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Construction of a Visible Light-Driven Hydrocarboxylation Cycle of Alkenes by the Combined Use of Rh(I) and Photoredox Catalysts

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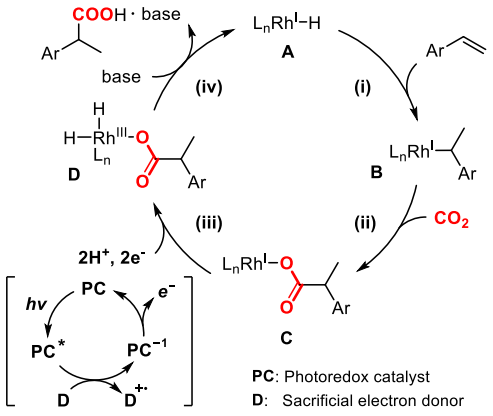
A visible light driven catalytic cycle for hydrocarboxylation of alkenes with CO_2 was established using a combination of Rh(I) complex as a carboxylation catalyst and $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridiyl) as a photoredox catalyst. Two key steps, the generation of the Rh(I) hydride species and nucleophilic addition of the π-benzyl Rh(I) species to CO_2, were found to be mediated by light.

Catalytic hydrocarboxylation of unsaturated hydrocarbons with CO_2 has recently attracted considerable attention as a method to utilize CO_2 as a carbon source for preparation of carboxylic acids from easily available materials.[1,2] This type of reaction usually necessitates the use of a stoichiometric amount of organometallic reductant such as $ZnEt_2$,[1a-d,2a,b] $AlEt_3$,[2c] or hydrosilanes[2d,e] to generate active metal hydride species from the corresponding metal carboxylates. Therefore it is highly desirable to develop a new system, which does not necessitate the use of a strong reductant and enables hydrocarboxylation reaction just using catalytic amounts of organometallic reagents.

To realize such system, we thought of the possibility of utilizing redox-photosensitized reaction with visible light. By the appropriate combination of a hydrocarboxylation catalyst and a photoredox catalyst in the presence of a sacrificial electron donor, it is expected that the key metal hydride species could be regenerated from the corresponding metal carboxylate by the successive protonation and reduction processes triggered by photoinduced electron transfer.[3] Recently, the single-electron transfer event has been widely used in organic synthesis,[4] and some dual catalytic systems combining transition metal and photoredox catalysts have also been developed.[5] However, there has been no report on their application to carboxylation reactions with CO_2, which could be regarded as a kind of artificial photosynthesis for the utilization of solar energy for preparation of organic molecules using CO_2.[6] We herein describe a novel cooperative photocatalytic cycle for hydrocarboxylation of alkenes using CO_2 by the combined use of catalytic amounts of a Rh(I) hydrocarboxylation catalyst and a photoredox catalyst.



Scheme 1 Proposed reaction mechanism for the photocatalytic hydrocarboxylation of alkenes with CO_2 by Rh/photoredox catalysis.

Our proposed catalytic cycle for hydrocarboxylation mediated by photoredox catalysis is shown in Scheme 1. We have chosen Rh(I) hydride complex **A** as the key catalytic species, as organorhodium(I) species are expected to have sufficient nucleophilicity towards CO_2[7] and some Rh(I) complexes are known to be active in redox-photosensitized reactions.[3c,8] Hydrometallation of an alkene, followed by nucleophilic carboxylation of the generated Rh(I) alkyl complex **B** with CO_2 would give Rh(I) carboxylate complex **C**. The next step is the regeneration of the Rh(I) hydride complex **A** from **C** with liberation of the carboxylated product by accepting two electrons and two protons, which is the most challenging step in the cycle. We expected that photoredox catalyst would enable the electron and proton transfers to generate Rh(III) dihydride **D**, which would be converted to Rh(I) monohydride **A** by eliminating the carboxylic acid in the presence of a base.

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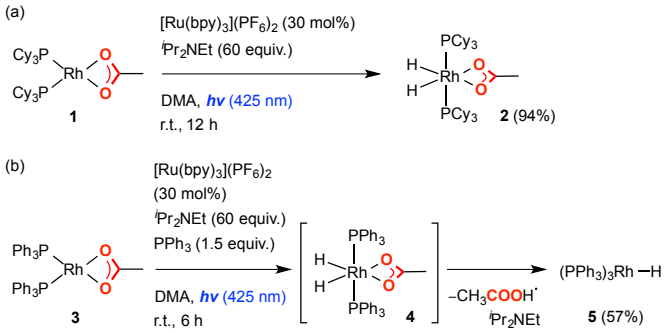
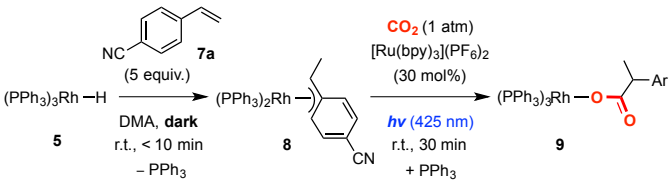
† Electronic Supplementary Information (ESI) available: Detailed experimental procedures, spectral data, analytical data. See DOI: 10.1039/x0xx00000x



