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Electrocatalytic Reduction of Carbon Dioxide with a Well-Defined PN^3–Ru Pincer Complex

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A well-defined PN^3–Ru pincer complex (**5**) bearing a redox-active bipyridine ligand with an aminophosphine arm has been established as an effective and stable molecular electrocatalyst for CO_2 reduction to CO and HCOOH with negligible formation of H_2 in a H_2O/MeCN mixture.

In addition to chemical transformation and reduction processes, the electrocatalytic reduction of CO_2 into valuable chemicals powered by the input of renewable energy is being pursued as a promising pathway to mitigate the depletion of carbon resources and environmental problems.[1] The rational design and development of electrocatalysts that are efficient, stable, and selective for this reaction is of great importance. Various metal electrocatalysts have been investigated experimentally and theoretically to rationalize their practical application in CO_2 electroreduction.[1d, 2] However, most of them commonly suffer from either low energy efficiency owing to the need for high overpotentials to activate CO_2 and/or low hydrocarbon selectivity owing to competitive water reduction. Despite this, several advances have been made recently to substantially enhance the activity and selectivity by using nanostructured noble-metal electrocatalysts and rational modification of existing electrocatalysts.[3] In addition, well-defined molecular electrocatalysts have gained tremendous attention because of their tunable reactivity and selectivity by varying the ligand structures and the coordinated metal centers.[4–6] A wide variety of transition-metal complexes with nitrogen-donor ligands have been found to be active for CO_2 reduction, but only a few of them show impressive performances,[5] and most of them still require quite a high overpotential or exhibit inferior selectivity and stability.

Transition-metal complexes supported by pincer ligands have recently emerged as versatile catalysts for a variety of organic transformation reactions owing to their high stability and the tunability of stereoelectronic properties by modifying the moieties on the ligand to afford exceptional chemical reactivities.[7] In particular, pincer catalysts have been developed and shown to exhibit superior activity and selectivity for the reversible chemical hydrogenation of CO_2 to formate, among them PCP–Ir,[8a–c] PNP–Ru,[8d,e] PNN–Ru,[8f–i] PNP–Fe,[8j–l] PNP–Co,[8m] and PNP–Ni.[8n] More recently, the utilization of pincer complexes has also been extended to electrocatalytic water and CO_2 reduction reactions.[9] Crabtree and co-workers reported that tridentate pincer-ligand-supported nickel complexes are active electrocatalysts for proton reduction to H_2 in both nonaqueous and aqueous solutions.[9a,b] Studies on electrocatalytic CO_2 reduction by Brookhart and co-workers showed that POCOP- and PCP-type Ir–dihydride pincer complexes are highly selective electrocatalysts for CO_2 reduction to formate in the presence of H_2O, and the electrocatalytic performance using this class of complexes was found to be further improved by using a gas-diffusion electrode.[9c–e] These studies clearly demonstrated a great potential of pincer complexes as highly efficient electrocatalysts for CO_2 reduction under mild conditions. We have recently developed a new class of dearomatized pyridine-based pincer complexes with an imine arm that exhibit unusual thermodynamic and kinetic properties.[10,11] This new class of complexes may show improved activity and selectivity for CO_2 reduction by fine-tuning their redox-active properties, thereby acquiring deep knowledge of the structure–performance relationship. In this communication, we synthesized various PN^3–Ru pincer complexes containing different redox-active (bi)pyridine-containing ligands, which are known as effective catalyst precursors for ester hydrogenation in the presence of H_2O.[11d] After optimizing the ligands and H_2O content, highly stable PN^3–Ru-based molecular catalysts have been identified that are selective for CO_2 reduction in MeCN/H_2O mixtures, with negligible H_2 formation.

