Research paper

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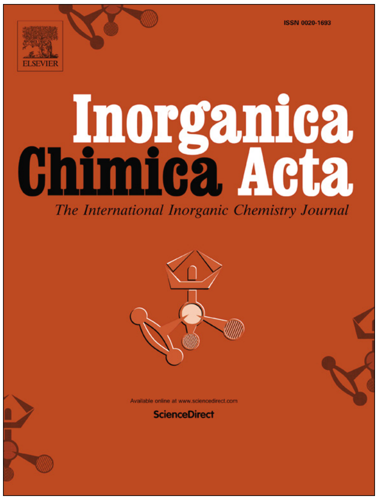

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Electrocatalytic CO_2 reduction using rhenium(I) complexes with modified 2-(2´-pyridyl)imidazole ligands

Soumalya Sinha,[a] Ellan K. Berdichevsky,[a] and Jeffrey J. Warren[a,b]*

[a]Simon Fraser University
Department of Chemistry
8888 University Drive
Burnaby BC V5A 1S6
Canada

[b]Canadian Institute for Advanced Research
Azrieli Global Scholars and Bio-Inspired Solar Energy Programs
Toronto, ON M5G 1Z8
Canada

Email: j.warren@sfu.ca

Abstract

The reduction of CO_2 to CO is an ongoing chemical challenge of great interest for the development of renewable and sustainable technologies. Coordination complexes of rhenium(I) are widely known as CO_2 reduction electrocatalysts, with emphasis on complexes bearing 2,2´-bipyridine (bpy) ligands. Recent research efforts have focused on incorporation of these catalysts into solid, electroactive supports, which can be challenging due to the requirement for synthetic modification to bpy ligands. Development of related ligand sets with modular syntheses is therefore an attractive goal. We investigated electrocatalytic CO_2 reduction using $ReCl(CO)_3$(N-N) complexes, where N-N is 2-(2´-pyridyl)imidazole (PyIm), 2-(2´-pyridyl)benzimidazole (PyBIm), 2-(2´-quinolyl)imidazole (QuIm), or 2-(2´-quinolyl)benzimidazole (QuBIm) ligands. In CO_2-saturated MeCN solutions, cyclic voltammograms of the Re-QuBIm complex showed current enhancement at a peak potential of –2.01 V vs. $Cp_2Fe^{+/0}$. The catalytic current was stable upon repeated cycling. Re-QuBim has an overpotential ~ 200 mV lower than related Re-bpy catalysts, but also is kinetically slower. The redox reactivity of each complex can be correlated to electronic parameters of the N-N chelating ligands. These results suggest that modular reduction potential tuning of CO_2 reduction catalysts is possible, but associated penalties to activity are important considerations.

Keywords: CO_2 reduction, electrocatalysis, ligand design, rhenium

Introduction

The development of catalysts that convert CO_2 value-added products (e.g., synthesis of liquid fuels via Fisher-Tropsch chemistry) is of great interest for sustainable chemistries. There are several approaches to utilizing CO_2, including the $2e^-$ reduction of CO_2 to CO (equation 1) using photochemical[1,2] or electrochemical catalysts,[3,4,5] or copolymerization,[6] to name a few. Homogeneous electrocatalysts have been extensively explored, including metal-2,2´-bipyridyl-based compounds,[4,7,8,9] porphyrinoid compounds,[10,11] metal carbene compounds,[12,13,14,15] and metal carbonyl compounds.[16] However, exploration of, and improvements to, catalyst design are still important goals. In addition, incorporation of molecular catalysts into materials also is an ongoing challenge.[17,18,19] Herein, we explore the electrochemical reduction of CO_2 using a series of molecular Re complexes bearing ligands derived from 2-(2´-pyridyl)imidazole as modular alternatives to bipyridyl ligands.

$$CO_2 + 2e^- + 2H^+ \rightarrow CO + H_2O \qquad (1)$$

Electrochemical reduction of CO_2 by ligand bidentate rhenium coordination complexes is well established.[7] For example, $ReX(CO)_3(bpy\text{-}R)$ ($X = Cl^-$, $CF_3SO_3^-$, bpy = 2,2´-bipyridyl, R = H, Me, CO_2H, ^tBu, OMe at the 4,4´positions of bpy) complexes have been extensively studied.[7,8] Investigation of electrochemical CO_2 reduction using these compounds showed that the onset of catalytic currents is correlated to the electronic properties of the ligands. The most active catalyst, with 4,4´-^{t}Bu-bpy as the N-N chelating ligand, showed impressive catalytic activity, but at more negative potentials than other complexes due to the electron donating ability of the *tert*-butyl group.[8]

Taking inspiration from the above work, others demonstrated that non-covalent[17,18] or covalent[19] immobilization of Re-diimine catalysts offers another strategy for investigating, and perhaps improving, their electrochemical CO_2 reduction properties. In all cases, spectroscopic data demonstrates that the molecular structures of the catalysts are intact. Electrochemical measurements show that the materials are active for electrochemical reduction of CO_2 to CO and H_2O. While these approaches show promise, synthetic modifications to the bipyridyl or phenanthroline ligands can be time consuming or involve low yielding and/or multistep reactions. In contrast, derivatives of 2-(2´-pyridyl)imidazole and 2-(2´-pyridyl)benzimidazole can be synthesized in one step and as such are widely used as N-N chelating ligands, analogous in many ways to bipyridine. Notable examples of relevance here include coordination complexes of metal ions such as Re(I), Ru(II), and Pt(II).[20,21,22,23] The externally directed NH group of imidazole ring can be readily modified (e.g., via *N*-alkylation[20,21]) in order to introduce new functional groups for attachment to other redox moieties, to photosensitizers, and/or to surfaces. Here, we explore the electrochemical CO_2 reduction activity of Re complexes of four ligands without modification to imidazole-NH: 2-(2´-pyridyl)imidazole (PyIm), 2-(2´-pyridyl)benzimidazole (PyBIm), 2-(2´-quinolyl)imidazole (QuIm), and 2-(2´-quinolyl)benzimidazole (QuBIm) (Figure 1).

