

Article

A Molecular Ruthenium Electrocatalyst for the Reduction of Carbon Dioxide to CO and Formate

Charles W. Machan, Matthew D. Sampson, and Clifford P. Kubiak

J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.5b03913 • Publication Date (Web): 18 Jun 2015

Downloaded from http://pubs.acs.org on June 21, 2015

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036 Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Page 1 of 24

A Molecular Ruthenium Electrocatalyst for the Reduction of Carbon Dioxide to CO and Formate

Charles W. Machan, Matthew D. Sampson, and Clifford P. Kubiak*

University of California – San Diego, Department of Chemistry and Biochemistry, 9500 Gilman

Drive 0358, La Jolla, CA 92023

* - ckubiak@ucsd.edu

Abstract

The use of a bulky bipyridine ligand, 6,6'-dimesityl-2,2'-bipyridine (mesbpy), to enable the reduction of carbon dioxide by a Ru-based molecular electrocatalyst is reported. Under catalytic conditions, this compound exhibits turnover frequencies of 1300 s⁻¹ and 95% Faradaic efficiency for the production of CO and H₂O from CO₂ in the presence of Brønsted acids. Mechanistic electrochemical and spectroelectrochemical studies, supplemented by the direct synthesis of relevant intermediates, indicate that this behavior is the result of the cooperative redox response of the bipyridine ligand and Ru metal center at negative potentials, as well as the inhibition of Ru–Ru bond formation through steric interactions.

Introduction

The eventual depletion of petrochemical feedstocks and rising levels of carbon dioxide (CO_2) continue to drive interest in the use of CO_2 as a C_1 source for liquid fuels.¹⁻⁶ Electrocatalytic reduction offers a way to close the fuel cycle by using CO_2 in the synthesis of energy-dense molecules.^{1,6} If done using renewable energy sources, this process could enable the storage of electrical energy in chemical bonds in an efficient and recoverable manner. Molecular catalysts have been shown to be active and selective for the electrocatalytic reduction of CO_2 to CO_2 , but often have limited turnover frequencies (TOFs), high overpotentials, and poor stabilities.

Recent progress has been made in benchmarking different catalysts for CO₂ reduction, however this is still a work in progress.⁷⁻¹⁰ To the limited extent to which the rates of molecular electrocatalysts can be compared, the 'state-of-the-art' catalysts reported so far are Re and $Mn(bpy)(CO)_3X$ (bpy = 2,2'-bipyridine, X = halide or a weakly coordinating anion), hydroxyphenyl-substituted Fe porphyrins, and Ni(cyclam)²⁺ (cyclam = 1.4.8.11tetraazacyclotetradecane).¹⁰⁻¹⁴ Generally, molecular Ru-based electrocatalysts have shown much lower activities.^{11,15,16} Under reducing conditions, complexes of the type Ru(bpy)(CO)₂Cl₂ have been shown to polymerize on the cathode through the formation of Ru-Ru bonds.¹⁷⁻¹⁹ The resultant metallopolymer is highly active for the reduction of CO₂ to CO as a heterogeneous catalyst. Our group has shown that the use of a bulky bpy ligand, 6,6'-dimesityl-2,2'-bipyridine (mesbpy, 1), inhibited metal-metal bond formation in the case of Mn tricarbonyl complexes, resulting in catalysts with TOFs in excess of 5000 s⁻¹.¹³ Recently, Kuramochi et al. also reported that the use of the same bulky bpy ligand (**mesbpy**), instead of an unfunctionalized bpy ligand, for complexes of the type Ru(bpy)(CO)₂Cl₂ resulted in the selective photocatalytic production of CO from CO₂²⁰ We reasoned that the use of the **mesbpy** ligand in the context of Ru-based molecular catalysts could have a similar effect on their electrocatalytic properties.

