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Low-overpotential CO_2 reduction by phosphine-substituted Ru(II) polypyridyl complex

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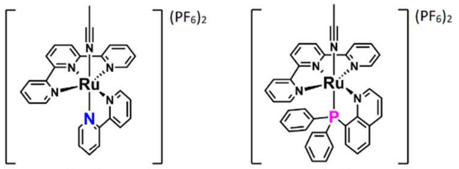
A Ru polypyridyl complex containing a phosphine donor promoted an electrocatalytic CO_2 reduction at a low overpotential. Mechanistic investigations revealed that the introduction of a phosphine donor at the *trans* position to the labile ligand is the key to reduce the overpotential for CO_2 reduction.

Catalytic CO_2 reduction into liquid fuels and commodity chemicals under benign condition has drawn tremendous attention, not only as a means to decrease the competition for limited fossil fuel reserves but also help to reduce the concentration of atmospheric CO_2.[1] There are a continuously increasing number of molecular catalysts to convert CO_2 into fuels, such as HCOOH[1] and deeply reduced products.[2] In addition, the reduction of CO_2 to carbon monoxide (CO)[3] is also favourable because a wide variety of fuels and commodity chemicals can be produced from CO via Fischer–Tropsch synthesis. Therefore, the development of a catalyst that can convert CO_2 to CO is an attractive research target and there have been numerous reports on transition metal complexes that can catalyse the reaction.[4]

Ru polypyridyl complexes with a monodentate ligand are known to exhibit promising CO_2 reduction activity by taking advantage of multiple accessible redox states.[4c-4d,5a] In these systems, polypyridine ligands play an essential role as an electron reservoir in addition to Ru ions as a CO_2-interaction site.[5b] A representative example of such catalysts is a Ru polypyridyl complex, $[Ru^{II}(tpy)(bpy)(MeCN)]^{2+}$ (**RuN**, where tpy = 2,2′:6′,2″-terpyridine; bpy = 2,2′-bipyridine, Fig. 1, left).[5a] This complex undergoes ligand-based multielectron reduction reaction to give $[Ru^{II}(tpy^{-})(bpy^{-})(MeCN)]^{0}$, and forms a CO_2 adduct, $[Ru^{II}(tpy)(bpy)(CO_2^{2-})]^{0}$, via a ligand exchange reaction, which results in the catalytic conversion of CO_2.[4c,5a-5b] However, the potentials required to access their active, two-electron reduced species causes the increase in overpotential (i.e., high energy is required to drive the catalytic reaction). In this connection, ligand modification of Ru polypyridyl complexes has extensively been studied to control over their redox properties and catalytic activity for CO_2 reduction.[5]



RuN **RuP**

Figure 1. Chemical structures of **RuN** and **RuP**.

Phosphine ligands are an attractive class of molecules[6] because these ligands can control the electronic structures of the metal centres of their complexes due to the σ-donating and π-accepting abilities of the phosphine donor. DuBois *et al.*, investigated the catalytic activity of a series of Pd complexes, $[Pd(PXP)(CH_3CN)](BF_4)_2$ (PXP = tridentate ligands; P and X denote coordinating atoms, where X = C, N, O, S, P, and As), and found that the introduction of a phosphine donor at the *trans* position to a labile ligand is the key to obtain an active catalyst for CO_2 reduction.[7] Thus, the introduction of phosphine donor(s) to Ru-based polypyridyl complexes can be a powerful strategy to control their CO_2 reduction activity. However, there is no study on CO_2 reduction by Ru-based complexes containing a phosphine-substituted polypyridine ligand.

Herein, we report electrochemical CO_2 reduction by a Ru complex with a mixed phosphine-pyridine ligand, *trans(P,MeCN)*-$[Ru^{II}(tpy)(pqn)(MeCN)]^{2+}$ (**RuP**, where pqn = 8-(diphenylphosphanyl)quinoline,[8] Fig. 1, right). Presented here are the catalytic activity of **RuP**, the electronic structures of catalytic intermediates, and a plausible catalytic mechanism.