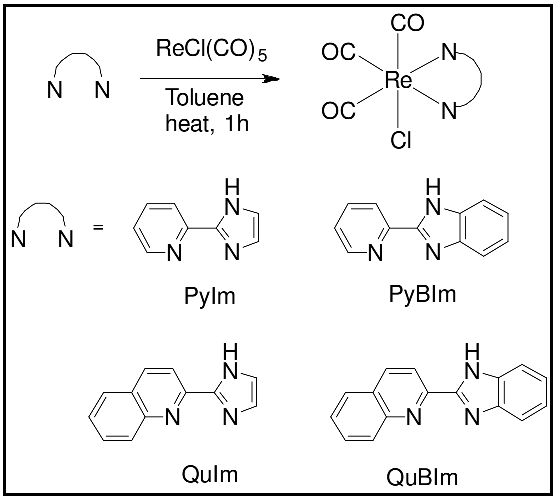

Figure 1. The chemical structures of PyIm, PyBIm, QuIm, QuBIm ligands and their corresponding Re-complexes.

Materials and methods

All reagents were purchased from Sigma-Aldrich unless otherwise noted and used without further purification. Chemicals obtained from other sources are as follows: 2-quinolinecarboxyaldehyde (TCI), *o*-phenylenediamine (Fisher), and $ReCl(CO)_5$ (Strem). Gases were obtained from Praxair Canada. ^1H NMR were recorded on a Bruker Ultrashield Plus 400 or 500 MHz instruments and ^{13}C NMR were recorded on a Bruker AVANCE II 600 MHz instruments equipped with a 5 mm QNP cryoprobe. Solvent residual signals ($CDCl_3$ and DMSO-d_6) used as references.[24] Mass spectrometry experiments were carried out using a Bruker microTOF instrument equipped with an electrospray ionization source. UV-visible spectra were recorded in MeCN solvent using a Cary100Bio UV-Vis spectrophotometer. All emission spectra and lifetime measurements were recorded in deoxygenated MeCN solution using a Fluorolog Jobin Yvon fluorometer with time-resolved single photon counting capability (TBX picosecond detector). The detector rise time is 1.0 ns and the LED (335 nm) pulse width is 1.4 ns. IR spectra were recorded on Thermo Nicolet NEXUS 670 FT-IR.

Basal plane graphite electrodes were prepared according to the literature.[25] Pyrolytic graphite was from www.graphitestore.com, Loctite Hysol 9460 epoxy was obtained from McMaster-Carr, and silver paint was from SPI Supplies. Electrochemical measurements were performed on a Gamry Instruments Interface1000 potentiostat, using a conventional three-electrode cell with a basal plane graphite working electrode (3 mm by 3 mm surface area), Pt wire counter electrode, and non-aqueous Ag/0.01M $AgNO_3$ in MeCN reference electrode (CH Instruments). The working electrode surfaces were prepared by lightly abrading with 4000 SiC paper, washing thoroughly with deionized water, followed by sonication (120 s) in isopropyl alcohol, and briefly drying with a heat gun. Ferrocene was used as an external standard for all electrochemical experiments and all potentials are reported with respect to the ferrocenium-ferrocene couple ($Cp_2Fe^{+/0}$). All Re-complexes or ligands were dissolved (1mM final concentration) in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte and were purged with argon or CO_2 before CVs were taken.

Ligand Syntheses. PyIm[26] and **QuIm**.[27] An ice-cold solution of the appropriate aldehyde (2-pyridinecarboxyaldehyde (4.668 mmol) or 2-quinolinecarboxyaldehyde (3.181 mmol) in 5 mL ethanol was added to an ice-cold solution of 40% aqueous glyoxal (0.2 mL) in 5 mL ethanol, and then ice-cold concentrated aqueous NH_4OH solution (0.15 mL) was added immediately. This solution was stirred at 0°C for 1 h, warmed to room temperature, and stirred for an additional 5 h. The solvent was removed under reduced pressure, and the resulting solution was extracted several times with diethyl ether. The combined organic extracts were evaporated under reduced pressure and crystalline solids were obtained upon recrystallization with diethyl ether.

PyIm. Pale yellow solid. Yield: 41%. ^1H NMR (400MHz, $CDCl_3$): δ (ppm) 11.7 (s, 1H) 8.51 (ddd, 1H, 4.9, 1.8, 1.0 Hz), 8.24 (dt, 1H, 8.0, 1.1 Hz), 7.80 (td, 1H, 7.8 1.7 Hz), 7.26 (ddd, 1H, 7.6, 4.9, 1.2 Hz), 7.17 (br s, 2H).

QuIm. Brown solid. Yield: 52%. ^1H NMR (400MHz, $CDCl_3$): δ (ppm) 11.13 (s, 1H) 8.35 (d, 1H, 8.6 Hz), 8.25 (d, 1H, 8.6 Hz), 8.02 (d, 1H, 8.6 Hz), 7.84 (d, 1H, 8.4 Hz), 7.70 (td, 1H, 7.6, 1.1 Hz), 7.53 (td, 1H, 7.6, 1.1 Hz), 7.31 (s, 1H), 7.19 (s, 1H).

PyBIm and **QuBIm.**[28] To a mixture of *o*-phenylenediamine (4.62 mmol for PyBIm and 1.59mmol for QuBIm) and 2-pyridinecarboxyaldehyde (4.62 mmol) or 2-quinolinecarboxyaldehyde (1.59mmol) in 5 mL of ethanol was added NH_4Cl (0.075g). In both cases, the resulting solution was stirred for 4h at 80°C. The reaction mixture was then poured into ice-cold water and the product was precipitated as a yellow solid. The solids were filtered and washed with water thoroughly and dried.