Results

Metallating **mesbpy**²¹ with the Ru(II) carbonyl precursor $[Ru(CO)_2Cl_2]_n^{22}$ (2) in refluxing toluene resulted in the isolation of *trans*-Cl-Ru(mesbpy)(CO)_2Cl_2 (3) as a pale yellow powder (Scheme 1).²⁰ X-ray crystallographic studies on single crystals grown from THF and pentanes show an octahedral coordination geometry around the Ru metal center, with the chloride ligands occupying axial positions, the bpy fully chelated in the equatorial plane, and two CO ligands at the remaining coordination sites (Figure 1, Table S1).^{17,18,20} All other characterization data are

consistent with this assignment. The plane of the bpy is slightly distorted: the N–C–C–N dihedral angle is 16.9(4)°. Scheme 1. Synthesis of 3 from 1 and 2.



Figure 1. Molecular structure of **3** obtained from single-crystal X-ray diffraction studies; Ru = cerulean, C = grey, N = blue, Cl = green, O = red; thermal ellipsoids at 50%, H atoms omitted for clarity.

An initial electrochemical survey under Ar saturation showed two reduction features at negative potentials; the first at -1.69 V vs Fc/Fc+ is irreversible, the second at -1.86 V vs Fc/Fc+ is quasi-reversible (**Figure 2**, $\Delta E_p = 0.61$ V; see Supporting Information). The current response of the first and second reduction features show a dependence on scan rate consistent with a freely diffusing molecule (**Figures S1, S2, and S3**). Based on these observations, we assign the first reduction to a bpy-based reduction of **3** to [Ru^{II}(mesbpy^{•-})(CO)₂Cl₂]⁻, followed by Cl loss through a ligand-to-metal charge transfer (LMCT) to yield [Ru(mesbpy)(CO)₂Cl]⁰, before a second bpy-based reduction to generate [Ru^I(mesbpy^{•-})(CO)₂Cl]⁻. The titration of phenol (PhOH) under Ar saturation revealed a new reduction feature (E_p = -2.12 V vs Fc/Fc+, **3**_{H+},

Figures 2 and S4). The potential of the first reduction shows a dependence on PhOH concentration, which is indicative of a protonation step coupled to electron transfer (Figure S5).^{13,23-25} The observed current response at the third reduction is consistent with second-order kinetic dependence on PhOH concentration (Figure S6). Bulk electrolysis experiments suggest that this new feature $(3_{H+}, Figure 2)$ represents the catalytic reduction of PhOH to H₂ (Table S2). No other gaseous products were detected by GC. Based on these observations, we assign the first feature (1, Figure 2) to an initial reduction followed by the formation of a cationic Ru-H, [Ru^{III}(mesbpy)(H)(CO)₂Cl]⁺, through a protonation by PhOH. Using the concentration of added PhOH and the corresponding shift in potential it is possible to determine a binding constant for H⁺ by Ru of $K_{\text{H}+} = 4.3 \pm 1.4 \text{ M}^{-1}$ under these conditions (Figure S5).^{13,23-25} The subsequent reduction of this cationic species (2, Figure 2) is expected to generate $Ru^{II}(mesbpy)(H)(CO)_2CI$. The third feature $(3_{H+}, Figure 2)$ corresponds to the reduction of Ru^{II}(mesbpy)(H)(CO)₂Cl to generate a species, presumably $[Ru^{II}(mesbpy^{\bullet-})(H)(CO)_2CI]^{-}$, which has sufficient hydricity to react with a proton and form H_2 . We note that catalytic H_2 production from PhOH on glassy carbon electrodes does not occur until -2.60V vs. Fc/Fc+.²⁶



Figure 2. Cyclic voltammograms of 3 under Ar saturation (black), Ar saturation with added PhOH (red), and CO_2 saturation with added PhOH (blue). First, second, and third reduction waves labeled for clarity. Conditions: 1 mM 3; 0.1 M TBAPF₆/MeCN; glassy carbon working

electrode, Pt counter electrode, Ag/AgCl pseudo-reference electrode; referenced to internal ferrocene standard; scan rate 100 mV/s.