Scheme 2 Photochemical generation of the rhodium hydride complexes.

We first examined transformation of Rh(I) carboxylate to Rh(I) hydride by photoredox catalysis, which is the key to construct the proposed catalytic cycle. Through screening of reaction conditions using $Rh(PCy_3)_2(OAc)$ **1** as a model complex of Rh(I) carboxylate, **1** was found to be transformed to $Rh(PCy_3)_2(OAc)(H)_2$ **2** (94% yield based on ^1H NMR using an internal standard) in the presence of a catalytic amount of $[Ru(bpy)_3](PF_6)_2$ as a photoredox catalyst, an excess amount of $^iPr_2NEt$ as a sacrificial electron donor under visible light irradiation (λ_{irr} = 425 nm) at room temperature (Scheme 2 (a)).[‡] Control experiments indicated that $[Ru(bpy)_3](PF_6)_2$, tertiary amine, and visible light were all essential for the transformation. Furthermore, when $Rh(PPh_3)_2(OAc)$ **3** was employed instead of **1** under the same reaction conditions in the presence of PPh_3 as an additional ligand, **3** was successfully transformed to the desired $Rh(PPh_3)_3H$ **5** (57% yield based on ^1H NMR using an internal standard and ca 30% of **3** recovered), accompanied by liberation of acetic acid as its ammonium salt (Scheme 2 (b)). $Rh(PPh_3)_2(OAc)(H)_2$ **4** was thought to be a possible intermediate in this transformation,[§] and it is likely that due to lower electron-donating ability of PPh_3 compared to PCy_3, elimination of acetic acid from **4** was facilitated by the action of $^iPr_2NEt$. Although detailed mechanism for the formation of Rh(III) dihydride complex has not been clarified, it would be generated by the two sets of protonation and single electron transfer to Rh(I) carboxylate complex mediated by the reductive quenching cycle of $[Ru(bpy)_3]^{2+}$ with $^iPr_2NEt$ (Scheme S6).[9]

The Rh(I) monohydride formation was similarly observed when Wilkinson's complex $Rh(PPh_3)_3Cl$ **6** was irradiated with visible light in the presence of $[Ru(bpy)_3](PF_6)_2$ and $^iPr_2NEt$, indicating Rh(I) hydride active species was also available from a chloro Rh(I) complex as a catalyst precursor (Scheme S3).



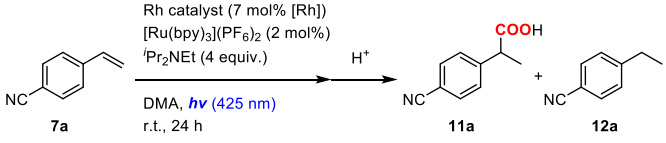
Scheme 3 Photochemical carboxylation of the π-benzyl rhodium complex.

Next, the nucleophilic addition of Rh(I) alkyl complex, which is another important step in the hydrocarboxylation cycle, was investigated (Scheme 3). When π-benzyl Rh(I) complex **8**, formed by insertion of 4-cyanostyrene **7a** to $Rh(PPh_3)_3H$ **5**, was subjected to CO_2 atmosphere, the carboxylation reaction did not proceed in the dark even upon heating at 60 °C.[§§] However, when **8** was exposed to visible light in the presence of $[Ru(bpy)_3](PF_6)_2$, clean formation of Rh(I) carboxylate **9** was observed (Figure S3), which was confirmed by alternative synthesis of **9**. This phenomenon could be regarded as a light-promoted nucleophilic addition to CO_2, which is a quite rare process.[10] Control experiments revealed that $[Ru(bpy)_3]^{2+}$ and visible light were essential but tertiary amine was not for this carboxylation reaction. The luminescence quenching study demonstrated that the emission from the triplet excited state of $[Ru(bpy)_3]^{2+}$ was quenched by **8** (Figure S5). As the electron transfer pathway is not likely in this reaction,[§§§] the triplet-triplet energy transfer from the photoexcited $[Ru(bpy)_3]^{2+}$ is considered to be a trigger for the carboxylation with CO_2.[11]