PyBIm. Off-white solid. Yield: 78%. ^1H NMR (400MHz, $CDCl_3$): δ (ppm) 10.76 (s, 1H), 8.66 (ddd, 1H, 4.8, 1.7, 0.9 Hz,), 8.46 (dt, 1H, 7.9, 1.1 Hz), 7.89 (td, 1H, 7.7, 1.7 Hz), 7.88 (br, 1H) 7.50 (br, 1H), 7.39 (ddd, 1H, 7.6, 4.8, 1.2 Hz), 7.33 (m, 2H).

QuBIm. Pale yellow solid. Yield: 86%. ^1H NMR (400MHz, $CDCl_3$): δ (ppm); 10.96 (s, 1H), 8.59 (d, 1H, 8.5 Hz), 8.34 (d, 1H, 8.7 Hz), 8.14 (d, 1H, 8.7 Hz), 7.91 (m, 1H), 7.90 (d, 1H, 8.7 Hz) 7.78 (ddd, 1H, 8.5, 6.8, 1.5 Hz), 7.60 (ddd, 1H, 8.1, 6.8, 1.2 Hz), 7.50 (m, 1H), 7.33 (m, 2H).

General synthetic procedure for $ReCl(CO)_3$(N-N) complexes. $ReCl(CO)_5$ and a requisite N-N ligand were dissolved in a 1:1 molar ratio in 50 mL of hot toluene and the reaction mixture was stirred at reflux for 1 hour, after which the mixture was allowed to cool to room temperature. A yellow precipitate formed during cooling.[8,29] Storing this solution at –20°C for an additional 1 hour promoted further precipitation. The mixture was then filtered and washed with cold toluene. Note that the numbering system for each ring is given with the NMR spectra shown in the Supporting Information. $ReCl(CO)_3(4,4'\text{-}^t\text{Bu-bpy})$ was prepared and characterized according to the literature.[8]

Re-PyIm.[20] Pale yellow solid. Yield: 92%. ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 14.28 (s, br, 1H, imidazole-N*H*) 8.91 (dt, 1H, 5.5, 1.3 Hz, H4), 8.28 (m, 2H, H1 and H2), 7.70 (d, 1H, 1.4 Hz, H5/H6), 7.63 (ddd, 1H, 7.4, 5.5, 2.0 Hz, H3), 7.51 (d, 1H, 1.4 Hz, H5/H6); ^{13}C NMR (600 MHz, DMSO-d_6): δ (ppm) 197.85, 197.40, 189.88, 153.27, 148.37, 146.88, 140.43, 130.48, 126.27, 121.98, 121.25. λ_{max}/nm (ε/$M^{-1}cm^{-1}$): 265 (10564), 302 (12115). IR (CH_3CN) υ(CO) (cm^{-1}): 2017, 1909, 1886. ESI-MS(+): 416.009 (M^+), 444.015 (M^+ + CO), 457.035 (M^+ + CH_3CN).

Re-PyBIm.[22] Pale yellow solid. Yield: 89%. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ (ppm) 9.04 (d, 1H, 5.3 Hz, H4), 8.51 (d, 1H, 7.5 Hz, H1), 8.37 (td, 1H, 7.8, 1.5 Hz, H2), 7.86-7.72 (m, 3H, H5, H8, and H3), 7.54-7.48 (m, 2H, H6 and H7); ^{13}C NMR (600 MHz, DMSO-d$_6$): δ (ppm) 198.37, 197.88, 189.68, 154.67, 153.66, 147.82, 141.34, 140.53, 135.69, 127.49, 125.12, 124.47, 123.27, 117.23, 114.48. λ_{max}/nm (ε/M^{-1}cm^{-1}): 321(14127), 333 (14127). IR (CH_3CN) υ(CO) (cm^{-1}): 2019, 1907, 1893. ESI-MS(+): 466.025 (M^+), 494.032 (M^+ + CO), 507.052 (M^+ + CH_3CN).

Re-QuIm. Brown solid. Yield: 81%. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ (ppm) 14.54 (s, 1H, imidazole-N*H*), 8.92 (d, 1H, 8.7 Hz, H2), 8.65 (dd, 1H, 8.7, 0.7 Hz, H3), 8.40 (d, 1H, 8.3, 1.4 Hz, H1), 8.21 (dd, 1H, 8.2, 1.5 Hz, H6), 8.11 (ddd, 1H, 8.7, 6.9, 1.5 Hz, H4), 7.85 (ddd, 1H, 8.0, 6.9, 1.0, H5), 7.82 (d, 1H, 1.4 Hz, H7/H8), 7.68 (d, 1H, 1.4 Hz, H7/H8); ^{13}C NMR (600 MHz, DMSO-d$_6$): δ (ppm) 198.53, 196.54, 189.73, 149.75, 149.21, 146.42, 141.62, 132.90, 131.20, 129.52, 128.61, 128.51, 128.18, 122.85, 118.14. λ_{max}/nm (ε/M^{-1}cm^{-1}): 283 (17181), 347 (11299). IR (CH_3CN) υ(CO) (cm^{-1}): 2017, 1909, 1887. ESI-MS(+): 466.025 (M^+), 494.031 (M^+ + CO), 507.052 (M^+ + CH_3CN).

Re-QuBIm. Orange solid. Yield: 83%. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ (ppm) 15.0 (s, br, 1H, imidazole-N*H*) 9.05 (d, 1H, 8.5 Hz, H2), 8.77 (d, 1H, 8.8 Hz, H3), 8.62 (d, 1H, 8.5 Hz, H1), 8.29 (d, 1H, 8.2 Hz, H6), 8.19 (ddd, 1H, 8.7, 6.9, 1.5 Hz, H4), 7.99 – 7.89 (m, 3H, H5 and BIm-*H*), 7.64 – 7.59 (m, 2H, BIm-*H*). Note that BIm-H indicates the protons (H_7 – H_{10}) from benzimidazole ring (see Supporting Information). ^{13}C NMR (600 MHz, DMSO-d$_6$): δ (ppm) 198.13, 197.22, 189.37, 155.01, 149.65, 146.80, 141.99, 141.39, 134.11, 133.35, 129.68, 129.31, 128.92, 128.82. 126.31, 125.42, 119.51, 117.71, 114.00. λ_{max}/nm (ε/M^{-1}cm^{-1}): 250 (22123), 297 (11084), 364 (14657). IR (CH_3CN) υ(CO) (cm^{-1}): 2017, 1905, 1891. ESI-MS(+): 516.041 (M^+), 544.047 (M^+ + CO), 557.068 (M^+ + CH_3CN).