We first investigated the electrocatalytic reduction of CO_2 using three PN^3–Ru pincer complexes **1**–**3** that have different substituents on one of the arms of the ligand (Scheme 1), by using cyclic voltammetry (CV) and controlled potential electrolysis (CPE) experiments at constant potential (−1.26 to −1.31 V versus a standard hydrogen electrode (SHE), depending on the complex used) on glassy carbon (GC) and carbon paper electrodes in a 3% H_2O/MeCN mixture, respectively (see the experimental details in the Supporting Information).

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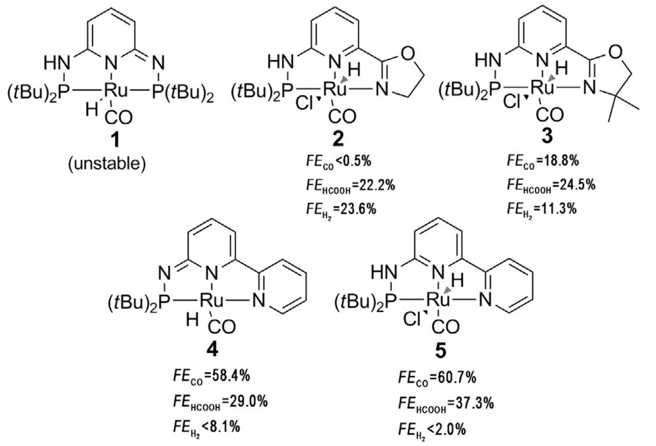


Scheme 1. PN^3–Ru pincer complexes **1**–**5** with different ligands that were investigated for electrocatalytic CO_2 reduction. CPE experimental conditions for **2**–**5**: Carbon-paper electrode, 2.4 cm^2, 3% H_2O/MeCN mixture. The *FE*s for CO and H_2 are the average values and that for HCOOH is a cumulative value over 12 h of electrolysis.

Dearomatized complex **1** was totally inactive and unstable under the electrochemical conditions. Complexes **2** and **3** with an oxazoline group were initially electrochemically active for CO_2 reduction but were deactivated quickly with time (Scheme 1; Figures S1 and S2 in the Supporting Information). The low activity and stability of these complexes are presumably due to the electrochemical ineffectiveness and/or unstable nature of these ligands in reduced form to accept electrons and to stabilize the reducing equivalents during the CO_2 reduction.

Previous studies reported that for nitrogen-donor ligand-supported Re, Mn, and Ru complexes, the incorporation of redox-active bipyridine ligands was essential for efficient CO_2 electroreduction,[6] which in turn influenced the product selectivity.[6g] Consistent with these observations, it was found that dearomatized bipyridine-containing complex **4** and its aromatized counterpart **5** (Figure 1 and Scheme 1) showed high activity for CO_2 reduction. Complexes **4** and **5** showed similar electrochemical behaviors in the presence of Ar, and there are two reduction waves with the latter showing quasi-reversibility during the reverse scan. In the presence of CO_2 and the addition of 3% H_2O, a clear enhancement in current was observed at these two reduction waves, indicative of the catalytic reduction of CO_2, which was also confirmed by experiments with controlled potentials (Figure 1C, D) at the first reduction waves. Complex **5** showed formation of CO (3.9%) and HCOOH (28.3%), even in the absence of H_2O. The addition of a small amount of H_2O (3%) significantly enhanced the electrocatalytic current with much higher Faradaic efficiencies (*FEs*) for CO (60.7%) and HCOOH (37.3%) (Figure 1D), with only negligible formation of H_2 (<2.0%) from H_2O reduction. No significant change was recorded in the UV-visible absorption spectra after the reaction during a two hour reaction (Figure S3 in the Supporting Information). NMR spectroscopy studies also showed that the chemical structure of **5** remained unchanged even in

