Title	fac-Re(2,2′ -bipyridine)$(CO)_3$Cl Catalyzes Visible-Light-Driven Functionalization of an Organic Substrate with CO_2
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fac-Re(2,2′-bipyridine)$(CO)_3Cl$ Catalyzes Visible-Light-Driven Functionalization of an Organic Substrate with CO_2

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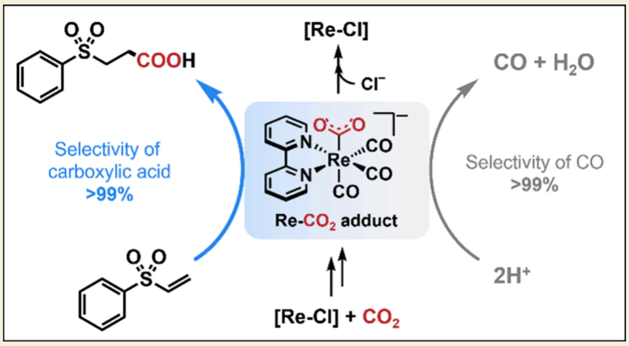
ABSTRACT: The molecular photocatalyst *fac*-Re(2,2′-bipyridine)$(CO)_3Cl$ ([**Re-Cl**]) is well established and has been extensively investigated for the highly active and selective conversion of CO_2 to CO. However, its reactivity in processes other than CO_2 reduction has rarely been explored. Herein, we report the application of [**Re-Cl**] as a catalyst for the visible-light-driven carboxylation of an alkene using CO_2, with phenyl vinyl sulfone (**1**) serving as a model substrate. The catalytic system successfully catalyzed the carboxylation of **1** to its corresponding carboxylic acid, with complete suppression of CO formation throughout the reaction. A turnover number (TON) of up to 2600, along with excellent regioselectivity, was achieved under optimized conditions. Control experiments revealed the key role of each reaction component, while isotope labeling with $^{13}CO_2$ confirmed that the carboxyl group originated from CO_2. Furthermore, mechanistic investigations suggested that the Re-CO_2 intermediate reacts directly with the alkene. These findings highlight the potential of Re-based molecular complexes for broader reactivities and expand their applicability in sustainable synthetic transformations.



KEYWORDS: *Re complex, photocatalysis, carboxylation, CO_2, visible light*

The development of novel catalytic systems for the efficient utilization of CO_2 as a C_1 building block in the synthesis of fuels and chemicals has attracted significant interest in recent decades.[1−3] In particular, visible-light-driven catalytic CO_2 reduction, which is regarded as a half-reaction of artificial photosynthesis, has gained considerable attention, prompting the extensive development of molecular catalysts.[4−8] In this context, the Re(I) tricarbonyl complex, *fac*-Re(2,2′-bipyridine)$(CO)_3Cl$ ([**Re-Cl**]), has been thoroughly investigated since its photocatalytic activity was first reported by Lehn et al. in 1983 (Figure 1a).[9] The complex exhibits excellent catalytic performance for the photoreduction of CO_2 to CO and demonstrates high stability owing to its substitution-inert coordination bonds. This intrinsic stability facilitates structural modifications, enabling molecular tuning and functionalization. Notably, the bipyridine moiety allows the introduction of additional functional moieties, thereby significantly enhancing photocatalytic performance.[10−18] Leveraging these features, Re complexes have been incorporated into various materials to further improve performance for photocatalytic CO_2 reduction.[19−26] These attributes make Re complexes ideal platforms for developing photocatalytic CO_2 reduction systems. Furthermore, extensive research has focused on elucidating the underlying mechanisms, leading to a comprehensive understanding of the catalytic system associated with [**Re-Cl**] and its derivatives.[27−44]

In the proposed mechanism for photochemical CO_2 reduction by [**Re-Cl**], one key intermediate is a Re-CO_2 adduct ([**Re-CO$_2$**]$^-$ in Figure 1b).[36,44] In this species, CO_2 is activated at the Re center and subsequently converted to CO and water following protonation. Given this reactivity, we hypothesize that, beyond serving as a substrate for CO formation, the activated CO_2 could also function as a reactive species capable of coupling with organic molecules. In this context, CO_2 can act as a C_1 building block for direct insertion into organic substrates. Although transformations in which CO_2 activated on a metal complex undergoes direct insertion