Result

Synthesis and Characterization. Each of the N-N chelating ligands was synthesized in moderate to good yields in a single step from commercially available starting materials. In all cases, ^{1}H NMR characterization data matched those reported in the literature. The corresponding $ReCl(CO)_3$(N-N) complexes were synthesized from a 1:1 mixture of ligand and $ReCl(CO)_5$ in refluxing toluene and were isolated in good yields. NMR (^{1}H and ^{13}C) spectra are presented in the Supporting Information. Of note is a downfield resonance (ca. 10-14 ppm) in most ^{1}H NMR spectra that is attributed to the imidazole or benzimidazole N*H*.

The electronic absorption and the emission spectra (λ_{ex} = 375 nm) for each complex in MeCN solvent are shown in Figures 2 and 3, respectively. In all absorption spectra, characteristic dπ-π* (MLCT) and π-π* transitions are observed. In analogy to the related bpy compounds,[29] the broad bands extending to ~400 nm (Re-PyIm and Re-PyBIm) and ~450 nm (Re-QuIm and Re-QuBIm) are attributed to the MLCT transitions, with $\varepsilon \sim 10^3$ M^{-1} cm^{-1}. The higher energy, sharper and more intense features, arise from intraligand transitions. For reference, spectra for each of the ligands are shown in the Supporting Information.

All four complexes also are luminescent, with $\lambda_{em, max}$ between 550 and 650 nm at 295 K. At the same concentrations, Re-PyIm and Re-PyBIm appear (qualitatively) more luminescent than Re-QuIm and ReQuBIm. Both the weak intensity and the band position of the Re-quinolyl complexes are similar to those reported for $ReCl(CO)_3$(2,2´-biquinoline).[29] The luminescence lifetimes (τ) in deoxygenated MeCN are: 3.5 μs (Re-PyIm), 3.3 μs (Re-PyBIm), 2.7 μs (Re-QuIm), and 5.6 μs (Re-QuBIm). These values also are in accord with those reported for related bipyridyl complexes[29,30,31]

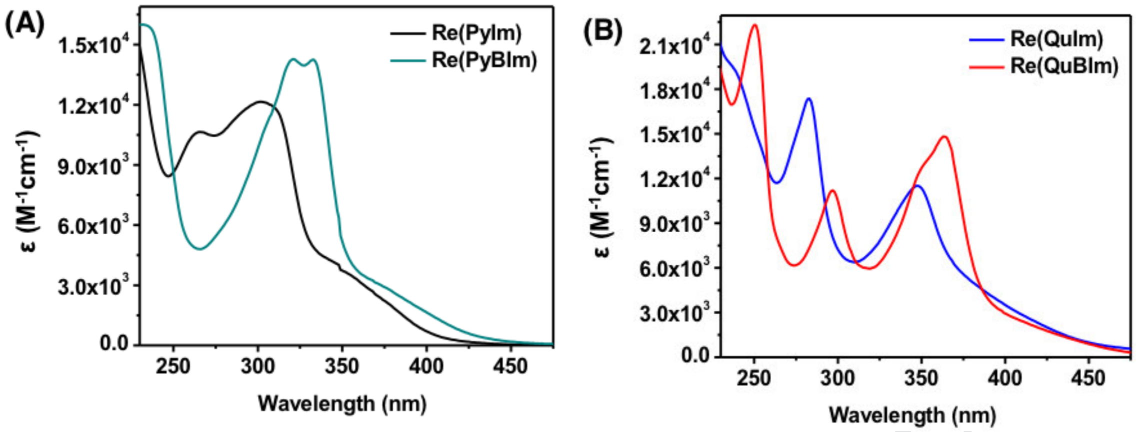

Figure 2. Electronic absorption spectra for Re-PyIm, Re-PyBIm (A), Re-QuIm, and Re-QuBIm (B) in MeCN.

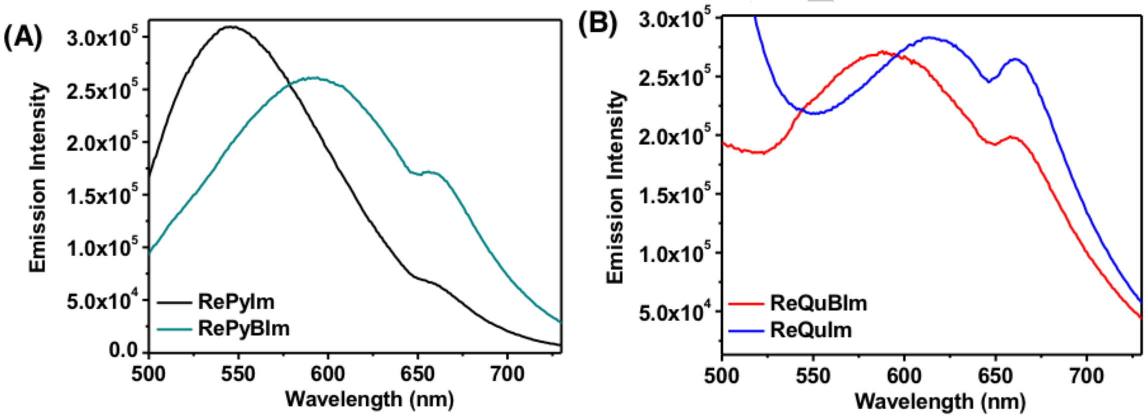

Figure 3. Emission spectra (λ_{ex} = 375 nm) for Re-PyIm, Re-PyBIm (A), Re-QuIm, and Re-QuBIm (B) in deoxygenated MeCN.