Sparging the solution to saturation with CO₂ in the presence of added PhOH altered all three of these reduction features (Figure 2). Although reactivity was observed with CO₂ only, the adventitious addition of trace amounts of H₂O through CO₂ sparging precluded isolation of the pure CO_2 response (Figure S7). As was the case under Ar saturation, the first reduction wave showed a positive potential shift with titration of PhOH under fixed CO₂ concentration (0.28 M, Figure S8). The second reduction feature, however, did not shift as the concentration of added PhOH increased. Varying CO₂ concentration under a fixed concentration of PhOH (0.28 M) showed that only the second reduction potential was dependent on CO₂ concentration (Figure S9). Note that in the presence of CO₂, the third reduction wave (3_{CO2} , $E_p = -2.05$ V vs Fc/Fc+; Figure 2) is both shifted >100 mV more positive than the feature in the presence of PhOH only $(\mathbf{3}_{H+})$ and there is a significant increase (~3x) in the catalytic current density. The titration of PhOH under CO₂ saturation (~0.28 M) also revealed that the current dependence of the third reduction feature was second order in [PhOH] (Figures S10 and S11). Bulk electrolysis under CO₂ saturation with added PhOH confirmed that at the third reduction (~-2.2 V vs Fc/Fc+), this system was catalytic, showing 95% current efficiency for CO production through 5.2 turnovers (relative to moles of **3** in solution, **Table S2**). The formation of H_2 was negligible by GC (~1%). When bulk electrolysis was repeated at the second reduction potential (~-1.7 V vs Fc/Fc+), the observed Faradaic efficiency for CO dropped to $63 \pm 16\%$ (H₂ accounted for $1.8 \pm 0.8\%$ of current passed under these conditions) and HCO₂H was observed by NMR (Figure S12). Insufficient current was observed at more positive potentials, precluding accurate product analysis. This indicates that the relative production of CO or HCO₂H is dependent on the applied potential. Similar effects on the ratio of CO to HCO₂H production have been observed for the

Ru(bpy)-based metallopolymer when the applied potential was varied.²⁷ Similar to the results under Ar, these data are consistent with the assignment of the first feature to an initial reduction followed by a protonation by PhOH to form [Ru^{III}(mesbpy)(H)(CO)₂Cl]⁺. The shift in potential at the first reduction feature when PhOH was varied approximates to a binding constant for H⁺ by Ru of $K_{\rm H^+} = 32 \pm 9.2 \text{ M}^{-1}$ (Figure S8).²³⁻²⁵ A Pourbaix diagram generated from this data exhibits a slope of approximately 60 mV/p K_a unit of PhOH under CO₂ saturation, which is also indicative of a 1e⁻/1H⁺ process (Figure S13).²⁸⁻³⁰ The increase in this binding constant under CO2 from the value obtained under Ar is the result of Nernstian shift from the favorable subsequent insertion of CO₂ into the Ru-H bond, vide infra. The second reduction is then expected to generate Ru^{II}(mesbpy)(H)(CO)₂Cl, which the data suggests undergoes a reaction with CO₂. The product of this reaction is expected to be a species similar to Ru^{II}(mesbpy)(η^1 -OCOH)(CO)₂Cl.³¹ A binding constant for CO₂ can be calculated from the change in potential at the second reduction under a fixed concentration of PhOH: $K_{CO2} = 28 \pm 5.0 \text{ M}^{-1}$ with 0.28 M PhOH (Figure S9). Based on a comparison of i_{cat}/i_p at the third reduction, which is proportional to the electrocatalytic rate constant and TOF, this catalyst is estimated to have a TOF for CO₂ reduction to CO of 1300 s⁻¹ with 0.91 M PhOH (see Supporting Information for details).¹³ The third reduction presumably corresponds to the reduction of $Ru^{II}(mesbpy)(\eta^1-OCOH)(CO)_2CI$ to $[Ru^{II}(mesbpy^{\bullet-})(\eta^1-OCOH)(CO)_2CI]^-$, which we did not expect to catalytically produce CO. In order to test these assignments more carefully, we explored the behavior of 3 further using spectroelectrochemistry.