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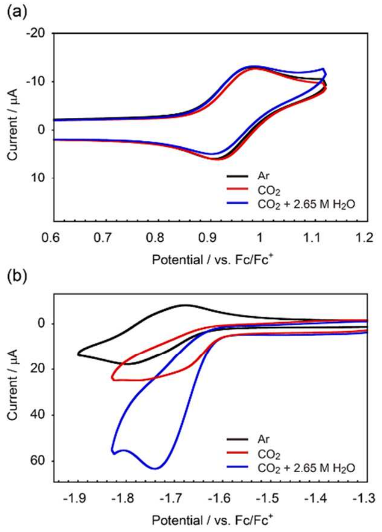


Figure 2. CVs of **RuP** (0.5 mM) in 0.1 M TEAP/MeCN under Ar (black line), CO_2 (0.28 M, red line), and CO_2 in the presence of 2.65 M H_2O (blue line). Working electrode, glassy carbon; counter electrode, Pt wire; reference electrode, Ag/Ag^+; scan rate, 0.1 Vs^{-1}. Potential sweeps were started from the open circuit potential (−0.27 V) for all measurements.

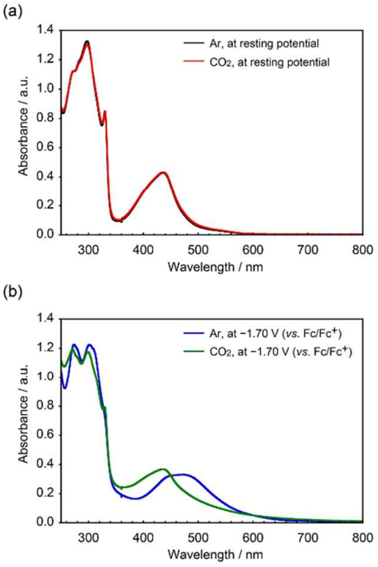


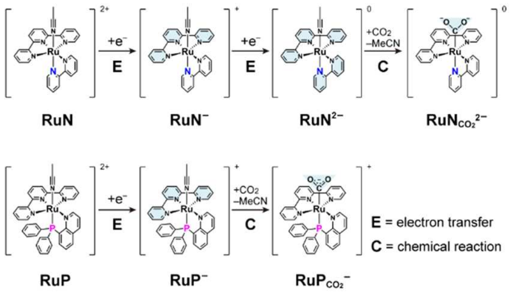
Figure 3. (**a**) UV-Vis absorption spectra of **RuP** (0.5 mM) at open circuit potential in 0.1 M TEAP/MeCN under Ar and CO_2. (**b**) UV-Vis absorption spectra of **RuP** (0.5 mM) under open circuit potential and at −1.70 V vs. Fc/Fc^+ in 0.1 M TEAP/MeCN under Ar and CO_2.

We also discussed the effect of the phosphine donor on the catalytic reaction in comparison with the relevant polypyridyl complex **RuN**.

RuP was synthesized and characterized following the procedure reported by our group.[9] In a cyclic voltammogram (CV) under an Ar atmosphere, **RuP** displayed one reversible oxidation wave in the positive potential region, attributed to a Ru(III)/Ru(II) redox couple at +0.95 V vs. ferrocene/ferrocenium (Fc/Fc^+, Fig. 2a, black line). In the negative potential region, one reversible redox wave was observed, and the half-wave potential ($E_{1/2}$) of the wave was −1.72 V (Fig. 2b, black line). As reported previously,[9b] the wave consists of two reversible one-electron processes with similar redox potentials ($E^{\circ\prime}_1$ = −1.69 V and $E^{\circ\prime}_2$ = −1.78 V, estimated from a simulation of CV (Fig. S1 and Table S1 in the Electronic Supplementary Information (ESI))). To assign the origin of the first reduction process, we calculated the molecular orbitals of **RuP** by density functional theory (DFT) calculations (for details, see the ESI). The LUMO of **RuP** is localized at the π* orbital of the tpy moiety, suggesting that the first reduction wave at –1.69 V originates from a tpy/tpy^- redox couple (Fig. S2). This observation is consistent with the electrochemical properties of the relevant Ru polypyridyl complexes.[5a] The peak currents (i_p) corresponding to the redox couples at −1.69 and −1.78 V have linear relationships with the square root of the scan rate ($v^{1/2}$) and follow the Randles-Sevcik equation (Figs. S3-4 and Table S2). This result indicates that **RuP** can facilitate rapid electron transfer reactions, as frequently observed for Ru polypyridyl complexes.[5a-5f]