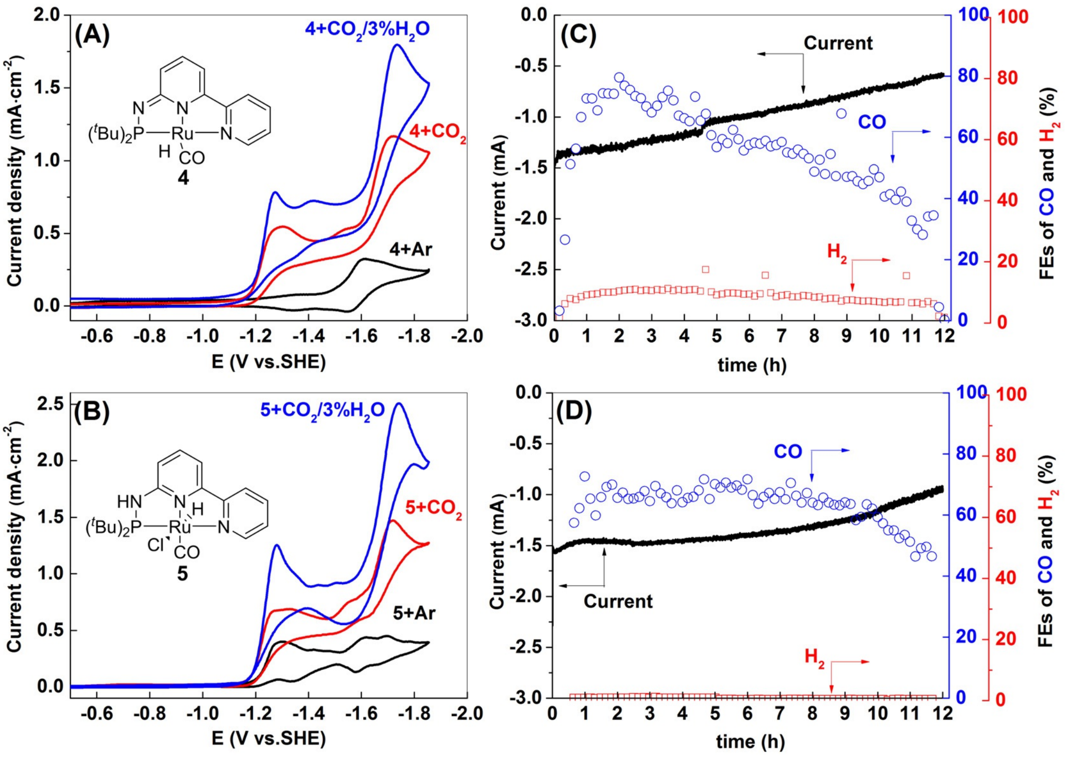


Figure 1. Cyclic voltammograms of 1.0 mM (A) **4** and (B) **5** in MeCN under Ar, CO_2, and CO_2 with addition of 3% H_2O. Conditions: Glassy carbon electrode, 7.1 mm^2, 0.1 M nBu_4NPF_6, 100 mV s^{-1}, 296.2 K. Current-time profiles CPE experiments of CO_2 reduction over (C) **4** and (D) **5** at −1.26 and −1.28 V (vs. SHE) in 3% H_2O/MeCN mixture, respectively. Conditions: carbon-paper electrode, 2.4 cm^2, 0.1 M nBu_4NPF_6.

