: 1939, 1869. ESI-MS (in acetonitrile): m/z 472 ([M-5PF₆⁻]⁵⁺), 627 ([M-4PF₆⁻]⁴⁺), 884 ($[M-3PF_6^{-}]^{3+}$). HRMS (ESI-TOF): $m/z [M-5PF_6^{-}]^{5+}$ Anal. Calcd for C₁₂₂H₁₀₄F₆N₁₄O₂P₂ReRu₂: 427.7107. Found: 472.7103. [M-4PF₆]⁴⁴ Anal. Calcd for C₁₂₂H₁₀₄F₁₂N₁₄O₂P₃ReRu₂: 627.1295. Found: 627.1312. $[M-3PF_6^{-}]^{3+}$ Anal. Calcd for $C_{122}H_{104}F_{18}N_{14}O_2P_4ReRu_2$: 884.4940. Found: 884.4962.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b01736.

UV–vis absorption spectrum of $[Ru(bpy)_2(dmb)](PF_6)$, cyclic voltammogram of $Ru(C=C)Re^{3+}$, Stern–Volmer plots, photophysical and electrochemical properties of $Ru(C=C)Re(C=C)Ru^{5+}$ and $Ru(CH-CH)Re(CH-CH)Ru^{5+}$, ESI–mass spectra of the reaction solution after photocatalyses, and ESI–mass spectrum of byproducts of the hydrogenation reaction in the case using $(EtO)Re(C=C)Re(Et)^{2+}$ (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Amadelli, R.; Argazzi, R.; Bignozzi, C. A.; Scandola, F. Design of Antenna-Sensitizer Polynuclear Complexes. Sensitization of Titanium Dioxide with $[Ru(bpy)_2(CN)_2]_2Ru(bpy(COO)_2)_2^{2-}$. J. Am. Chem. Soc. **1990**, 112, 7099–7103. (b) Morimoto, T.; Nishiura, C.; Tanaka, M.; Rohacova, J.; Nakagawa, Y.; Funada, Y.; Koike, K.; Yamamoto, Y.; Shishido, S.; Kojima, T.; Saeki, T.; Ozeki, T.; Ishitani, O. Ring-Shaped Re(I) Multinuclear Complexes with Unique Photofunctional Properties. J. Am. Chem. Soc. **2013**, 135, 13266–13269.

(2) (a) Koike, K.; Naito, S.; Sato, S.; Tamaki, Y.; Ishitani, O. Architecture of supramolecular metal complexes for photocatalytic CO_2 reduction III: Effects of length of alkyl chain connecting photosensitizer to catalyst. J. Photochem. Photobiol., A **2009**, 207, 109–114. (b) Tamaki, Y.; Morimoto, T.; Koike, K.; Ishitani, O. Photocatalytic CO_2 reduction with high turnover frequency and selectivity of formic acid formation using Ru(II) multinuclear complexes. Proc. Natl. Acad. Sci. U. S. A. **2012**, 109, 15673–8.