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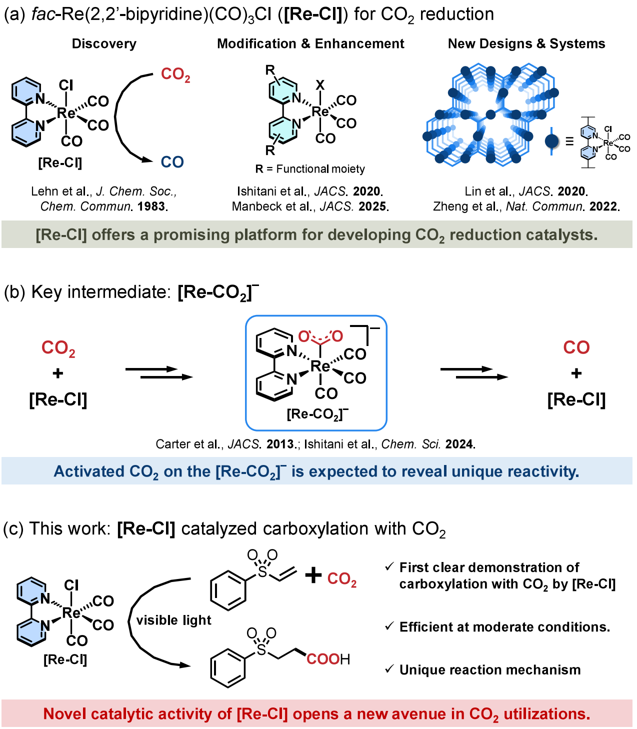
(a) *fac*-Re(2,2′-bipyridine)(CO)$_3$Cl (**[Re-Cl]**) for CO_2 reduction



Lehn et al., *J. Chem. Soc., Chem. Commun.* **1983**.

Ishitani et al., *JACS*. **2020**. Manbeck et al., *JACS*. **2025**.

Lin et al., *JACS*. **2020**. Zheng et al., *Nat. Commun*. **2022**.

[Re-Cl] offers a promising platform for developing CO_2 reduction catalysts.

Carter et al., *JACS*. **2013**.; Ishitani et al., *Chem. Sci*. **2024**.

Activated CO_2 on the [Re-CO_2]$^-$ is expected to reveal unique reactivity.

- ✓ First clear demonstration of carboxylation with CO_2 by [Re-Cl]
- ✓ Efficient at moderate conditions.
- ✓ Unique reaction mechanism

Novel catalytic activity of [Re-Cl] opens a new avenue in CO_2 utilizations.

Figure 1. Overview of research on [**Re-Cl**]: (a) Discovery of its catalytic activity and recent achievements. (b) Key intermediate based on mechanistic studies. (c) This study.

into organic molecules remain unexplored, such processes would mark a significant advancement in sustainable chemistry. Motivated by these considerations, we investigated the catalytic potential[26] of [**Re-Cl**] in visible-light-driven transformations involving CO_2 and organic molecules.

In this study, we introduce a Re-based molecular catalyst for functionalizing an organic substrate with CO_2 (Figure 1c). This photocatalytic system produced the desired carboxylic acid with a high turnover number (TON) of 2600. Control experiments, including ^{13}C isotope labeling, confirmed the catalytic activity of [**Re-Cl**] in driving the organic transformation reaction. Moreover, mechanistic studies revealed a plausible catalytic cycle involving Re-CO_2 active species. Although photochemical carboxylation with CO_2 has become a highly active research area in recent years,[45−68] particularly involving iridium-[53,57−62] and nickel-based[63−68] catalytic systems, our study introduces a distinct and intriguing mechanism in which activated CO_2 on the Re center serve as a nucleophile to react with a substrate. This mechanism is in sharp contrast to the reported systems, where the organic substrate is first activated to act as a nucleophile toward CO_2. Notably, this study is the first to clearly demonstrate the catalytic activity of a Re(I) diimine complex for the utilization of CO_2 as a substrate in a chemical reaction other than CO_2 reduction.