Infrared spectroelectrochemistry (IR-SEC) experiments, which allow for characterization of changes in the IR signature with respect to potential and time, were used to investigate the behavior of **3** at negative potentials with and without substrate present.³²⁻³⁴ At resting potentials

under N₂ saturation, two IR bands are observed for **3** in TBAPF₆/MeCN at 2058 and 1995 cm⁻¹ (Figure 3).^{17,18,20} When the applied negative potential is increased stepwise to the first reduction observed by CV (~-1.5 V vs Fc/Fc+), these bands are replaced by two new bands at 2014 and cm^{-1} (with other minor species, *vide infra*). We assign this primary species to [Ru(mesbpy)(CO)₂(MeCN)Cll⁰, which results from a single-electron reduction, chloride loss from the parent species **3**, Ru^{II}(mesbpy)(CO)₂Cl₂, and MeCN solvent coordination. This assignment is consistent with the irreversible reduction observed by CV. The other minor bands observed at this potential likely correspond to two species: the six-coordinate anion, $[Ru^{II}(mesbpy^{\bullet-})(CO)_2Cl_2]^{-}$, which forms before Cl dissociation to form the major species, and the five-coordinate, neutral complex, $[Ru(mesbpy)(CO)_2Cl]^0$, which forms before solvent coordination. These assignments are supported by chemical reduction experiments with potassium-intercalated-graphite (KC₈, Figure S14). Other constitutional isomers, i.e. CO ligands at axial positions and solvent coordination in various positions, can occur upon losing the Cl ligand.^{17-19,35-37} Increasing the applied negative potential again to that of the second reduction (~-1.7 V vs Fc/Fc+) resulted in the appearance of two major bands at 1904 and 1884 cm⁻¹. These bands are consistent with a five-coordinate, anionic complex, [Ru^I(mesbpy^{•-})(CO)₂Cl]⁻ (see Figure S14 for more information on this assignment). This bpy-based reduction is consistent with the reversible redox feature observed by CV. The other minor bands observed at this second reduction potential could be results of the following: incomplete reduction to the doubly-reduced complex, other isomers (as previously discussed), and MeCN solvent coordination.³⁵⁻³⁷



Figure 3. IR-SEC of **3** under N_2 saturation showing the species at resting potential (black), the first reduction (red), and the second reduction PhOH (blue). Conditions: 3.5 mM **3**; 0.1 M TBAPF₆/MeCN; Pt working electrode, Pt counter electrode, Ag pseudo-reference electrode.

A second set of experiments with added PhOH (0.5 M) under N₂ saturation conditions indicated that at applied potential a reaction with PhOH was occurring. At resting potential, bands consistent with the starting material **3** were observed at 2058 and 1995 cm^{-1} (Figure S15). When the negative potential of the IR-SEC cell was increased stepwise to that of the first reduction observed by CV (~-1.5 V vs Fc/Fc+), these bands diminished in intensity and were replaced by a species with absorbances at 2051 and 1984 cm⁻¹, with a minor species also cm^{-1} . The and former is observable at tentativelv assigned to $[Ru^{III}(mesbpy)(H)(CO)_2Cl]^+$, vide infra, and the latter is assigned to $[Ru^{II}(mesbpy^{\bullet-})(CO)_2Cl_2]^-$ (Figure S14).^{35,36} If the cell potential is increased again to more negative potentials corresponding to the second reduction (~-1.7 V vs Fc/Fc+), the major species observable by IR becomes Ru^{II}(mesbpy)(H)(CO)₂Cl, with intense bands at 2029 and 1948 cm⁻¹, consistent with previous reports.^{35,38} Although the shift in the observed carbonyl frequencies from 2051 and 1984 cm⁻¹ to 2029 and 1948 cm⁻¹ is not necessarily diagnostic of a change in oxidation state, it is clear from these experiments that the former is a product of a Ru^{1} reaction with H^{+} and from

literature precedent and direct synthesis that the latter represents a Ru^{II}–H species, *vide infra* (see Experimental).