the presence of H_2O and after exposure to air for three days (Figure S4 in the Supporting Information). These preliminary results show that a new, high-performance, water- and air-stable Ru-based pincer electrocatalyst **5** for CO_2 reduction has been established by rationally modulating the redox properties of the ligand framework. In an effort to obtain more kinetic details on the electrocatalytic reduction of CO_2, cyclic voltammograms of **5** under different reaction conditions were investigated at a glassy carbon electrode in detail, as shown in Figure 2A–C. Under Ar in dry MeCN at 100 $mV\,s^{-1}$(Figure 1B), a reduction wave at about -1.30 V versus a standard hydrogen electrode (SHE) was observed, likely arising from ligand-related reduction,[6e,j,12] which was consistent with that of recently reported *trans*-Cl-[Ru(mesbpy)$(CO)_2Cl_2$] with a bulky bpy ligand (mesbpy).[13] The peak current density ($i_{p,c}$) of this reduction wave demonstrates a linear dependence on the square root of the scan rate ($\upsilon^{1/2}$) from 50 to 3000 $mV\,s^{-1}$, which indicates a diffusion-limited reduction process of the catalyst at the electrode (Figure 2A, Figures S5 and S6 in the Supporting Information). Only at faster scan rates ($>$400 $mV\,s^{-1}$), was an oxidation peak observed at -1.25 V (vs. SHE), with a linear correlation of the peak current density ($i_{p,a}$) with $\upsilon^{1/2}$ (Figure S5a in the Supporting Information), also indicative of a diffusion-limited process. This observation is consistent with a mechanism in which an initial electron transfer takes place to form the radical anion, which can be reversible, followed by an irreversible chemical step, most likely the loss of chloride to form Ru^I species coordinated with solvent molecule(s). Similar processes were observed with other bipyridine-related transition-metal complexes containing Cl ligand(s).[6f,h,j,13] It is also noted that only one reduction wave is observed for **5** under Ar in the potential range of -1.2 to -1.5 V (vs. SHE), which suggests that complex **5** is capable of mediating a two-electron reduction process to produce the neutral species after the chloride loss (Figures S6 and S7 in the Supporting Information), in agreement with our aforementioned kinetic analysis and the observation in an NHC-containing Mn molecular electrocatalyst.[6g] At slower scan rates, the irreversibility is attributed to a fast irreversible chemical step following the initial electron transfer, whereas at higher scan rates, the reversible behavior of **5** suggests that the loss of chloride is slower than the reoxidation of the radical anion formed upon the initial reduction.

Under CO_2 bubbling in dry MeCN, the reduction peak current density at around -1.28 V (vs. SHE) for **5** was nearly doubled from 0.38 to 0.69 $mA\,cm^{-2}$ (Figure 1B), which suggests catalytic CO_2 turnover. The catalytic peak current density (i_{cat}) for CO_2 reduction also shows scan-rate-dependent electrochemical behavior (Figure 2B, and Figure S8a in the Supporting Information). The complete absence of oxidation currents in the presence of CO_2 even at higher scan rates suggests that the active species (probably a neutral radical) formed by an initial electron transfer (Figure S7 in the Supporting Information) is likely transformed immediately by the reaction with CO_2. The similar onset potential for the CO_2 reduction wave is consistent