(c) Tamaki, Y.; Watanabe, K.; Koike, K.; Inoue, H.; Morimoto, T.; Ishitani, O. Development of highly efficient supramolecular CO₂ reduction photocatalysts with high turnover frequency and durability. Faraday Discuss. 2012, 155, 115-127. (d) Tamaki, Y.; Koike, K.; Morimoto, T.; Ishitani, O. Substantial improvement in the efficiency and durability of a photocatalyst for carbon dioxide reduction using a benzoimidazole derivative as an electron donor. J. Catal. 2013, 304, 22-28. (e) Gholamkhass, B.; Mametsuka, H.; Koike, K.; Tanabe, T.; Furue, M.; Ishitani, O. Architecture of Supramolecular Metal Complexes for Photocatalytic CO₂ Reduction: Ruthenium-Rhenium Bi- and Tetranuclear Complexes. Inorg. Chem. 2005, 44, 2326-2336. (f) Kato, E.; Takeda, H.; Koike, K.; Ohkubo, K.; Ishitani, O. Ru(ii)-Re(i) binuclear photocatalysts connected by $- CH_2XCH_2 - (X = O, S, S)$ CH₂) for CO₂ reduction. Chem. Sci. 2015, 6, 3003-3012. (g) Meister, S.; Reithmeier, R. O.; Ogrodnik, A.; Rieger, B. Bridging Efficiency within Multinuclear Homogeneous Catalysts in the Photocatalytic Reduction of Carbon Dioxide. ChemCatChem 2015, 7, 3562-3569. (h) Kou, Y.; Nakatani, S.; Sunagawa, G.; Tachikawa, Y.; Masui, D.; Shimada, T.; Takagi, S.; Tryk, D. A.; Nabetani, Y.; Tachibana, H.; Inoue, H. Visible light-induced reduction of carbon dioxide sensitized by a porphyrin-rhenium dyad metal complex on p-type semiconducting NiO as the reduction terminal end of an artificial photosynthetic system. J. Catal. 2014, 310, 57-66. (i) Fujita, E.; Milder, S. J.; Brunschwig, B. S. Photophysical Properties of Covalently Attached $Ru(bpy)_3^{2+}$ and $Mcyclam^{2+}$ (M = Ni, H₂) Complexes. Inorg. Chem. 1992, 31, 2079-2085. (j) Kimura, E.; Bu, X.; Shionoya, M.; Wada, S.; Maruyama, S. A New Nickel(II) Cyclam (cyclam = 1,4,8,11-Tetraazacyclotetradecane) Complex Covalently Attached to Ru- $(phen)_{3}^{2+}$ (phen = 1,10-Phenanthroline). A New Candidate for the Catalytic Photoreduction of Carbon Dioxide. Inorg. Chem. 1992, 31, 4542-4546. (k) Kitagawa, Y.; Takeda, H.; Ohashi, K.; Asatani, T.; Kosumi, D.; Hashimoto, H.; Ishitani, O.; Tamiaki, H. Photochemical Reduction of CO2 with Red Light Using Synthetic Chlorophyll-Rhenium Bipyridine Dyad. Chem. Lett. 2014, 43, 1383-1385. (1) Schneider, J.; Vuong, K. Q.; Calladine, J. A.; Sun, X. Z.; Whitwood, A. C.; George, M. W.; Perutz, R. N. Photochemistry and Photophysics of a Pd(II) Metalloporphyrin: Re(I) Tricarbonyl Bipyridine Molecular Dyad and its Activity Toward the Photoreduction of CO₂ to CO. Inorg. Chem. 2011, 50, 11877-89. (m) Ozawa, H.; Yokoyama, Y.; Haga, M. A.; Sakai, K. Syntheses, characterization, and photo-hydrogen-evolving properties of tris(2,2'bipyridine)ruthenium(II) derivatives tethered to a cis-Pt(II)Cl₂ unit: insights into the structure-activity relationship. Dalton Trans. 2007, 1197-206. (n) Ozawa, H.; Sakai, K. Photo-hydrogen-evolving molecular devices driving visible-light-induced water reduction into molecular hydrogen: structure-activity relationship and reaction mechanism. Chem. Commun. 2011, 47, 2227-42. (o) Stoll, T.; Gennari, M.; Fortage, J.; Castillo, C. E.; Rebarz, M.; Sliwa, M.; Poizat, O.; Odobel, F.; Deronzier, A.; Collomb, M.-N. An Efficient Ru^{II}-Rh^{III}-Ru^{II} Polypyridyl Photocatalyst for Visible-Light-Driven Hydrogen Production in Aqueous Solution. Angew. Chem., Int. Ed. 2014, 53, 1654-1658. (p) Arachchige, S. M.; Brown, J. R.; Chang, E.; Jain, A.; Zigler, D. F.; Rangan, K.; Brewer, K. J. Design Considerations for a System for Photocatalytic Hydrogen Production from Water Employing Mixed-Metal Photochemical Molecular Devices for Photoinitiated Electron Collection. Inorg. Chem. 2009, 48, 1989-2000. (q) Li, F.; Jiang, Y.; Zhang, B.; Huang, F.; Gao, Y.; Sun, L. Towards A Solar Fuel Device: Light-Driven Water Oxidation Catalyzed by a Supramolecular Assembly. Angew. Chem., Int. Ed. 2012, 51, 2417-2420. (r) House, R. L.; Iha, N. Y. M.; Coppo, R. L.; Alibabaei, L.; Sherman, B. D.; Kang, P.; Brennaman, M. K.; Hoertz, P. G.; Meyer, T. J. Artificial photosynthesis: Where are we now? Where can we go? J. Photochem. Photobiol., C 2015, 25, 32-45.