When these experiments were repeated under CO₂ saturation with added PhOH (0.5 M), bands were observed which are consistent with the initial formation of a Ru-H species followed by rapid CO₂ insertion (Figure 4). At the first reduction potential (\sim -1.5 V vs Fc/Fc+), two species are observed, with the first set of bands at 2050 and 1983 cm⁻¹ and the second set of bands at 2032, 1958, and 1949 cm⁻¹. Over the course of 5 minutes the system equilibrates almost entirely to the second of these two species at this potential. Based on the previously described experiments, the former is tentatively assigned to $[Ru^{III}(mesbpy)(H)(CO)_2CI]^+$ and the latter is assigned to Ru^{II}(mesbpy)(n¹-OCHO)(CO)₂Cl (Figure S16).³¹ We attribute the observation of products from an additional reduction at this potential to the Nernstian shift of the second reduction potential from the favorable binding of CO₂ by Ru^{II}–H. The region where Ru– $(\eta^{1}-$ OCHO) adducts are expected $(1500-1600 \text{ cm}^{-1})$ is obscured by the strong solvent absorbance.^{39,40} At the second reduction potential (~-1.7 V vs Fc/Fc+) new bands appear at 2016, 1989, 1945, and 1890 cm⁻¹, which are the only observable IR features at the second reduction potential and after the third reduction potential (~-2.0 V vs Fc/Fc+, Figure 2). These species are likely isomers of the type $[Ru^{II}(mesbpy^{\bullet-})(\eta^1-OCOH)(CO)_2L]^X$ or $[Ru^{I}(mesbpy)(\eta^1 OCOH)(CO)_2L^{X}$, where L = MeCN or Cl (Figure S17).³⁵⁻³⁷



Figure 4. IR-SEC of **3** under CO_2 saturation with added PhOH (0.5 M) showing the species at resting potential (black) and those which grow in at the first reduction (red to blue) over the course of 5 minutes. Conditions: 8.6 mM **3**; 0.1 M TBAPF₆/MeCN; glassy carbon working electrode, Pt counter electrode, Ag pseudo-reference electrode.

Discussion

In general, the reduction of CO_2 proceeds by either a hydroxycarbonyl (*a*) or a $HCO_2^-(b)$ bound intermediate (1).



Mechanistic studies show that a hydroxycarbonyl complex is usually obtained by direct interaction of a reduced metal center with CO₂, followed by protonation.⁴¹ A HCO₂⁻ adduct is usually produced by a metal hydride reacting with CO₂ to produce the C–H bond, followed by rearrangement to the O-bonded species, b.^{42,43} To our knowledge, there exists no detailed discussion concerning the potential isomerization between *a* and *b*. The results described here suggest that the relative thermodynamic stabilities of *a* and *b* can depend on the redox states of the metal ions involved. Indeed, Ru(bpy) complexes have previously been reported to

electrocatalytically or photocatalytically produce mixtures of HCO₂^{-/}HCO₂H and CO from CO₂ with varying efficiencies.^{17,18,20,27,44-47} Our proposed reduction mechanism for the electrocatalytic process to HCO_2^- is shown in Scheme 2. The irreversibility of the observed CV response of 3 (i) at the first reduction is indicative of a bpy-based reduction followed by a fast ligand-to-metal charge transfer (LMCT) resulting in Cl loss, vielding $[Ru(mesbpv)(CO)_2Cl(L)]^0$ (*ii*). This interpretation of the reduction feature is also supported by DFT calculations, which suggest that the LUMO of *i* is localized on the π^* orbital of the bpy ligand (Figure S18). $[Ru(mesbpy)(CO)_2Cl(L)]^0$ reacts with H⁺ to generate $[Ru^{III}(mesbpy)(H)(CO)_2Cl]^+$ (iii). Additional DFT calculations on the presumptive 5-coordinate intermediate generated by L loss from ii, [Ru(mesbpy)(CO)₂Cl]⁰, indicate a cooperative metal-ligand redox response; the added charged in the SOMO is distributed between the d_z^2 orbital of the metal center and the π^* orbital of the bpy ligand (Figure S19). Under applied potential under CO₂ saturation, however, this species is rapidly reduced to Ru^{II} (mesbpy)(H)(CO)₂Cl, *iv*. An insertion reaction involving CO₂ and *iv* generates Ru^{II} (mesbpy)(η^1 -OCHO)(CO)₂Cl, *v*. Bulk electrolysis at this potential shows that both CO and HCO₂⁻/HCO₂H are generated. For CO production to occur, a dehydration reaction must take place involving the formato species: Ru complexes have previously been observed to catalyze the dehydration of HCO₂H.^{22,48-50} Interestingly, the synthesis of the Ru(II) precursor used in these studies seems to rely on a similar mechanism to generate [Ru(CO)₂Cl₂]_n from RuCl₃, HCl (aq.), and HCO₂H.²²

Scheme 2. Proposed overall mechanism for the reduction of CO_2 to CO and H_2O or HCO_2H by 3, Ar = mesityl, L = MeCN.