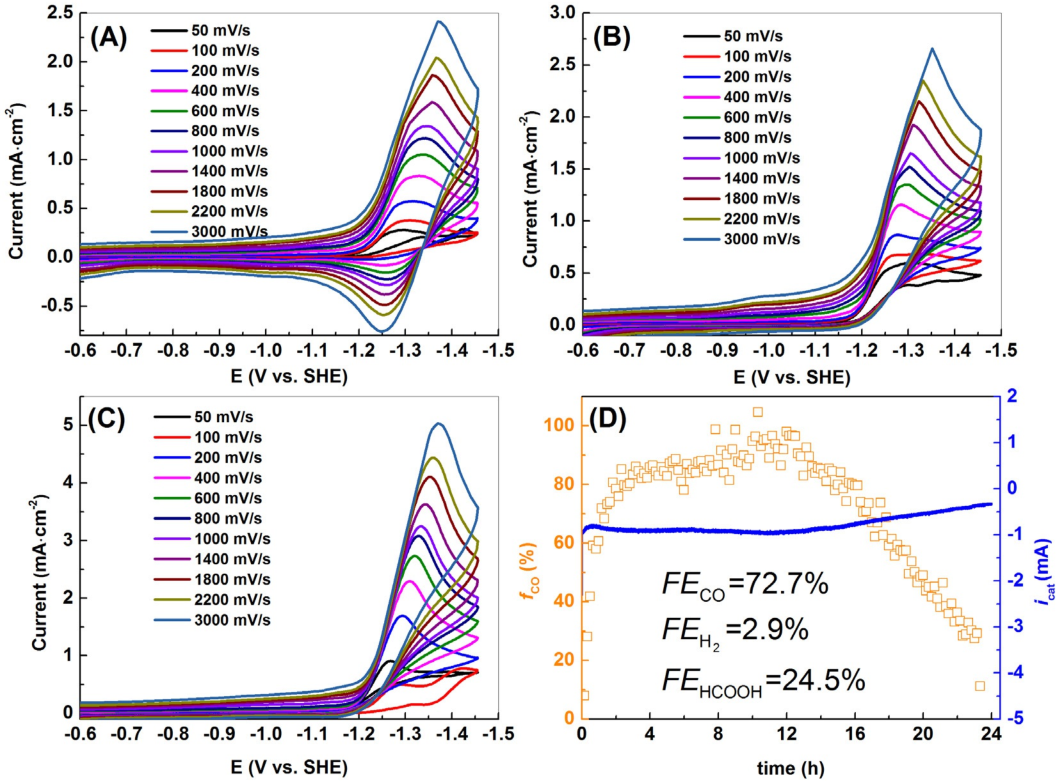


Figure 2. Cyclic voltammograms of 1 mM **5** in MeCN under (A) Ar, (B) CO_2, and (C) CO_2 with addition of 3% H_2O, at various scan rates. Conditions: Glassy carbon electrode, 7.1 mm^2, 0.1 M nBu_4NPF_6, 296.2 K. (D) Long-term CPE at -1.28 V (vs. SHE) in 3% H_2O/MeCN mixture (carbon-paper electrode, 1.2 cm^2). The *FE*s for CO and H_2 are average values and that for HCOOH is a cumulative value over 24 h of electrolysis.

with the fact that the reduced **5** as a result of the initial electron transfer is an active species for CO_2 reduction catalysis. By measuring the ratio of peak currents with CO_2 (i_{cat}) and without CO_2 ($i_{p,c}$) as a function of $\upsilon^{-0.5}$ (Figure S8b in the Supporting Information),[8c–e] the pseudo-first-order rate constant (k_{cat}) for CO_2 reduction under one atmosphere of CO_2 ($[CO_2]=0.28$ M) is calculated to be 0.66 s^{-1}. Long-term CPE experiments (12 h) (Table 1, entry 1) confirmed the successful CO_2 reduction even without H_2O, but with low *FE*s to CO (3.2%) and HCOOH (15.4%). Note that control experiments confirmed a lack of incremental catalytic currents when either no CO_2 or **5** was present (Figure S9 in the Supporting Information).

As reported previously, the presence of H_2O (or some other proton sources) is effective to further improve the catalytic performance for CO_2 reduction.[5,6] When the CV of **5** under CO_2 was recorded in CH_3CN with increasing amounts of added H_2O, a gradual increase in catalytic current at −1.28 V (vs. SHE) was observed (Figure S10a in the Supporting Information) and i_{cat} reached a maximum of 1.25 mA cm^{-2} at 2–3% H_2O, with an onset for CO_2 reduction appearing at approximately −1.15 V (vs. SHE), corresponding to overpotentials of 0.629 and 0.549 V for CO and HCOOH production, respectively, which is comparable to most recently reported Ir–pincer[9c] and Mn–carbonyl complexes.[6f–h] In contrast, there was no significant current enhancement under Ar at −1.28 V (vs. SHE) with added H_2O up to 3%, instead there was a significant contribution to the current enhancement at more negative potentials, probably due to the background water reduction (Figure S10b in the Supporting Information). Diffusion-limited kinetic behavior was also observed for CO_2 reduction with 3% H_2O added (Figure 2C, and Figure S11 in the Supporting Information), and a much larger k_{cat} of 4.44 s^{-1} was achieved. This value is comparable to that of polypyridyl-supported Ru complexes (≈5.1 s^{-1} with 10% H_2O),[6i] but much lower than the value obtained with Ir–dihydride pincer complex (20 s^{-1} with 5% H_2O).[9c] Controlled potential electrolysis experiments showed that, with 1 mM of **5** and in the presence of 3% H_2O, the average *FE*s for both CO and HCOOH production over a 12 hour reaction were considerably higher than those in dry MeCN, with negligible formation of H_2 (Table 1, entry 2, and Figure 2D). As expected, when more H_2O (10%) or less **5** was present, the reduction of water to H_2 became more favorable than CO_2 reduction (Table 1, entries 3 and 4). It was reported that for Re– and Mn–tricarbonyl complexes the presence of water not only serves as a proton source to lower overpotentials for CO_2 reduction, but also stabilizes the metal–CO_2 intermediate through protonation, thus facilitating the reduction of CO_2.[6] A similar beneficial effect of water was also reported for the electrocatalytic reduction of CO_2 to formate with an Ir–dihydride pincer complex.[9c] Kinetic studies showed that the catalytic peak current, i_{cat}, varies linearly with [**5**] under one atmosphere of CO_2 and linearly with $[CO_2]^{0.5}$ with 1 mM of **5** (Figures S12 and S13 in the Supporting Information), which indicates that the catalytic reaction is first order in both concentrations of **5** and CO_2.[9c,d]