Figure 2a shows the proposed catalytic cycle for photochemical CO_2 reduction using [**Re-Cl**].[29,31,32,36,37,39,40,42−44] Upon absorbing photon energy, [**Re-Cl**] forms an excited state ([**Re-Cl**]*), which subsequently undergoes reductive quenching to generate the one-electron-reduced species, [**Re-Cl**]$^-$. Following the dissociation of the Cl^- ligand, the 5-coordinated intermediate [**Re**] receives one electron and coordinates to the carbon atom of CO_2, forming [**Re-CO$_2$**]$^-$. Theoretical calculations have suggested the formation of [**Re-CO$_2$**]$^-$, which is reported to be thermodynamically favorable.[36,44] In the presence of a proton source, protonation of [**Re-CO$_2$**]$^-$ leads to the release of CO and water. However, we hypothesize that this particular activated CO_2 in [**Re-CO$_2$**]$^-$ may also attack organic substrates, resulting in a functionalization reaction to produce carboxylic acids.[69−71] In either case, coordination to the Cl^- ligand regenerates [**Re-Cl**], thereby completing the catalytic cycle.

Based on our hypothesis, we conducted two distinct experiments involving CO_2 activation using [**Re-Cl**] as the catalyst. First, we investigated the photocatalytic reduction of CO_2 under visible-light irradiation. The reaction was performed in the presence of [**Re-Cl**] using a solvent mixture of *N*,*N*-dimethylacetamide (DMA) and triethanolamine

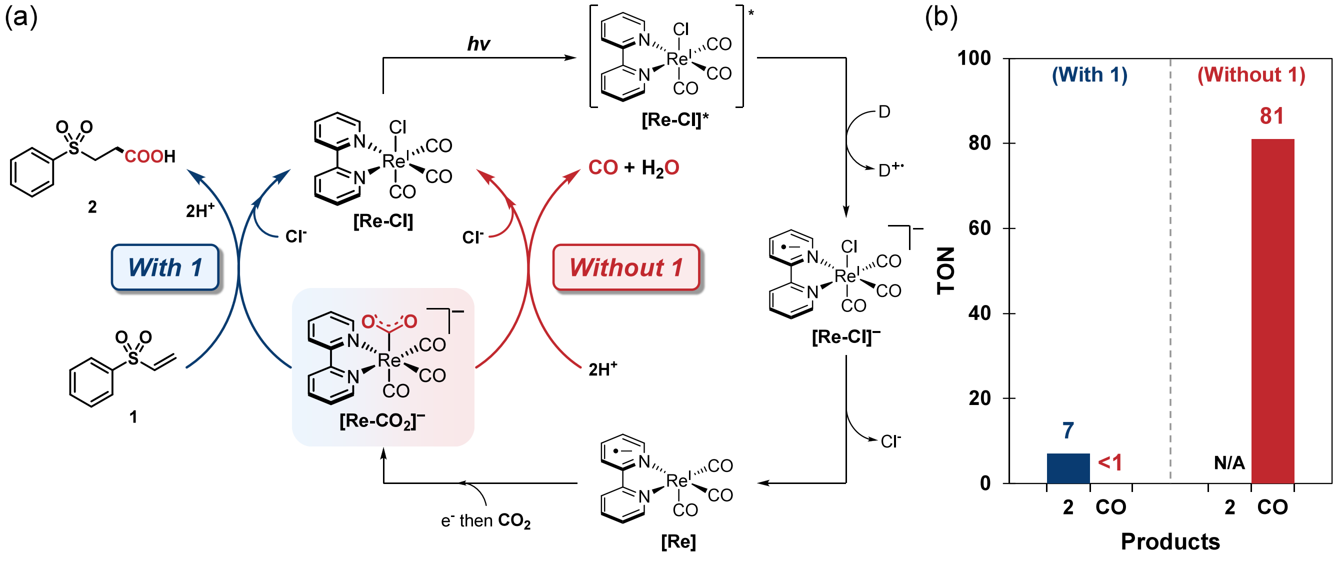
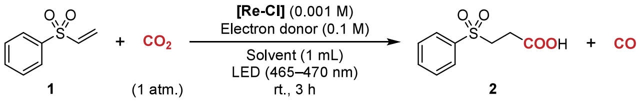