If an additional reduction reaction involving v takes place, the dehydration reaction is accelerated, as evidenced by the increased current response for CO production observed at the third reduction feature by CV. Current efficiency for CO is almost quantitative at this potential, suggesting an efficient inter-conversion of HCO₂⁻ and H⁺ to CO and H₂O. Generating CO from solvated HCO₂H is predicted to be favored over a decarboxylation reaction at room temperature as a result of the favorable solvation effects of producing H₂O as a co-product.⁵¹ The necessity of additional electrochemical driving force to enhance the catalytic response in a similar manner has been previously observed in other molecular electrocatalysts for CO₂ reduction.^{13,52} It is also noteworthy that a Ru^{II}(EDTA) complex has even been shown to convert HCO₂⁻ and HCO₂H to CO.⁵³

A mechanism for the Ru-catalyzed dehydration reaction of HCO_2H has not yet been proposed. Previous reports have shown that a carboxylate ester of an analogous compound, $Ru^{II}(bpy)(\eta^1-C(O)OCH_2CH_2OH)(CO)_2CI$, could be converted to $[Ru^{II}(bpy)(CO)_3CI]^+$ in the presence of HCl.³⁶ A carboxylate intermediate would be consistent with other observations and proposed mechanisms involving Ru(bpy) complexes, although a Ru–[η^1 -C(O)OH] species is not

Journal of the American Chemical Society

observed here experimentally.^{20,27,54,55} Although many mechanisms could allow for this, we favor the one proposed below for the conversion of the HCO_2^- adduct to CO (**Scheme 3**).

The O-bound HCO_2^- species *vi* is capable of a hydride elimination reaction, to yield a Ru hydride with a $[CO_2]$ molecule in close proximity, *vii*. A concomitant LMCT generates a Ru^I metal center that can immediately reduce CO₂ to form a hydroxycarbonyl species, *viii*. Species *viii* is expected to be weakly hydridic as a result of the Ru^{III} oxidation state. It is therefore likely for a proton shift to occur, especially when considering the expected basicity of the bound hydroxycarbonyl. Such a protonation reaction would generate a Ru^I–[η^1 -C(O)OH] species, *ix*, which would favor protonation by an external acid to cleave the C–O bond and lose H₂O. As an octahedral 19-electron complex the resulting Ru^I species, *x*, should rapidly lose CO. The loss of CO as an axial ligand would regenerate *ii*, which is the entry point to the catalytic cycle that was discussed in **Scheme 2**. Consecutive protonation and reduction steps will generate a hydride, which can undergo a CO₂ insertion reaction to generate Ru^{II}–(η^1 -OCHO) again.

Scheme 3. Proposed dehydration mechanism for production of CO from HCO_2^- by 3.



To test certain elements of this proposed mechanism, a series of experiments were performed with HCO₂H and tetraethylammonium formate (TEA⁺[HCO₂⁻]).⁵⁶ Bulk electrolysis experiments at \sim -2.2 V vs Fc/Fc+ with **3** and an excess of either HCO₂H or TEA[HCO₂⁻]

showed that CO was produced in both circumstances.^{53,57} Heating complex **3** to reflux in MeCN with $TEA^{+}[HCO_{2}^{-}]$ under a static N₂ blanket with a gas bubbler attached via tubing to a reflux condenser allowed us to confirm by GC that CO was produced under these conditions as well as CO₂ and H₂. Any attempts to abstract or displace a chloride with a HCO₂⁻ salt resulted in similar behavior. Interestingly, the preparation of a partially chloride-abstracted species with trifluoromethanesulfonic acid (HOTf), Ru^{II}(mesbpy)(CO)₂[OTf]Cl, 4, did not allow for the isolation of a stable formato species. Electrochemical characterization of the directly synthesized presumptive Ru–H intermediate, Ru^{II}(mesbpy)(CO)₂(H)Cl 5, by CV was also consistent with the proposed mechanism. Under Ar saturation a single irreversible wave was observed at -1.98 V vs Fc/Fc+ (Figures S20 and S21). Similar to the observed behavior of 3 in the presence of a fixed concentration of PhOH, an increased current response consistent with catalysis is observed under CO₂ saturation at potentials ~100 mV more positive than Ar saturation for 5 (Figures 5 and S21). Additionally, the voltages at peak current under CO₂ saturation ($E_p = -2.07$ V vs Fc/Fc+) and Ar saturation ($E_p = -2.14$ V vs Fc/Fc+) for **5** are also comparable to those observed for **3** (Figure 5).