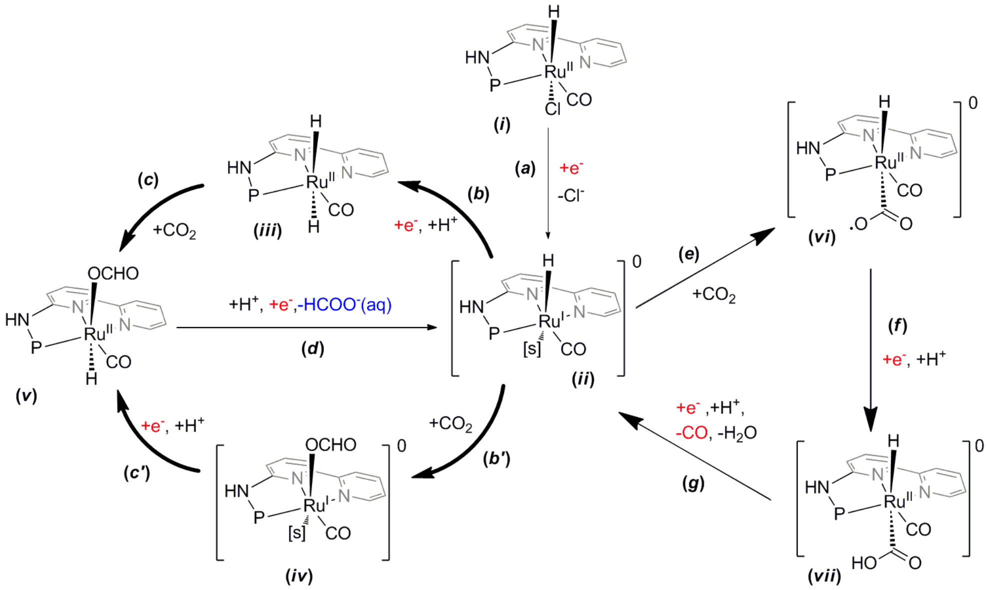
Scheme 2 shows a plausible electrocatalytic reduction mechanism of CO_2 reduction over **5**. The irreversibility of the CV response of **5** (*i*) at the first reduction potential is a bpy-based reduction pathway followed by a fast ligand-to-metal charge transfer resulting in the Cl^- loss, which yields Ru^I species (*ii*) (step (*a*)). The Ru^I species readily accepts an electron and reacts with H^+ to generate the neutral dihydride Ru^{II} species (*iii*) (step (*b*)) followed by an insertion reaction of CO_2 into one of the Ru–H bonds of (*iii*) to give intermediate (*v*) (step (*c*)) under an applied potential. In another possible pathway, CO_2 may insert into the Ru–H bond of Ru^I species (*ii*) directly to give a neutral Ru^I species (*iv*) (step (*b'*)) under CO_2-saturation conditions and then undergoes a proton-coupled electron-transfer process to form (*v*). Subsequently, bulk electrolysis at the first reduction potential may generate HCO_2^-/HCO_2H via step (*d*). The CO formation may be a result of decarbonylation from a metallocarboxylate intermediate (*vi*) through steps (e)–(g).[6,14] The formation of intermediate (*v*) was supported by a control experiment using complex **4** with the addition of one equivalent of HCOOH under otherwise identical conditions, which gave a similar activity and selectivity for CO_2 reduction to that of **4** without the addition of HCOOH (Figures S14 in the Supporting Information).