Figure 2. (a) Proposed mechanism based on our hypothesis for the visible-light-driven carboxylation of **1** with CO_2 catalyzed by [**Re-Cl**]. (b) Photocatalytic reactions for the production of **2** and CO. Reaction conditions: A 1 mL solution of DMA:TEOA (5:1 v/v) containing **1** (0.1 M or none), [**Re-Cl**] (1.0 mM), and an electron donor (0.1 M) was saturated with CO_2 for 15 min and then irradiated (465−470 nm) for 3 h.

(TEOA), with 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[*d*]imidazole (BIH) as a sacrificial electron donor, and a blue LED (λ = 465−470 nm) as the light source, under a CO_2 atmosphere. Consequently, CO was formed with a TON of 81 after 3 h (Figure 2b and Table 1, entry 1), which is in line with previously reported results.[9,10] In the second experiment, phenyl vinyl sulfone (**1**) was used as the model alkene substrate under the same reaction conditions. In this case, only trace amounts of CO were detected, indicating suppression of the CO_2 reduction pathway, and 3-(phenylsulfonyl)propanoic acid (**2**) was formed instead, with a TON of 7 (Figure 2b and Table 1, entry 2). These results demonstrate that [**Re-Cl**] exhibits catalytic activity for the carboxylation of organic molecules under visible-light irradiation.

Table 1. Screening of Reaction Conditions[a]



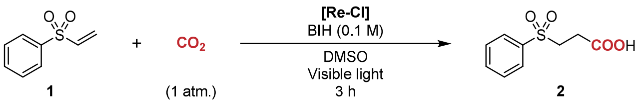
Entry	Solvent	Electron donor	TON of 2[b]	TON of CO
1[c]	DMA:TEOA (5:1 v/v)	BIH	-	81
2	DMA:TEOA (5:1 v/v)	BIH	7	<1
3	DMF:TEOA (5:1 v/v)	BIH	8	<1
4	MeCN	BIH	14	<1
5	DMSO	BIH	22	<1
6[d]	DMSO	TEA	0	-
7[d]	DMSO	Ascorbic acid	0	-

[a] Reaction conditions: A 1 mL solution containing **1** (0.1 M), [**Re-Cl**] (0.001 M), and an electron donor (0.1 M) was saturated with CO_2 (1 atm) for 15 min and then irradiated (465−470 nm) for 3 h. [b] Calculated based on crude ^{1}H NMR using 1,2-dibromoethane as the internal standard. [c] Reaction conducted without **1**. [d] Reaction duration of 16 h.

Encouraged by these initial findings, we examined the optimal reaction conditions. Starting with the solvent investigation, a mixture of *N*,*N*-dimethylformamide (DMF) and TEOA, a well-known effective medium for photocatalytic CO_2 reduction using [**Re-Cl**],[72] produced **2** with a TON comparable to that of DMA:TEOA (Table 1, entries 2 and 3). The use of acetonitrile (MeCN) increased the TON of **2** to 14 (Table 1, entry 4). The optimum solvent was found to be dimethyl sulfoxide (DMSO), which yielded a TON of 22 (Table 1, entry 5). Other common solvents, including DMF, DMA, methanol, tetrahydrofuran, and chloroform, were ineffective (Table S1, entries 5−9). Notably, CO was detected at trace levels in all solvent investigation experiments. Next, we screened various electron donors, including triethylamine (TEA), ascorbic acid, and other commonly used compounds. However, **2** was not produced in any of these cases (Table 1, entries 6 and 7; Table S1, entries 12−16).

To further enhance the TON of **2**, an optimization study was conducted. As shown by the reaction time profile (Figure S1), extending the reaction time beyond 3 h did not improve the TON of **2**. In contrast, doubling the solution volume resulted in a higher TON of 30, even without increasing the loading of [**Re-Cl**] (Table 2, entry 2). In addition, using a Xe lamp (300 W, ≥400 nm) further increased the TON to 36 (Table 2, entry 3), possibly due to the higher absorption intensity of [**Re-Cl**] around the 400 nm region (Figure S17). Finally, the highest TON of 2600 was obtained by reducing the catalyst loading to 0.005 mM (Table 2, entry 4). Notably, **2** was the only regioisomer formed in all experiments, demonstrating excellent regioselectivity for the linear isomer under the optimized conditions (see Scheme S1 for details).