The carbonyl infrared spectra for each Re-complex are given in the Supporting Information and the band positions for the three observed carbonyl stretches are set out in Table 1. The bands are consistent with the pseudo-C_s symmetry about Re, and are similar to those reported for the same or related complexes (e.g., Re-PyBIm recorded in the solid state[22] and the *N*-ethyl analog of Re-PyBIm recorded in KBr[32]). Also shown in Table 1 are characteristic data for related 2,2´-bipyridyl derivatives for comparison.[8] The slightly lower IR stretching frequencies for Re-PyIm, Re-PyBIm, Re-QuIm, and Re-QuBIm are in qualitative agreement with the differences in electronic properties of imidazole-containing ligands versus bpy ligands (e.g., PyIm is a somewhat weaker π-acceptor[33]), that results in greater electron density on the metal.

Table 1. Carbonyl IR stretching frequencies for $ReCl(CO)_3(N\text{-}N)$ compounds[a]

bpy[8]	^{t}Bubpy[8]	$bpyCO_2H$[8]	PyIm	PyBIm	QuIm	QuBIm
2025	2023	2037	2017	2019	2017	2017
1918	1916	1935	1909	1907	1909	1905
1902	1898	1911	1886	1893	1887	1891

[a] bpy = 2,2´-bipyridyl, ^{t}Bubpy = 4,4´-*tert*-butyl-2,2´-bipyridyl, $bpyCO_2H$ = 4,4´-dicarboxylicacid-2,2´-bipyridyl. Data for all complexes collected in MeCN solvent.

Electrochemical behavior under inert atmosphere. Electrochemical studies of the series of Re-complexes (1 mM) were carried out in MeCN solution with 0.1 M $^nBu_4NPF_6$ supporting electrolyte. The working electrode was basal plane graphite and potentials are reported with respect to $Cp_2Fe^{+/0}$. Other experimental details are given above. In argon saturated solution, Re-PyIm and Re-QuIm show one irreversible reduction wave at –1.74 and –1.72 V (peak potentials), respectively. RePyBIm and Re-QuBIm each show two irreversible waves. The first irreversible wave appears at –1.74 and –1.57 V, respectively followed by an additional wave at –2.20 and –2.01V, respectively. Oxidative scans also showed irreversible waves. All observed peak potentials are summarized in Table 2. The potentials measured for Re-PyBIm are close to those reported in MeCN solvent in two independent reports of the electrochemical properties of the closely related *N*-methyl-PyBIm Re complex (–1.83, –2.27, 0.88 V[34] and –1.79, –2.14, 0.87 V,[35] respectively; potentials are versus $Cp_2Fe^{+/0}$).

Table 2. Peak reduction potentials (in MeCN versus $Cp_2Fe^{+/0}$) for Re-complexes under Ar

Compound	E_{red}^1 (V)	E_{red}^2 (V)	E_{ox} (V)
Re-PyIm	–1.74	--	0.93
Re-PyBIm	–1.74	–2.20	0.96
Re-QuIm	–1.72	--	0.98
Re-QuBIm	–1.57	–2.01	0.95

Electrochemical behavior under CO_2. Cyclic voltammograms for all four complexes were collected in CO_2-saturated MeCN solution. The addition of CO_2 reproducibly shifted the reduction peak potential to –2.05 V for Re-PyIm, but did not increase the intensity. Addition of methanol, as a proton source, also did not affect the peak position or current. The origin of this unusual behavior is not yet known. In the case of Re-PyBIm, ≤5% current enhancement at the second reduction peak (–2.24 V) is observed under CO_2. A steeply rising wave is observed for this complex, but it is convoluted with signal from the electrochemical window. Addition of MeOH has no effect on the observed currents.

The two quinolyl-containing complexes (Re-QuIm and Re-QuBIm) were more active for reduction of CO_2. CVs collected under CO_2 atmosphere for ReQuIm showed current enhancement (160 μA cm^{-2} to 630 μA cm^{-2} at –2.24 V) after the first reduction wave (Figure 4). The response is near the limit of the electrochemical window, but is not attributable to background alone. Re-QuBIm also is active for CO_2 reduction, exhibiting 2-fold current enhancement (285 μA cm^{-2} to 560 μA cm^{-2} at –2.01 V) at the second reduction potential in the presence of CO_2 (Figure 4). In controlled potential experiments under CO_2 atmosphere, Re-QuBIm remains active with –2 V applied potential for about 40 minutes (see Supporting Information). Furthermore, with the addition of 1M MeOH, the reduction potential shifted by about 20mV anodically with the negligible change in current intensity. For reference, CVs of ligands alone (under Ar and under CO_2) are presented in the Supporting Information. Addition of CO_2 causes negligible increases in current upon ligand reduction.

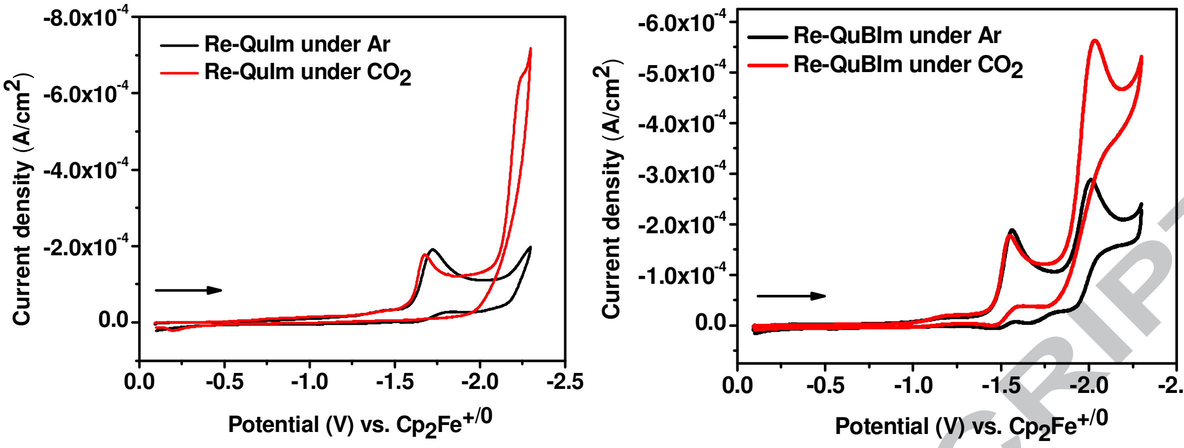

Figure 4. Cyclic voltammograms for 1mM Re-QuIm (left) and Re-QuBIm (right) under Ar (black) and CO_2 (red) saturated 0.1M $^{n}Bu_4NPF_6$ MeCN solution at 100 mV/sec scan rate. The arrow indicates the scan direction.