(3) (a) Hwang, I.-W.; Ko, D. M.; Ahn, T. K.; Yoon, Z. S.; Kim, D.; Peng, X.; Aratani, N.; Osuka, A. Excitation Energy Migration in A Dodecameric Porphyrin Wheel. *J. Phys. Chem. B* **2005**, *109*, 8643– 8651. (b) Yamamoto, Y.; Sawa, S.; Funada, Y.; Morimoto, T.; Falkenström, M.; Miyasaka, H.; Shishido, S.; Ozeki, T.; Koike, K.; Ishitani, O. Systematic Synthesis, Isolation, and Photophysical Properties of Linear-Shaped Re(I) Oligomers and Polymers with 2–20 Units. J. Am. Chem. Soc. **2008**, 130, 14659–14674. (c) Yamamoto, Y.; Takeda, H.; Yui, T.; Ueda, Y.; Koike, K.; Inagaki, S.; Ishitani, O. Efficient light harvesting via sequential two-step energy accumulation using a Ru-Re₅ multinuclear complex incorporated into periodic mesoporous organosilica. Chem. Sci. **2014**, *5*, 639–648.

(4) Yamazaki, Y.; Takeda, H.; Ishitani, O. Photocatalytic reduction of CO₂ using metal complexes. *J. Photochem. Photobiol., C* **2015**, *25*, 106–137.

(5) Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. Designing Dendrimers Based on Transition-Metal Complexes. Light-Harvesting Properties and Predetermined Redox Patterns. *Acc. Chem. Res.* **1998**, *31*, 26–34.

(6) Ren, T. Peripheral Covalent Modification of Inorganic and Organometallic Compounds through C–C Bond Formation Reactions. *Chem. Rev.* **2008**, *108*, 4185–4207.

(7) (a) Yamazaki, Y.; Morimoto, T.; Ishitani, O. Synthesis of novel photofunctional multinuclear complexes using a coupling reaction. *Dalton Trans.* **2015**, *44*, 11626–35. (b) Locos, O. B.; Arnold, D. P. The Heck reaction for porphyrin functionalisation: synthesis of *meso-* alkenyl monoporphyrins and palladium-catalysed formation of unprecedented *meso-* β ethene-linked diporphyrins. *Org. Biomol. Chem.* **2006**, *4*, 902–916.

(8) (a) Connors, P. J.; Tzalis, D.; Dunnick, A. L.; Tor, Y. Coordination Compounds as Building Blocks: Single-Step Synthesis of Heteronuclear Multimetallic Complexes Containing Ru^{II} and Os^{II}. *Inorg. Chem.* 1998, 37, 1121–1123. (b) Tzalis, D.; Tor, Y. Coordination compounds as building blocks: single-step synthesis of multi-ruthenium(II) complexes. *Chem. Commun.* 1996, 1043–1044. (c) Goeb, S.; De Nicola, A.; Ziessel, R. Controlled Synthesis of Multinuclear Metal Complex Arrays by Cross Coupling of Coordinated Ligands. *J. Org. Chem.* 2005, 70, 6802–6808.