Table 2. Optimization Study[a]

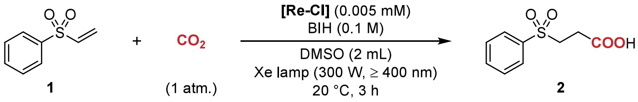


Entry	Total volume	Irradiation	[**Re-Cl**] loading	TON of **2**[b]
1	1 mL	LED[c]	1 mM	22
2	2 mL	LED[c]	0.5 mM	30
3	2 mL	Xe lamp[d]	0.5 mM	36
4	2 mL	Xe lamp[d]	0.005 mM	2600

[a] Standard reaction conditions: A 1 mL DMSO solution containing **1** (0.1 M), [**Re-Cl**], and BIH (0.1 M) was saturated with CO_2 (1 atm) for 15 min and then irradiated (465−470 nm) for 3 h. [b] Calculated based on crude ^{1}H NMR using 1,2-dibromoethane as the internal standard. [c] 465−470 nm. [d] 300 W, ≥400 nm; the temperature of the reaction vial was maintained at 20 °C.

Several control experiments were performed to verify the necessity of each component in the carboxylation reaction. Significantly decreased yield was observed in the absence of [**Re-Cl**], and no product was formed in the absence of BIH, confirming that both the Re catalyst and sacrificial electron donor are critical components (Table 3, entries 1−3). Similarly, no reaction occurred without photoirradiation or a CO_2 atmosphere (Table 3, entries 4−5). Collectively, these results indicate that all the components are essential for successful carboxylation reactions (for details, see the SI, pp S12−S14).

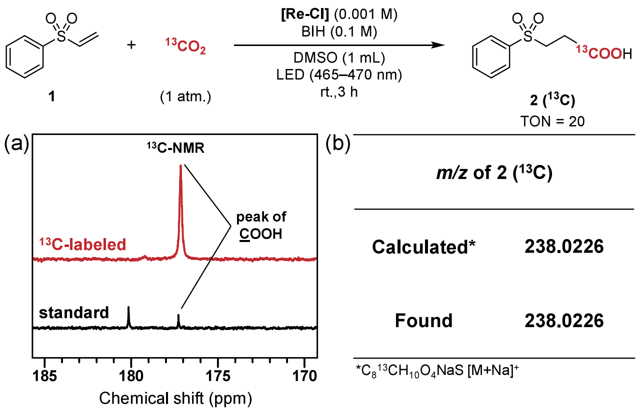
Table 3. Control Experiments[a]



Entry	Catalyst	Electron donor	Irradiation	Gas	TON of **2**[b]
1	[**Re-Cl**]	BIH	Xe lamp	CO_2	2600
2	–	BIH	Xe lamp	CO_2	(8%)[c,d]
3	[**Re-Cl**]	–	Xe lamp	CO_2	0
4	[**Re-Cl**]	BIH	–	CO_2	0
5	[**Re-Cl**]	BIH	Xe lamp	Ar	0

[a] Reaction conditions: A 2 mL DMSO solution containing **1** (0.05 M), [**Re-Cl**] (0.005 mM), and BIH (0.1 M) was saturated with CO_2 (1 atm) for 15 min and then irradiated under a Xe lamp (300 W, ≥400 nm, 20 °C) for 3 h. [b] Calculated based on crude ^{1}H NMR using 1,2-dibromoethane as the internal standard. [c] The yield is shown instead of TON. [d] For the reason behind the obtained yield (8%), please see the SI (pp S12−S14).