Further optimization of the electrolyte conditions was attempted to improve the electrocatalytic performance of CO_2

Table 1. Results of controlled potential electrolysis (CPE) experiments for 12 hours.[a]

Entry	Comments	*E* vs. SHE [V]	Charge passed [C]	FE_{CO} [%] (TON)[f]	FE_{HCOOH} [%] (TON)[f]	FE_{H_2} [%]	Total *FE* [%]
1	**5** (1.0 mM) in MeCN/CO_2	−1.28	34.8	3.2 (0.2)	15.4 (0.9)	n.d.	18.6
2	**5** (1.0 mM) in MeCN (3% H_2O)/CO_2	−1.28	57.9	60.7 (6.1)	37.3 (4.2)	<2.0	≈100
3	**5** (0.2 mM) in MeCN (3% H_2O)/CO_2	−1.28	10.9	20.3 (2.0)	40.1 (7.5)	26.8	87.2
4	**5** (1.0 mM) in MeCN (10% H_2O)/CO_2	−1.28	58.2	60.9 (6.1)	13.9 (1.4)	13.2	88.0
5	**5** (1.0 mM) in MeCN (3% H_2O)/CO_2	−1.75	75.1	36.4 (4.7)	34.3 (4.5)	5.3	76.0
6	**5** (1.0 mM) in MeCN (3% H_2O)/CO_2[b]	−1.28	67.0 (24 h)	72.7 (8.4)	24.5 (2.8)	<3.0	≈100
7	MeCN (3% H_2O)/CO_2/used electrode[c]	−1.28	10.7	n.d.	18.4 (0.3)	35.4	53.8
8	MeCN/CO_2/bare electrode[d]	−1.28	7.3	n.d.	18.3 (0.5)	n.d.	18.3
9	MeCN (3% H_2O)/CO_2/bare electrode[e]	−1.28	38.5	n.d.	8.5 (0.3)	89.3	97.8

[a] Conditions: Carbon-paper electrode, 2.4 cm^2, 1 atm CO_2, 0.1 M nBu_4NPF_6, 296.2 K. [b] A 1.2 cm^2 carbon-paper electrode was used. [c] Electrode used for entry 2 experiment was reused after thoroughly rising with acetonitrile and acetone, and recharged with fresh solution without **5** added. [d] Clean carbon electrode was used without addition of **5** and H_2O. [e] Clean carbon electrode was used without addition of **5**. [f] The TON was calculated based on the amount of **5** used. n.d. = not detectable. The *FE*s for CO and H_2 are average values and that for HCOOH is a cumulative value during the electrolysis reaction.



Scheme 2. Proposed overall mechanism for the reduction of CO_2 to CO and HCO_2H by **5** in H_2O/MeCN mixture.

using **5**. When adding 3% aqueous HCl solution with concentrations varying from 10^{-5} to 10^{-1} M instead of pure water (Table S1 in the Supporting Information), a slight decrease in CO selectivity and negligible increase in H_2 selectivity were observed compared with the values obtained with pure water (Table 1, entry 2), together with a slight decrease in HCOOH selectivity, further confirming the high activity of **5** for CO_2 reduction over proton reduction. When the reaction was carried out in an aqueous $KHCO_3$ solution in the presence of the required amount of MeCN to dissolve **5** (Table S1 in the Supporting Information), the production of H_2 (21.8%) became more favorable with concurrent HCOOH formation (9.2%), which might still show potential for applications of **5** in aqueous CO_2 reduction.