(9) (a) Haak, R. M.; Martinez Belmonte, M.; Escudero-Adan, E. C.; Benet-Buchholz, J.; Kleij, A. W. Olefin metathesis as a tool for multinuclear Co(iii)salen catalyst construction: access to cooperative catalysts. *Dalton Trans.* **2010**, *39*, 593–602. (b) Haak, R. M.; Castilla, A. M.; Martinez Belmonte, M.; Escudero-Adan, E. C.; Benet-Buchholz, J.; Kleij, A. W. Access to multinuclear salen complexes using olefin metathesis. *Dalton Trans.* **2011**, *40*, 3352–3364.

(10) (a) Arm, K. J.; Williams, J. A. G. A cross-coupling strategy for the synthesis of dimetallic assemblies containing mixed bipyridineterpyridine bridging ligands: luminescence and energy transfer properties. *Dalton Trans.* **2006**, 2172–2174. (b) Whittle, V. L.; Williams, J. A. G. Cyclometallated, bis-terdentate iridium complexes as linearly expandable cores for the construction of multimetallic assemblies. *Dalton Trans.* **2009**, 3929–3940. (c) Welter, S.; Salluce, N.; Belser, P.; Groeneveld, M.; De Cola, L. Photoinduced electronic energy transfer in modular, conjugated, dinuclear Ru(II)/Os(II) complexes. *Coord. Chem. Rev.* **2005**, 249, 1360–1371.

(11) Cassidy, L.; Horn, S.; Cleary, L.; Halpin, Y.; Browne, W. R.; Vos, J. G. Synthesis of asymmetric supramolecular compounds using a Ni(0) catalysed homo-coupling approach. *Dalton Trans.* **2009**, 3923–3928.

(12) Bian, Z.-Y.; Wang, H.; Fu, W.-F.; Li, L.; Ding, A.-Z. Two bifunctional Ru^{II}/Re^{I} photocatalysts for CO₂ reduction: A spectroscopic, photocatalytic, and computational study. *Polyhedron* **2012**, *32*, 78–85.

(13) Bian, Z.-Y.; Chi, S.-M.; Li, L.; Fu, W. Conjugation effect of the bridging ligand on the CO_2 reduction properties in difunctional photocatalysts. *Dalton Trans.* **2010**, *39*, 7884–7.

(14) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. The Preparation and Properties of Tris(triphenylphosphine)halogenorhodium(I) and Some Reactions Thereof including Catalytic Homogeneous Hydrogenation of Olefins and Acetylenes and their Derivatives. *J. Chem. Soc. A* **1966**, 1711.

(15) Crabtree, R. Iridium Compounds in Catalysis. Acc. Chem. Res. 1979, 12, 331–337.

(16) Takeda, H.; Yamamoto, Y.; Nishiura, C.; Ishitani, O. Analysis and Isolation of Cationic Rhenium(I) and Ruthenium(II) Multinuclear Complexes Using Size-Exclusion Chromatography. Anal. Sci. 2006, 22, 545–549.

(17) (a) Pac, C.; Ihama, M.; Yasuda, M.; Miyauchi, Y.; Sakurai, H. Ru(bpy)₃²⁺-Mediated Photoreduction of Olefins with 1-Benzyl-1,4dihvdronicotinamide: A Mechanistic Probe for Electron-Transfer Reactions of NAD(P)H-Model Compounds. J. Am. Chem. Soc. 1981, 103, 6495-6497. (b) Ishitani, O.; Ihama, M.; Miyauchi, Y.; Pac, C. Redox-Photosensitised Reactions. Part 12. Effects of Magnesium(II) Ion on the $[Ru(bpy)_3]^{2+}$ -Photomediated Reduction of Olefins by 1-Benzyl-1,4-dihydronicotinamide: Metal-ion Catalysis of Electron Transfer Processes Involving an NADH Model. J. Chem. Soc., Perkin Trans. 1 1985, 1527. (c) Pac, C.; Miyauchi, Y.; Ishitani, O.; Ihama, M.; Yasuda, M.; Sakurai, H. Redox-Photosensitized Reactions. 11. Ru(bpy)₃²⁺-photosensitized Reactions of 1-Benzyl-1,4-dihydronicotinamide with Aryl-substituted Enones, Derivatives of Methyl Cinnamate, and Substituted Cinnamonitriles: Electron-Transfer Mechanism and Structure-Reactivity Relationships. J. Org. Chem. 1984, 49, 26-34.