Discussion and Conclusions

Modifications of the 2-(2´-pyridyl)imidazole (PyIm) backbone provide a facile approach for tuning the electronic properties of transition metal complexes. Here, we investigated the spectroscopic properties and CO_2 reduction behavior of four Re(I) complexes of the general form $ReCl(CO)_3$(N-N) (N-N = 2-(2´-pyridyl)imidazole (PyIm), 2-(2´-pyridyl)benzimidazole (PyBIm), 2-(2´-quinolyl)imidazole (QuIm), and 2-(2´-quinolyl)benzimidazole (QuBIm)). Each of the complexes displays properties consistent with related coordination complexes bearing a *fac*-$Re(CO)_3$ core, including IR features and luminescence. As for 2,2´-bipyridyl derived Re complexes, the four complexes described in this work also have reduction potentials at > 1V ($Re^{II/I}$) and < –1 V (ligand-centered reduction). As for related Re[29] and Ru[36] pyridyl complexes, coordination of the ligand to a metal shifts the ligand-centered reduction to potentials more positive than the ligand alone (see Supporting Information).

Lever's parameterization of ligand properties and metal complex reduction potentials[37,38] offers one way in which to rationalize the electrochemical behavior of our four Re complexes. The parameters (E_L) are: 0.12 (imidazole), 0.17 (bibenzimidazole), 0.25 (pyridine), and 0.29

(biquinoline). Note that values are not known individually for benzimidazole and quinolone, but E_L values are given for each coordinating atom (i.e., ΣE_L for biquinoline is 2•0.17). Bearing this in mind, the ΣE_L values for PyIm, PyBIm, QuIm, and QuBIm are 0.37, 0.42, 0.41, and 0.46, respectively. For comparison, ΣE_L for 4,4´-dimethly-2,2´-bipyridine is 0.46;[37] values for the *tert*-butyl analog are not reported. The E_L values for CO and Cl^- are 0.99 and –0.24, respectively. Larger E_L values are correlated to higher $Re^{II/I}$ potentials. In theory, this also should qualitatively correspond to higher (less negative) $Re^{I/0}$ potentials. Here, this would correspond to potentials at which CO_2 is reduced, since input of two electrons (ligand + Re reduction) is required for catalysis. The calculated $Re^{II/I}$ couples are 0.78, 0.81, 0.81, and 0.84 V versus $Cp_2Fe^{+/0}$. Note that Lever's approach gives values with respect to NHE, which we converted using known parameters.[39] The calculated values do not quantitatively reproduce the observed peak potentials, as expected for irreversible waves. However, the trend in $E_{p,c}$ is in agreement with the calculation and indicates that the potentials of Re-based CO_2 reduction catalysts can be rationally tuned with ligands other than bpy.

The ability of each ligand to support radical anion character (non-innocence) increases with increasing aromatic ring size. We do not observe reduction of the PyIm ligand itself, and the corresponding Re complex has the most negative potential (Table 2). The slightly larger. aromatic system in PyBIm supports some additional catalytic activity. In contrast, the QuBIm ligand has the highest reduction potential ($QuBIm^{0/-}$, see Supporting Information), as does the corresponding Re complex. Re-QuIm also exhibits catalytic activity. These data demonstrate that that the ability of a system to accept $2e^-$ is an important feature for molecular catalysis in these complexes. Similar behavior is observed for related Re and porphyrin CO_2 reduction catalysts.[3,5,7] We note that it was recently demonstrated that ligand non-innocence is not a requirement for metal-mediated CO$_2$ reduction,[16] but complexes that are able to accept multiple reducing equivalents are generally superior catalysts, exhibiting lower overpotentials and more rapid turnover frequencies.[10,11]

The activity of Re-QuBIm is interesting to compare to that of ReCl(CO)$_3$(4,4´-^{t}Bu-bpy)[8] under similar reaction conditions. The overall electrochemical properties (based on Lever's parameters) are similar, but the activities are different. Re-QuBIm has current onset for CO$_2$ reduction at potentials about 200 mV more positive than ReCl(CO)$_3$(4,4´-^{t}Bu-bpy). This is a notable shift in onset potential, but the overpotential (η) for CO$_2$ reduction by Re-QuBIm is still high.[40] However, analysis of the peak current response[41] for Re-QuBIm (or Re-QuIm) shows CO$_2$ reduction kinetics, with a rate constant of about 5 M^{-1} s^{-1}. [42] Note that our rate constant is approximate due to the irreversibility of the CV response in the absence of CO$_2$. This value is almost 10^3-fold more sluggish than reported for ReCl(CO)$_3$(4,4´-^{t}Bu-bpy).[8] We were surprised by this large difference in activity for such similar compounds, so we collected CVs of ReCl(CO)$_3$(4,4´-^{t}Bu-bpy) under CO$_2$ using experimental conditions identical to those we used for Re-QuIm and Re-QuBIm (see Supporting Information). Based on a comparison the intensity of the catalytic waves, Re-QuIm and Re-QuBIm are only ca. 15 times more sluggish CO$_2$ reduction catalysts than ReCl(CO)$_3$(4,4´-^{t}Bu-bpy). We conclude that the ~200 mV decrease in overpotential is coupled to modest losses in CO$_2$ reduction kinetics.