Figure 5. Cyclic voltammograms of **3** and **5** under Ar saturation (red, maroon) and CO_2 saturation (blue, navy) with added PhOH (0.91 M, red/blue; 0.5 M, maroon/red). (A) current response and detail (B) at negative potentials. Conditions: 1 mM **3** or **5**; 0.1 M TBAPF₆/MeCN;

glassy carbon working electrode, Pt counter electrode, Ag/AgCl pseudo-reference electrode; referenced to internal ferrocene standard; scan rate 100 mV/s.

Based on these experimental results, we note several key points about the observed behavior. Because of the thermodynamic considerations and factors that relate the production of CO and HCO₂H from CO₂, it is remarkable that such a delicate balance can be achieved in this system. It is possible to rationalize this by considering the equilibrium that relates CO and HCO₂H. The common intermediate shared by CO₂ and the potential products (CO, HCO₂H) in this system is a Ru–H species. In the absence of applied potential, the Ru^{II} metal center decomposes HCO₂⁻ and HCO₂H to CO₂ and H₂, which suggests that the Ru^{II}–H is less hydridic than HCO₂H or HCO₂⁻. Under electrochemical conditions, intermediate applied potential is enough to disrupt this equilibrium, favoring the production of HCO₂H and HCO₂⁻ from CO₂ by increasing the relative hydricity of the Ru–H species. At high applied potential, the observed rate of catalysis increases, which is consistent with the expected increase in the hydricity of the Ru– H. At these potentials it also appears that this reduced Ru species is capable of reacting directly with CO₂ through hydride elimination from HCO₂⁻/HCO₂H. Further study is in order to increase our understanding of the branching ratio between CO and HCO₂H.

Conclusion

Mechanistic electrochemical and spectroelectrochemical studies, supplemented by the synthesis of relevant intermediates, indicate that this catalytic behavior is the result of the cooperative redox response of the bpy ligand and Ru metal center at negative potentials, as well as the inhibition of Ru–Ru bond formation through sterics.^{13,20} In this system CO₂ binding is the result of an insertion reaction, preceded by Ru–H bond formation, which is observed by IR-SEC. The resulting species is likely similar to Ru^{II}(mesbpy)(η^1 -OCOH)(CO)₂Cl. In similar Ru systems where more than one hydride is available, high pressure is used, or relevant substrate molecules

are added, HCO_2^- is observed from this insertion product.⁵⁸⁻⁶⁴ In this case, however, an additional reduction reaction seems to accelerate a thermal process: the dehydration of HCO_2^- in the presence of H⁺ to CO and H₂O. The results of these two studies suggest that the equilibria relating HCO_2H , CO_2 and H_2 , and CO and H_2O can have significant consequences on the catalytic functionalization of CO_2 under electrochemical conditions. We are currently exploring additional modifications of the overall ligand structure and primary coordination sphere of the Ru metal center to further investigate this behavior.

Experimental and Procedures

General. ¹H NMR spectra were recorded on a Varian 400 or Jeol 500 MHz spectrometer at 298 K and referenced to residual solvent shifts. Data manipulations were completed using *ACD*. Infrared spectra were taken on a Thermo Scientific Nicolet 6700 or a Bruker Equinox 55 spectrometer. Microanalyses were performed by Midwest Microlab for C, H, and N.

Solvents and chemicals. All solvents were obtained from Fisher Scientific. All solvents were dried in house by storing in a moisture free environment and dried on a custom drying system running through two alumina columns under an argon atmosphere prior to use. All compounds were obtained from Fisher Scientific, Alfa Aesar, or Sigma-Aldrich and used as obtained unless otherwise specified. Tetrabutylammonium hexafluorophosphate (TBAPF₆, Aldrich, 98%) was recrystallized from CH₃OH twice and dried at 90°C overnight before use in electrochemistry.