(18) (a) Van Houten, J.; Watts, R. J. Photochemistry of Tris(2,2'bipyridyl)ruthenium(II) in Aqueous Solutions. *Inorg. Chem.* **1978**, *17*, 3381–3385. (b) Durham, B.; Caspar, J. V.; Nagle, J. K.; Meyer, T. J. Photochemistry of Ru(bpy)₃²⁺. *J. Am. Chem. Soc.* **1982**, *104*, 4803– 4810. (c) Kalyanasundaram, K. Photophysics, photochemistry and solar energy conversion with tris(bipyridyl)ruthenium(II) and its analogues. *Coord. Chem. Rev.* **1982**, *46*, 159–244.

(19) The cone angles of $P(OEt)_3$ and PEt_3 are 109° and 132° , respectively. These values are smaller than that of PPh₃ (145°), which is contained in Ru(C=C)Re³⁺, cf.: Tolman, C. A. Chem. Rev. **1977**, 77, 313.

(20) (a) Hawecker, J.; Lehn, J.-M.; Ziessel, R. Photochemical and Electrochemical Reduction of Carbon Dioxide to Carbon Monoxide Mediated by (2,2'-Bipyridine)tricarbonylchlororhenium(I) and Related Complexes as Homogeneous Catalysts. Helv. Chim. Acta 1986, 69, 1990-2012. (b) Kurz, P.; Probst, B.; Spingler, B.; Alberto, R. Ligand Variations in [ReX(diimine) (CO)₃] Complexes: Effects on Photocatalytic CO2 Reduction. Eur. J. Inorg. Chem. 2006, 2006, 2966-2974. (c) Hori, H.; Johnson, F. P. A.; Koike, K.; Ishitani, O.; Ibusuki, T. Efficient photocatalytic CO₂ reduction using [Re(bpy) (CO)₃{P-(OEt)₃}]⁺. J. Photochem. Photobiol., A **1996**, 96, 171–174. (d) Hori, H.; Johnson, F. P. A.; Koike, K.; Takeuchi, K.; Ibusuki, T.; Ishitani, O. Photochemistry of $[\text{Re(bipy)} (\text{CO})_3(\text{PPh}_3)]^+$ (bipy = 2,2'-bipyridine) in the presence of triethanolamine associated with photoreductive fixation of carbon dioxide: participation of a chain reaction mechanism. J. Chem. Soc., Dalton Trans. 1997, 1019-1024. (e) Koike, K.; Hori, H.; Ishizuka, M.; Westwell, J. R.; Takeuchi, K.; Ibusuki, T.; Enjouji, K.; Konno, H.; Sakamoto, K.; Ishitani, O. Key Process of the Photocatalytic Reduction of CO₂ Using [Re(4,4'-X₂-bipyridine) (CO)₃PR₃]⁺(X = CH₃, H, CF₃; PR₃= Phosphorus Ligands): Dark Reaction of the One-Electron-Reduced Complexes with CO2. Organometallics 1997, 16, 5724-5729. (f) Takeda, H.; Koike, K.; Inoue, H.; Ishitani, O. Development of an Efficient Photocatalytic System for CO₂ Reduction Using Rhenium(I) Complexes Based on Mechanistic Studies. J. Am. Chem. Soc. 2008, 130, 2023-2031. (g) Morimoto, T.; Nakajima, T.; Sawa, S.; Nakanishi, R.; Imori, D.; Ishitani, O. CO₂ Capture by a Rhenium(I) Complex with the Aid of Triethanolamine. J. Am. Chem. Soc. 2013, 135, 16825-16828. (h) Hawecker, J.; Lehn, J.-M.; Ziessel, R. Efficient Photochemical Reduction of CO₂ to CO by Visible Light Irradiation of Systems Containing Re(bipy) (CO)₃X or Ru(bipy)₃²⁺ $-Co^{2+}$ Combinations as Homogeneous Catalysts. J. Chem. Soc., Chem. Commun. 1983, 536-538. (i) Kutal, C.; Weber, M. A.; Ferraudi, G.; Geiger, D. A Mechanistic Investigation of the Photoinduced Reduction of Carbon Dioxide Mediated by Tricarbonylbromo(2,2'-bipyridine)rhenium(I). Organometallics 1985, 4, 2161-2166. (j) Koike, K.; Okoshi, N.; Hori, H.; Takeuchi, K.; Ishitani, O.; Tsubaki, H.; Clark, I. P.; George, M. W.; Johnson, F. P. A.; Turner, J. J. Mechanism of the Photochemical Ligand Substitution Reactions of fac- $[Re(bpy) (CO)_3(PR_3)]^+$ Complexes and the Properties of Their Triplet Ligand-Field Excited States. J. Am. Chem. Soc. 2002, 124, 11448-11455.