Isotope labeling was employed to verify the original source of the carboxyl group. The reaction was conducted using $^{13}CO_2$, and the isolated product was analyzed using ^{13}C NMR and high-resolution mass spectrometry (HRMS). The ^{13}C NMR spectrum (Figure 3a) shows a prominent signal at 177.1 ppm, corresponding to the carbon atom of the −COOH group. In addition, HRMS analysis revealed a species with an m/z value of 238.0226, which matches the calculated value for **2** (^{13}C) with a Na^+ ion ($[M+Na]^+$, m/z = 238.0226) (Figure



m/z of 2 (^{13}C)	
Calculated*	238.0226
Found	238.0226

*$C_8{}^{13}CH_{10}O_4NaS$ [M+Na]$^+$

Figure 3. (a) ^{13}C NMR spectra (CD_3OD) showing the signal of the carboxyl carbon (177.1 ppm) for the isolated products from the isotope labeling experiment (red line) and the standard conditions (black line). (b) HRMS analysis of the product from the isotope labeling experiment.

3b). Thus, these results confirm that the carboxyl group originated from CO_2.

We conducted the following mechanistic studies to elucidate the reaction mechanism. First, emission-quenching experiments were performed. The emission intensity of [**Re-Cl**] changed negligibly in the presence of either **1** or CO_2 (Figures 4a and b), whereas it decreased markedly in the presence of BIH (Figure 4c). The Stern−Volmer plot of I_0/I versus BIH concentration exhibits a linear correlation, yielding a K_{eq} value of 129.54 M^{-1} (Figure 4d). These findings indicate that the excited state of [**Re-Cl**] was quenched only by BIH in this system, supporting the reductive quenching of [**Re-Cl**]* to generate [**Re-Cl**]$^-$, as shown in Figure 2a.

Next, the electrochemical behavior of [**Re-Cl**] was assessed using cyclic voltammetry (CV) in MeCN solution. The CV curve of [**Re-Cl**] under an Ar atmosphere exhibits a reversible wave corresponding to the reduction of the 2,2′-bipyridine ligand and an irreversible wave corresponding to the reduction of Re(I) ions (Figure 4e, black line). We then performed CV measurements under a CO_2 atmosphere. Notably, a large irreversible current was observed after the two-electron reduction of [**Re-Cl**] (Figure 4e, red line).[27] This result is consistent with the proposed mechanism in Figure 2a, where coordination between [**Re-Cl**] and CO_2 follows the two-electron reduction, leading to the generation of [**Re-CO$_2$**]$^-$. In contrast, the presence of **1** under an Ar atmosphere did not affect the redox behavior of [**Re-Cl**] (Figure 4f). Moreover, **1** exhibited a highly negative reduction potential (Figure S12). These results indicate that the two-electron reduced species of [**Re-Cl**] can interact with CO_2, whereas neither an interaction between [**Re-Cl**] and **1** nor the direct reduction of **1** occurs in this system.

The reaction mechanism was further investigated by examining the regioselectivity of the product (see Scheme S1 for details). Two possible pathways for the coupling of **1** with CO_2 were considered: (A) nucleophilic attack of a radical anion of **1**, generated via one-electron reduction, on CO_2; or (B) nucleophilic attack of an activated CO_2, which is coordinated to [**Re-CO$_2$**]$^-$, on **1**. In pathway A, the radical anion of **1** localizes the negative charge at the α-position to the phenylsulfonyl group, which is stabilized by resonance with the sulfonyl moiety, as evidenced by density functional theory (DFT) calculations (for details, see the SI, pp S20−S23). Nucleophilic attack from the carbanion on CO_2 would preferentially yield the branched isomer (Scheme S1, pathway A). In contrast, in pathway B, the activated CO_2 coordinated to [**Re-CO$_2$**]$^-$ nucleophilically attacks **1**, leading to the formation of the linear isomer (Scheme S1, pathway B). Our experimental investigations consistently showed that only the linear isomer **2** was formed in all cases. These observations support pathway B, in which the activated CO_2 species at the Re center reacts directly with the substrate (for investigations on other substrates, see the SI, pp S15−S16).