As the CV scan of **5** was expanded to more negative potentials (Figure 1B), one more reductive process was observed under an atmosphere of argon, with an additional catalytic reduction wave appearing at −1.75 V (vs. SHE) under CO_2 in the presence of H_2O. Electrolysis of CO_2 at this potential, however, only showed lower CO selectivity and total *FE* for CO_2 reduction (CO and HCOOH), due to the background proton reduction and/or decomposition of the catalyst (Table 1, entry 5). The product selectivity was also affected by the applied potentials (Table S2 in the Supporting Information). The CO/HCOOH ratio increased with an increase in applied potential from about −1.15 to −1.35 V (vs. SHE). The catalytic current was highest at about −1.28 V (vs. SHE), consistent with the CV result (Figure 1B), with the highest total FE of CO_2 reduction products reaching as high as 98%.

At the optimal potential (−1.28 V vs. SHE), the current for CO_2 reduction electrolysis was sustained without significant decrease for at least 12 hours using a carbon-paper working electrode (Figure 2D). The *FE* of CO approaches an average value of 85.2% (Table 1, entry 6) without a change in the ratio of CO and HCOOH by assuming that the total *FE* of the main products equals 100%, which suggests a robustness of the catalytic species from **5** during this period of time. In the next 12 hours of electrolysis, there was a gradual decrease in both the catalytic current and *FE* for CO (Figure 2D). An overall turnover number (TON) of about 11.2 for CO_2 reduction was achieved over 24 hours of electrolysis. The decrease in activity was presumably due to the decomposition of the catalyst caused by the hydrolysis of the P–N bond of the aminophosphine arm when more formic acid was formed,[15] as evidenced by a visible color change in both the carbon-paper electrode and electrolyte solutions, and the formation of a white precipitate in solution. X-ray photoelectron spectroscopy (XPS) (Figure S15 in the Supporting Information) confirmed that the surface of the carbon electrode contained Ru and N after the long-term electrocatalytic reaction, in which Ru 3p peaks show both oxidized and metallic forms. The deactivation of **5** during CO_2 electrolysis also resulted in the change of the CO/HCOOH ratio as the decomposed catalytic species may be involved in the electrolysis.

To investigate whether the deposited material was catalytically active, the used electrode was subjected to an additional 12 hours of electrolysis after removing **5** and recharging with fresh solution, under otherwise identical conditions. As a result, H_2 appeared to be the main product, with no CO detected (Table 1, entry 7). These results are similar to those obtain from background CPE experiments with a clean carbon-paper electrode without **5** irrespective of H_2O presence (Table 1, entries 8 and 9). From these control experiments, the presence of **5** drastically improved not only the amount of charge passed but specifically the CO_2 reduction over H_2 evolution. These observations indicated that any Ru species deposited on the electrode was not responsible for the observed CO_2 electrocatalysis and **5** indeed worked as a homogeneous catalyst for electrocatalytic reduction of CO_2.

In summary, the PN^3–Ru pincer complex **5** has been demonstrated as an effective and stable electrocatalyst for CO_2 reduction. When an appropriate amount of water is present, CO_2 is reduced to CO and HCOOH at high *FE*s. Importantly, formation of H_2 from background water reduction during CO_2 reduction is only negligible, which is indicative of the high activity of this complex toward CO_2 reduction over water reduction. Moreover, a lack of CO_2 reduction activity with a used carbon electrode confirmed that the dissolved molecular complex in homogeneous phase is solely responsible for the observed CO_2 electrocatalysis. This study reveals a new ligand platform for the development of high-performance electrocatalysts of pincer-based metal complexes with versatile functionality and reactivity for CO_2 conversion. Further studies involving pulse radiolysis with time-resolved infrared detection to elucidate the detailed mechanism are currently underway.[16]

Acknowledgements

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