To estimate the effect of the energy transfer in the carboxylation reaction, theoretical analysis was conducted in terms of the ground state (S_0) and lowest triplet excited state (T_1) of **8** which would be generated in the photochemical process. The TD-DFT result indicated that metal-to-(metal-ligand) charge transfer from the Rh center to the Rh-benzyl unit has major contribution to the T_1 state (Table S4). This transition caused (i) the change in coordination mode of the benzyl ligand from η^3-benzyl to η^1-benzyl form as indicated in the optimized structure of the T_1 state, and (ii) increase in the electron density of the benzylic position (Table S3). These changes would promote the subsequent nucleophilic addition to CO_2.

As all the elementary steps of the catalytic cycle were found to be feasible, we then examined the catalytic reaction. Using 4-cyanostyrene **7a** as substrate, the combination of $Rh(PPh_3)_3H$ **5** and $[Ru(bpy)_3](PF_6)_2$ was found to give the desired hydrocarboxylated product **11a** in 33% yield upon visible light irradiation ($\lambda_{irr.}$ = 425 nm) in the presence of an excess amount of $^iPr_2NEt$ under atmospheric pressure of CO_2 at room temperature (Table 1, entry 1). In this reaction, significant amounts of hydrogenated product **12a** and polymers were also produced. When the catalytic reaction was followed by $^{31}P\{^1H\}$ NMR spectroscopy, the accumulation of **9** was observed, suggesting the resting-state of the catalytic reaction under visible light irradiation was the Rh(I) carboxylate complex (Figure S4). A series of control experiments confirmed that the rhodium catalyst, photoredox catalyst, tertiary amine and visible light were all essential for the reaction progress (entries 2 – 5). Wilkinson's complex **6** and chloro-bridged bis(phosphine) dimer **10a** were found to be applicable as a precatalyst (entries 6, 7).

Table 1 Screening of catalytic conditions for the hydrocarboxylation of 4-Cyanostyrene by Rh/photoredox catalysis.

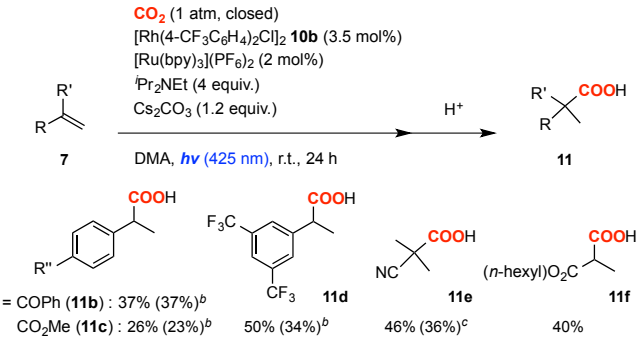


Entry	Rh catalyst	Conv. /%	Yield /%	
			11a[a]	**12a**[b]
1	$Rh(PPh_3)_3H$ (**5**)	60	33	18
2[c]	$Rh(PPh_3)_3H$ (**5**)	8	n.d.	n.d.
3[d]	$Rh(PPh_3)_3H$ (**5**)	1	1	n.d.
4[e]	$Rh(PPh_3)_3H$ (**5**)	<1	n.d.	n.d.
5	none	12	n.d.	n.d.
6	$Rh(PPh_3)_3Cl$ (**6**)	56	31	13
7	$[Rh(PPh_3)_2Cl]_2$ (**10a**)	60	21	16
8	$[Rh(P(4\text{-}CF_3C_6H_4)_3)_2Cl]_2$ (**10b**)	95	54	25
9[f]	$[Rh(P(4\text{-}CF_3C_6H_4)_3)_2Cl]_2$ (**10b**)	70	67[g]	1
10	$[Rh(P(4\text{-}CNC_6H_4)_3)_2Cl]_2$ (**10c**)	80	45	12
11	$[Rh(P(3,5\text{-}(CF_3)_2C_6H_3)_3)_2Cl]_2$ (**10d**)	34	11	3
12	$[Rh(P(p\text{-tolyl})_3)_2Cl]_2$ (**10e**)	32	14	3
13	$[Rh(PCy_3)_2Cl]_2$ (**10f**)	22	6	7

[a]NMR yield. [b]GC yield. [c]without $[Ru(bpy)_3](PF_6)_2$. [d]without $^iPr_2NEt$. [e]under dark. [f]1.2 equiv. of Cs_2CO_3 was added. [g]Isolated yield (62%) was obtained after methyl esterification in a larger scale experiment, see the supporting Information for detail.