In sum, we synthesized, characterized, and investigated the electrochemical reduction of CO$_2$ using four *fac*-Re(CO)$_3$ complexes with N-N chelating ligands derived from 2-(2´-pyridyl)imidazole. The modular framework that comprises the four N-N chelating ligands (PyIm, PyBIm, QuIm, and QuBIm) allows for the electronic properties of the complex to be tuned and for catalytic overpotentials to be consequently altered, although our results suggest that there can be a cost with respect to CO_2 reduction kinetics. Re-QuBIm, with the largest aromatic system, showed good catalytic activity at a peak potential of –2.01V versus $Cp_2Fe^{+/0}$. Conversely, the complex with the smallest aromatic system, Re-PyIm, showed the least catalytic activity under the identical electrochemical conditions. In ongoing work, we are investigating methods of covalent[43,44] and non-covalent[17] attachment of these catalysts to carbon electrodes via the external imidazole-NH.

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References

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1. A. J. Morris, G. J. Meyer, E. Fujita. Acc. Chem. Res. 42 (2009) 1983.
2. B. Kumar, M. Llorente, J. Froehlich, T. Dang, A. Sathrum, C. P. Kubiak. Annu. Rev. Phys. Chem. 63 (2012) 541.
3. J.-M. Savéant. Chem. Rev. 108 (2008) 2348.
4. E. E. Benson, C. P. Kubiak, A. J. Sathrum, J. M. Smieja. Chem. Soc. Rev. 38 (2009) 89.
5. C. Costentin, M. Robert, J.-M. Savéant. Chem. Soc. Rev. 42 (2013) 2423.
6. D. J. Darensbourg. Inorg. Chem. 49 (2010) 10765.
7. K. A. Grice, C. P. Kubiak. *In Adv. Inorg. Chem.* Volume 66: CO2 Chemistry. *Edited by* A. Michele, R. van Eldik. Academic Press, 2014. pp. 163-188.

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8. J. M. Smieja, C. P. Kubiak. Inorg. Chem. 49 (2010) 9283.
9. J. M. Smieja, M. D. Sampson, K. A. Grice, E. E. Benson, J. D. Froehlich, C. P. Kubiak. Inorg. Chem. 52 (2013) 2484.
10. C. Costentin, M. Robert, J.-M. Savéant. Acc. Chem. Res. 48 (2015) 2996.
11. C. Costentin, S. Drouet, M. Robert, J.-M. Savéant. Science. 338 (2012) 90.
12. J. A. Therrien, M. O. Wolf, B. O. Patrick. Inorg. Chem. 53 (2014) 12962.
13. C. J. Stanton, C. W. Machan, J. E. Vandezande, T. Jin, G. F. Majetich, H. F. Schaefer, C. P. Kubiak, G. Li, J. Agarwal. Inorg. Chem. 55 (2016) 3136.
14. N. P. Liyanage, H. A. Dulaney, A. J. Huckaba, J. W. Jurss, J. H. Delcamp. Inorg. Chem. 55 (2016) 6085.
15. J. Agarwal, T. W. Shaw, C. J. Stanton, G. F. Majetich, A. B. Bocarsly, H. F. Schaefer. Angew. Chem. Int. Ed. 53 (2014) 5152.
16. K. A. Grice, C. Saucedo. Inorg. Chem. (2016) 6240.
17. J. D. Blakemore, A. Gupta, J. J. Warren, B. S. Brunschwig, H. B. Gray. J. Am. Chem. Soc. 135 (2013) 18288.
18. M. E. Louis, T. G. Fenton, J. Rondeau, T. Jin, G. Li. Comment. Inorg. Chem. 36 (2016) 38.
19. S. Oh, J. R. Gallagher, J. T. Miller, Y. Surendranath. J. Am. Chem. Soc. 138 (2016) 1820.
20. M. E. Viguri, Pérez, Julio, L. Riera. Chem. Eur. J. 20 (2014) 5732.
21. N. M. Shavaleev, Z. R. Bell, T. L. Easun, R. Rutkaite, L. Swanson, M. D. Ward. Dalton Trans. (2004) 3678.
22. B.-C. Tzeng, B.-S. Chen, C.-K. Chen, Y.-P. Chang, W.-C. Tzeng, T.-Y. Lin, G.-H. Lee, P.-T. Chou, Y.-J. Fu, A. H.-H. Chang. Inorg. Chem. 50 (2011) 5379.
23. K. M. Lancaster, J. B. Gerken, A. C. Durrell, J. H. Palmer, H. B. Gray. Corrd. Chem. Rev. 254 (2010) 1803.
24. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg. Organometallics. 29 (2010) 2176.
25. J. D. Blakemore, N. D. Schley, D. Balcells, J. F. Hull, G. W. Olack, C. D. Incarvito, O. Eisenstein, G. W. Brudvig, R. H. Crabtree. J. Am. Chem. Soc. 132 (2010) 16017.
26. R. Wang, J.-C. Xiao, B. Twamley, J. M. Shreeve. Org. Biomol. Chem. 5 (2007) 671.
27. A. Wada, Q. Zhang, T. Yasuda, I. Takasu, S. Enomoto, C. Adachi. Chem. Commun. 48 (2012) 5340.

28. D. Kathirvelan, P. Yuvaraj, K. Babu, A. S. Nagarajan, B. S. R. Reddy. Indian J. Chem. B. 52B (2013) 1152.

29. M. Wrighton, D. L. Morse. J. Am. Chem. Soc. 96 (1974) 998.

30. L. Sacksteder, A. P. Zipp, E. A. Brown, J. Streich, J. N. Demas, B. A. Degraff. Inorg. Chem. 29 (1990) 4335.

31. L. Sacksteder, M. Lee, J. N. Demas, B. A. Degraff. J. Am. Chem. Soc. 115 (1993) 8230.

32. K. Wang, L. Huang, L. Gao, L. Jin, C. Huang. Inorg. Chem. 41 (2002) 3353.

33. W. J. Eilbeck, F. Holmes. J. Chem. Soc. A (1967) 1777.

34. A. Albertino, C. Garino, S. Ghiani, R. Gobetto, C. Nervi, L. Salassa, E. Rosenberg, A. Sharmin, G. Viscardi, R. Buscaino, G. Croce, M. Milanesio. J.Organomet. Chem. 692 (2007) 1377.