To examine the catalytic CO_2 reduction activity of **RuP**, CVs of **RuP** were measured under CO_2 using anhydrous acetonitrile as the solvent. **RuP** exhibited irreversible reduction waves at E_{pc} = −1.67 and −1.76 V (Fig. 2b, red line). These reduction occurred at a more positive potential than those under Ar (Fig. S5). We also performed controlled-potential electrolysis (CPE) at −1.70V, and almost negligible amount of CO (faradaic efficiency (FE) < 1.0 %) was detected. Similar measurements were subsequently performed using acetonitrile containing 2.65 M H_2O as a weak Brønsted acid as the solvent. In this condition, current enhancement was observed near E_{pc} = −1.73 V (Fig. 2b, blue line), and the intensity of the current was dependent on the concentrations of CO_2 and H_2O (Fig. S6). In CPE conducted at −1.70 V, approximately 1.75 C of charge passed during 1 h of electrolysis (Fig. S7 and Table S3, Entry 1), and the formation of CO (5.1 μmol, FE: 55.8%), HCOOH (0.6 μmol, FE: 6.6%), and a negligible amount of H_2 (0.04 μmol, FE: 0.5%) was confirmed. These results clearly indicate that **RuP** can promote electrochemical CO_2 reduction in the presence of H_2O. We also calculated the overpotential of **RuP** for CO_2 reduction to be 0.4 V based on the potential at half of the catalytic current ($E_{cat/2}$ = −1.65 V).[5e,10] The value is substantially lower than those of the relevant polypyridyl complexes including **RuN** (Table S4).[5a-5b] The turnover frequency (TOF) and the turnover number (TON) for CO production were determined to be 4.7 s^{-1} and 1.7 x 10^4, respectively (for details, see the ESI).

Details of the reactions of **RuP** under CO_2 were investigated under anhydrous conditions, where the catalytic reaction does not proceed (*vide supra*). When the concentration of CO_2 was increased, the first reduction peak gradually became irreversible, and the position of cathodic peak shifted to more positive potentials (Fig. S5). This result indicates that CO_2 and the one-electron reduced state of **RuP** (**RuP**$^-$) interact. The position of the first reduction peak remained unchanged in the case of **RuN** (Fig. S8), which is known to show no interactions with CO_2 in its one-electron reduced state.[5a] The reactions

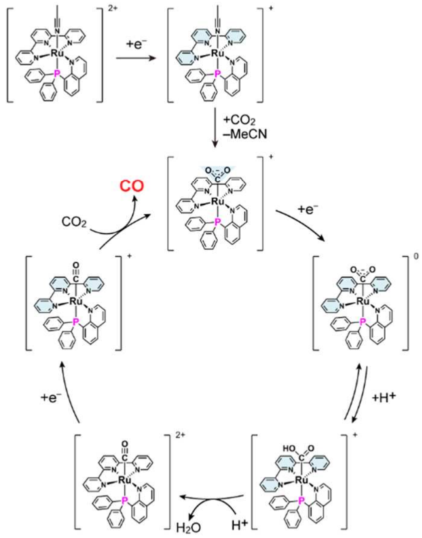


Scheme 1. Proposed mechanism for the formation of metallocarboxylate intermediate of **RuN** via EEC mechanism (top) and that for **RuP** via EC mechanism (bottom). **E** indicates electron transfer while **C** indicates chemical reaction. Reduced ligands are highlighted with pale blue.