Then various combinations of rhodium and photoredox catalysts were examined to improve the yield of the desired product **11a**. With regard to its ancillary ligand, triarylphosphines possessing electron-withdrawing groups significantly improved the yield (entries 8, 10). This reactivity enhancement was likely due to the acceleration of the reduction process of the Rh(I) carboxylate, which was the resting-state of the catalytic cycle. When PCy_3 was introduced to the rhodium center, only a small amount of the carboxylated product **11a** was obtained (entry 13), which coincided with the result shown in Scheme 2(a). Thus, fine-tuning of the electronic nature of the rhodium complex by ancillary ligands was quite important for the catalytic efficiency. Choice of photoredox catalyst, solvent, and ratio of the rhodium/photoredox catalyst also affected the product distribution as well as the reaction rate (Tables S1, S2). Very importantly, addition of a small excess amount of Cs_2CO_3 almost completely suppressed the hydrogenation and polymerization reactions and significantly improved the yield of the hydrocarboxylated product (entry 9). Through these optimizations, employment of 2.0 mol% of $[Ru(bpy)_3](PF_6)_2$, 3.5 mol% of $[Rh(P(4\text{-}CF_3C_6H_4)_3)_2Cl]_2$ **10b** (7.0 mol% as Rh metal), 4 equiv. of $^iPr_2NEt$ and 1.2 equiv. of Cs_2CO_3 in DMA gave the best yield of **11a** (67%, TON = 9.6 based on Rh). The quantum yield of this reaction under the optimized conditions was 0.0036 (Figure S6). The catalytic reaction upon on-and-off irradiation demonstrated the repeatable switching of the catalytic activity with the high photoresponsivity (Figure S7). Selective formation of the ^{13}C-labelled product in the reaction using a mixed gas of ^{13}C-labelled CO_2 and non-labelled CO (Scheme S5) confirmed that this reaction did not proceed *via* carboxylation reaction associated with release of CO by reduction of CO_2, which could also give the same carboxylation product.[12] This hydrocarboxylation reaction was also applicable to other styrenes possessing an electron-withdrawing group. Although the yields became considerably lower as the substrate became less electron-deficient, the conversion yields were generally good. Other electron-deficient alkenes such as methacrylonitrile and an alkyl acrylate also gave the corresponding hydrocarboxylated product (Table 2).

Table 2 Photocatalytic hydrocarboxylation of other electron-deficient alkenes by Rh/photoredox catalysis.[a]



[a]NMR yield. GC yields of the hydrogenated byproduct were <1% for all entries. [b]isolated yield after methyl esterification. [c]isolated yield after acid-base extraction.

The redox-photosensitized reaction with multi-electron transfer processes has been used for CO_2 reduction to organic feedstock such as CO, formic acid and methanol as well as hydrogen generation reactions.[13] Although single electron transfer by photoredox catalyst has been used actively in organic synthesis, application of such multielectron transfer processes to other C-C bond forming reactions has been quite limited, and the reaction with CO_2 has not been reported yet. In addition to the photoinduced electron transfer, activation of the Rh(I) benzyl complex by photoinduced energy transfer enabled the carboxylation reaction. The combination of different types of activation of the Rh catalyst by light energy *via* photoredox catalyst is the key to construct such a novel photocatalytic cycle.

In conclusion, the visible light-driven catalytic hydrocarboxylation of alkenes with CO_2 was achieved for the first time by using the Rh(I) hydride complex generated by photoredox catalysis. Each elementary step of the proposed catalytic cycle was found to be feasible and visible light energy was required for the multiple steps. In contrast to the previous related systems which required more than stoichiometric amounts of highly reactive metallic species, this strategy realized a reaction which employs only catalytic amounts of two metal complexes. These results would open up a new possibility in the field of CO_2 fixation chemistry.

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‡ Gaseous H_2 was not detected by GC-TCD during the reaction.
§ **5** was found to be in equilibrium with **4** in the presence of AcOH-$^{i}Pr_2NEt$ in C_6D_6 (see Scheme S1, S2). This equilibrium shifted completely to **5** when the reaction was performed in DMA.
§§ Decomposition of **8** occurred at higher temperature.
§§§ In the cyclic voltammetry measurement of **8** (generated *in situ* by the reaction of **5** with 5 equiv. of **7a**), no reduction wave was observed in the range of -2.0 – 0 V (0.1 M $[Bu_4N][PF_6]$ / DMF vs. E (Fc/Fc^{+})).

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