(21) (a) Ishida, H.; Terada, T.; Tanaka, K.; Tanaka, T. Photochemical CO₂ Reduction Catalyzed by $[Ru(bpy)_2(CO)_2]^{2+}$ Using Triethanolamine and 1-Benzyl-1,4-dihydronicotinamide as an Electron Donor. *Inorg. Chem.* **1990**, *29*, 905–911. (b) Lehn, J.-M.; Ziessel, R. Photochemical reduction of carbon dioxide to formate catalyzed by 2,2'-bipyridine- or 1,10-phenanthroline-ruthenium(II) complexes. *J. Organomet. Chem.* **1990**, *382*, 157–173. (c) Kuramochi, Y.; Ishitani, O. Iridium(III) 1-Phenylisoquinoline Complexes as a Photosensitizer for Photocatalytic CO₂ Reduction: A Mixed System with a Re(I) Catalyst and a Supramolecular Photocatalyst. *Inorg. Chem.* **2016**, *55*, 5702–9.

(22) Allen, G. H.; White, R. P.; Rillema, D. P.; Meyer, T. J. Synthetic Control of Excited-State Properties. Tris-Chelate Complexes Containing the Ligands 2,2'-Bipyrazine, 2,2'-Bipyridine, and 2,2'-Bipyrimidine. J. Am. Chem. Soc. **1984**, 106, 2613–2620.

(23) Ohkubo, K.; Yamazaki, Y.; Nakashima, T.; Tamaki, Y.; Koike, K.; Ishitani, O. Photocatalyses of Ru(II)-Re(I) binuclear complexes connected through two ethylene chains for CO₂ reduction. *J. Catal.* **2016**, in press. DOI: 10.1016/j.jcat.2015.12.025.

(24) Baron, A.; Herrero, C.; Quaranta, A.; Charlot, M. F.; Leibl, W.; Vauzeilles, B.; Aukauloo, A. Click Chemistry on a Ruthenium Polypyridine Complex. An Efficient and Versatile Synthetic Route for the Synthesis of Photoactive Modular Assemblies. *Inorg. Chem.* **2012**, *51*, 5985–7.

(25) Mauzerall, D.; Westheimer, F. H. 1-Benzyldihydronicotinamide—A Model for Reduced DPN. *J. Am. Chem. Soc.* **1955**, 77, 2261– 2264.

(26) Gärtner, F.; Cozzula, D.; Losse, S.; Boddien, A.; Anilkumar, G.; Junge, H.; Schulz, T.; Marquet, N.; Spannenberg, A.; Gladiali, S.; Beller, M. Synthesis, Characterisation and Application of Iridium(III) Photosensitisers for Catalytic Water Reduction. *Chem. - Eur. J.* **2011**, *17*, 6998–7006.