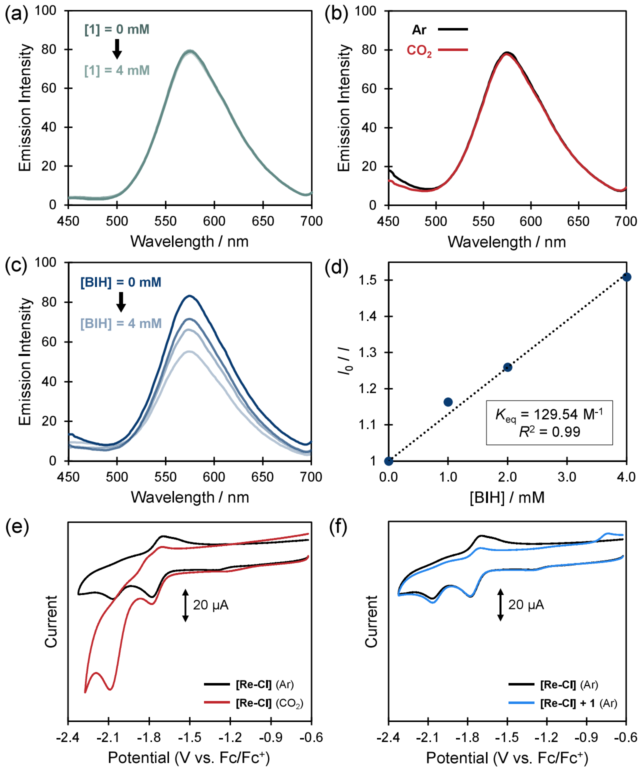


Figure 4. (a) Emission quenching of [**Re-Cl**] in the presence of **1**. (b) Emission quenching of [**Re-Cl**] under a CO_2 atmosphere. (c) Emission quenching of [**Re-Cl**] in the presence of BIH. Measurements were conducted using a DMSO solution of [**Re-Cl**] (50 μM), with quencher concentrations of 1.0, 2.0, or 4.0 mM. The samples were degassed with a stream of Ar or CO_2 for 20 min prior to measurement. (d) Stern−Volmer plot of the emission quenching of [**Re-Cl**] in the presence of BIH. (e) CV curves of [**Re-Cl**] (0.5 mM) under an Ar atmosphere, and a CO_2 atmosphere. (f) CV curves of [**Re-Cl**] (0.5 mM) in the absence and presence of **1** (0.5 mM). CV was performed in an acetonitrile solution containing 0.1 M tetrabutylammonium hexafluorophosphate at a scan rate of 100 mV s^{-1} using glassy carbon as the working electrode, Ag/Ag$^+$ as the reference electrode, and Pt wire as the counter electrode.

The results from the mechanistic studies corroborate the hypothesis shown in Figure 2a. In this mechanism, the two-electron reduced species of [**Re-Cl**] interacts with CO_2 to form a Re-CO_2 adduct, which subsequently reacts with the substrate to produce the carboxylation product. X-ray absorption spectroscopy (XAS) experiments support the electron donation from the Re center to the coordinated CO_2, leading to the formation of a reduced CO_2 species (for details, see the SI, pp S24−S26). Notably, this mechanism differs significantly from conventional carboxylation systems,[61,73−75] where the organic substrate is first activated before reacting as a nucleophile toward CO_2. Thus, our findings reveal a new mode of CO_2 activation and open new avenues for CO_2 utilization.

In conclusion, this study provides the first clear demonstration of using a Re-based molecular catalyst for the functionalization of organic molecules with CO_2. The [**Re-Cl**] catalyst enabled visible-light-driven carboxylation of **1** with CO_2, affording the corresponding carboxylic acid **2** with excellent regioselectivity. Notably, CO_2 reduction to CO was completely suppressed under identical conditions. Under the optimized conditions, the TON for **2** reached 2600. Control and isotope labeling experiments confirmed the reactivity of [**Re-Cl**] in the carboxylation of **1** with CO_2. Moreover, mechanistic studies supported the proposed catalytic cycle. Thus, this study opens a new avenue for the application of Re complexes in other organic transformations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.5c00665.

> Detailed experimental procedures, screening of reaction conditions, study of reaction time course, characterization of the carboxylation products, further mechanistic studies (quenching experiment, CV, examining of product selectivity, theoretical calculation, X-ray absorption spectroscopy and UV−visible absorption spectrum) (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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