were also monitored by UV-vis spectro-electrochemical measurements. At the open circuit potential (E = −0.27 V), **RuP** exhibits an absorption band centred at 436 nm, which is attributed to a metal-to-ligand charge transfer (MLCT) transition (Fig. 3). The UV-vis absorption spectra under Ar and CO_2 were almost identical at this potential, indicating that **RuP** does not interact with CO_2 before the electrochemical reaction proceeds. By scanning the potential to the negative potential region, distinct spectral changes under Ar and CO_2 were observed. Under Ar, the MLCT band redshifted from 436 to 475 nm with isosbestic points (Fig. S9) due to the reduction at tpy moiety.[11] Under CO_2, the MLCT band initially shifted from 436 to 460 nm (from open circuit potential to −1.60 V, Fig. S10), followed by a blueshift to 440 nm (from −1.60 to −1.70 V). These results suggest that **RuP**$^-$, formed after one-electron reduction of **RuP**, rapidly reacts with CO_2 and that the generated CO_2-bound species is further reduced at around −1.65 V.

The aforementioned reactivity of **RuP** with CO_2 under reductive conditions is completely different from that of **RuN**.[5a-5b] The **RuN** complex initially undergoes two one-electron reductions at the tpy and bpy ligands, and a two-electron reduced species, [Ru^{II}(tpy$^-$)(bpy$^-$)(MeCN)]^0 (**RuN**$^{2-}$), forms at near −1.85 V. **RuN**$^{2-}$ undergoes an exchange between the MeCN ligand and a CO_2 molecule to generate the metallocarboxylate intermediate [Ru^{II}(tpy)(bpy)($CO_2{}^{2-}$)]^0 (**RuN**$_{CO_2}{}^{2-}$, Scheme 1, top, EEC mechanism, where E and C indicate electron transfer and chemical reactions, respectively). In other words, **RuN** cannot react with CO_2 before 2e$^-$ reduction, and thus, the electrocatalytic CO_2 reduction can proceed only after the second reduction.[5a-5b] In contrast, one-electron reduced species of **RuP** (**RuP**$^-$) can react with CO_2 (EC mechanism, *vide supra*) and be further reduced to generate the catalytic active intermediate near −1.65 V, resulting in **RuP** mediating CO_2 reduction at a lower overpotential than **RuN** (Fig. S11).

This superior reactivity of **RuP** with CO_2 can be explained by considering the nature of the coordinating phosphine donor. First, the σ-donating character of the phosphine group can destabilize the bond between the Ru centre and the nitrogen atom of the MeCN ligand (*trans* influence). The previously reported crystal structures of **RuP** and **RuN** clearly demonstrate that the bond between the Ru centre and the nitrogen atom of the MeCN is significantly elongated upon the introduction of a phosphine donor at the position *trans* to the MeCN: 2.127(5) Å[9b] for **RuP** and 2.030(1) Å[12] for **RuN**. Second, the π-accepting character of the phosphine group can stabilize the bond between the Ru centre and the carbon atom of CO_2. DFT calculations revealed that the HOMO of the CO_2 adduct formed after one-electron reduction of **RuP** (**RuP**$_{CO_2}{}^-$) is mainly located on the metal-bound CO_2, whereas the HOMO of **RuP**$^-$ is localized on the tpy ligand (Fig. S12). These results indicate that the intramolecular electron transfer from the tpy moiety to the CO_2 proceeds upon the exchange of the MeCN ligand. In other words, the electronic structure of **RuP**$_{CO_2}{}^-$ can be best described as [Ru^{II}(tpy)(pqn)($CO_2{}^{\bullet-}$)]$^+$ (Scheme 1, bottom). The HOMO of **RuP**$_{CO_2}{}^-$ is also located on the phosphine donor of the pqn ligand, indicating that the phosphine donor of the pqn ligand contributes to the stabilization of the Ru-C($CO_2{}^{\bullet-}$) bond of **RuP**$_{CO_2}{}^-$ via π-back donation.



Scheme 2. Proposed reaction mechanism for the electrochemical CO_2 reduction by **RuP** in the presence of the weak Brønsted acid, H_2O. Reduced ligands are highlighted with pale blue.