35. R. Czerwieniec, A. Kapturkiewicz, J. Lipkowski, J. Nowacki. Inorg. Chim. Acta. 358 (2005) 2701.

36. F. Pichot, J. H. Beck, C. M., Elliott, C. M. J. Phys. Chem. A 103 (1999) 6263.

37. A. B. P. Lever. Inorg. Chem. 29 (1990) 1271.

38. A. B. P. Lever. Inorg. Chem. 30 (1991) 1980.

39. V. V. Pavlishchuk, A. W. Addison. Inorg. Chim. Acta. 298 (2000) 97.

40. M. L. Pegis, J. A. S. Roberts, D. J. Wasylenko, E. A. Mader, A. M. Appel, J. M. Mayer. Inorg. Chem. 54 (2015) 11883.

41. J. M. Savéant, E. Vianello. Electrochim. Acta. 8 (1963) 905.

42. The rate constant was calculated using the following equation: $i_c = nFA[cat](Dk[CO_2])^{1/2}$, where i_c is the catalytic peak current, n is the number of electrons (2, in this case), F is Faraday's constant, A is the electrode surface area (0.09 cm^2), [cat] = 1 mM, D is the diffusion coefficient of the catalyst (approximated as 8×10^{-6} cm^2 s^{-1} from Ref. 8), and $[CO_2]$ = 0.25 M (from Ref. 11).

43. A. Devadoss, C. E. D. Chidsey. J. Am. Chem. Soc. 129 (2007) 5370.

44. J. C. Lennox, R. W. Murray. J. Electroanal. Chem. 78 (1977) 395.

Electrocatalytic CO_2 reduction using rhenium(I) complexes with modified 2-(2´-pyridyl)imidazole ligands

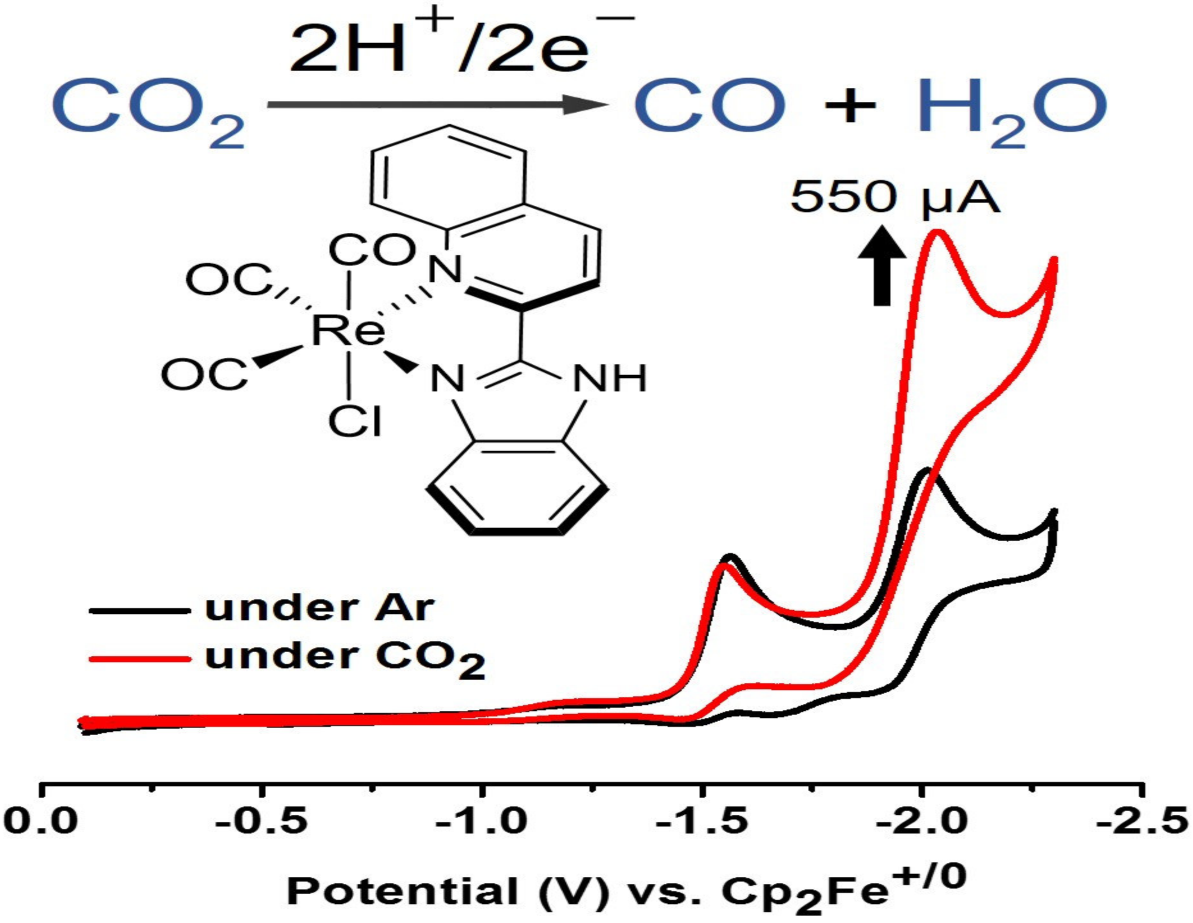
Soumalya Sinha, Ellan K. Berdichevsky, and Jeffrey J. Warren*

Simon Fraser University
Department of Chemistry
8888 University Drive
Burnaby BC V5A 1S6
Canada

Email: j.warren@sfu.ca

Highlights:

- A series of Re(I) coordination complexes with bidentate ligands were prepared.
- Complexes with quinolone-derived ligands are active for electrochemical CO_2 reduction.
- Reactivity can be correlated to ligand electronic properties.


CO2
2H+/2e−
CO + H2O
OC
OC
CO
Re
Cl
N
N
NH
550 μA
under Ar
under CO2
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
Potential (V) vs. Cp2Fe+/0