The effect of the phosphine donor was further confirmed by electrochemical measurements in a non-coordinating solvent, γ-butyrolactone. The CV of **RuP** under Ar exhibits irreversible reduction waves at E_{pc} = −1.64 and −1.81 V (Fig. S13a). Upon addition of MeCN to the solution, these waves gradually disappeared, and one quasi-reversible wave was observed at $E_{1/2}$ = −1.75 V (Fig. S13b). In contrast, the CVs of **RuN** did not change upon the addition of MeCN (Fig. S14). These observations suggest that the MeCN ligand easily dissociates from the Ru centre after the first one-electron reduction step in the case of **RuP**. Moreover, under CO_2, the first reduction wave of **RuN** remained unchanged (Fig. S15a), whereas the reduction wave of **RuP** was positively shifted to E_{pc} = −1.55 V (Fig. S15b), supporting the idea that CO_2 can easily bind **RuP**$^-$. These results are fully consistent with the consideration that phosphine donor of **RuP** contributes to the destabilization of the Ru- N(MeCN) bond via σ-donation and the stabilization of the Ru-C($CO_2{}^{\bullet-}$) bond via π-back donation.

Based on these results, we propose a plausible reaction mechanism of CO_2 reduction catalysed by **RuP** as depicted in

Scheme 2. First, a one-electron reduction of **RuP** occurs at the tpy ligand, and the ligand exchange between the MeCN ligand and CO_2 then proceeds (EC mechanism); simultaneous intramolecular electron transfer from the tpy moiety to the coordinated CO_2 affords the key catalytic intermediate, $[Ru^{II}(tpy)(pqn)(CO_2^{\bullet-})]^+$ ($\mathbf{RuP_{CO_2}}^-$). This charge redistribution enables a further one-electron accommodation on the tpy moiety of $\mathbf{RuP_{CO_2}}^-$ to generate $[Ru^{II}(tpy^-)(pqn)(CO_2^{\bullet-})]^0$ ($\mathbf{RuP_{CO_2}}^{2-}$).[5e] This consideration was supported by DFT calculations on $\mathbf{RuP_{CO_2}}^-$, which indicated that the LUMO is mainly located on the tpy ligand (Fig. S12). It should be noted that the further reduction of $\mathbf{RuP_{CO_2}}^{2-}$ cannot proceed under anhydrous conditions. However, in the presence of H_2O, a protonation reaction occurs to produce the hydroxycarbonyl intermediate, $[Ru^{II}(tpy^-)(pqn)(CO_2H)]^+$. Further protonation and dehydration of $[Ru^{II}(tpy^-)(pqn)(CO_2H)]^+$ afford the CO-coordinated species, $[Ru^{II}(tpy)(pqn)(CO)]^{2+}$.[4d,5c] The obtained $[Ru^{II}(tpy)(pqn)(CO)]^{2+}$ is easily reduced at a given potential,[13] the subsequent ligand exchange between the coordinated CO and CO_2 regenerates $\mathbf{RuP_{CO_2}}^-$, and CO is obtained as the major product of the catalytic reaction.

In summary, we have shown that **RuP** can promote electrocatalytic CO_2 reduction to produce CO with a low-overpotential. The results of electrochemical and spectro-electrochemical measurements and quantum chemical calculations suggested that the phosphine donor destabilizes the bond between the Ru centre and the nitrogen atom of the MeCN ligand via σ-donation (*trans* influence) and stabilizes the bond between the Ru centre and the carbon atom of the coordinated CO_2 molecule via π-back donation. As a result, **RuP** can react with CO_2 upon one-electron reduction to form the key intermediate, $[Ru^{II}(tpy)(pqn)(CO_2^{\bullet-})]^+$ ($\mathbf{RuP_{CO_2}}^-$), via an EC mechanism. Recently, Ott *et al.*, also reported that the catalyst that can undergo EC reaction can promote CO_2 reduction at a low overpotential.[5e] In their study, the steric effect of the bulky substituents embedded in the ligand is the key to induce the EC reaction.[5f] It is also reported that the introduction of cationic substituents,[14a] and the addition of Lewis acid[14b] can reduce the overpotentials. In the current study, a simple introduction of a phosphine moiety to the ligand largely affect the reactivity of the Ru centre, which collectively allow **RuP** to reduce CO_2 with low overpotentials. The present work provides a novel versatile strategy to reduce the overpotential of molecular catalysts for CO_2 reduction, which is possibly applicable to a wide variety of catalytic systems.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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