Synthetic Methods

The ligand 6,6'-dimesityl-2,2'-bipyridine, tetraethylammonium formate, and $[Ru(CO)_2Cl_2]$ were prepared according to literature methods.^{13,20-22,56}

trans-Cl-Ru(6,6'-dimesityl-2,2'-bipyridyl)(CO)₂Cl₂, **3**. A round bottom flask was charged with $[Ru(CO)_2Cl_2]_n$ (0.288 g, 1.26 mmol) and 6,6'-dimesityl-2,2'-bipyridine (0.500 g, 1.26 mmol) in dry toluene (25 mL). A reflux condenser was attached to the flask and the mixture heated to reflux and left overnight (18 h) in the dark. After this time the solution was allowed to cool to room temperature and placed in a freezer at -20° C for 1 h. Over the course of an hour a pale yellow powder precipitated, which was isolated by vacuum filtration and washed with pentanes (2 x 10 mL). Yield (recovered) 580 mg, 74%. Removing the solvent from the filtrate under reduced pressure isolated a pale yellow solid from which further material could be obtained by recrystallization from THF solution with pentanes. ¹H NMR (d₂-CD₂Cl₂, 400 MHz): δ 8.32 (d,

2H, Ar*H*), 8.13 (d-d, 2H, Ar*H*), 7.45 (d, 2H, Ar*H*), 6.98 (s, 4H, Ar*H*), 2.34 (s, 6H, $-CH_3$), 2.14 (s, 12H, $-CH_3$). ¹³C{¹H} NMR (d₂-CD₂Cl₂, 500 MHz): δ 191.26, 165.19, 157.98, 141.38, 140.21, 139.75, 138.09, 130.40, 129.58, 129.39, 123.51, 115.96, 21.96, 21.74. IR (CH₂Cl₂) v_{CO}: 2062, 1999 cm⁻¹. ESI-MS (*m*/*z*) [M+Na⁺]⁺: Calcd. 643.05. Found: 643.17. Elemental Analysis for C₃₀H₂₈Cl₂N₂O₂Ru Calc'd: C 58.04, H 4.55, N 4.51; Found: C 58.21, H 4.60, N 4.32.

Ru(6,6'-dimesityl-2,2'-bipyridyl)(CO)₂(**CF**₃**SO**₃)**Cl**, **4.** A Schlenk flask was charged with **4** (0.100 g, 0.16 mmol) in dry CH₂Cl₂ (2 mL) under N₂ atmosphere. An excess of trifluoromethanesulfonic acid (0.30 mL, 3.2 mmol) was added slowly via syringe. The mixture was stirred 1 h in the dark under N₂ atmosphere. After this time diethyl ether (20 mL) was added to the solution and a white precipitate formed which was collected by filtration. Yield (recovered) 84 mg, 61%. ¹H NMR (d₂-CD₂Cl₂, 400 MHz): δ 8.69 (br m, 2H, Ar*H*), 8.58 (br m, 2H, Ar*H*), 7.95 (br m, 2H, Ar*H*), 7.05 (s, 4H, Ar*H*), 2.36 (s, 6H, -C*H*₃), 2.12 (s, 12H, -C*H*₃). IR (CH₂Cl₂) v_{CO}: 2086, 2014 cm⁻¹. Elemental Analysis for C₃₁H₂₈ClF₃N₂O₅RuS Calc'd: C 50.72, H 3.84, N 3.82; Found: C 50.38, H 4.34, N 3.84.

Ru(6,6'-dimesityl-2,2'-bipyridyl)(CO)₂(**COOMe)Cl.** A round-bottom flask was charged with **mesbpy** (0.193 g, 0.49 mmol) and dichlorotricarbonylruthenium (II) dimer (0.125 g, 0.24 mmol) in dry methyl formate (10 mL) under N₂ atmosphere. The mixture was stirred at reflux for 2 h in the dark. After this time the solution was condensed under reduced pressure and recrystallized from a mixture of CH₂Cl₂ and pentanes. Yield (recovered) 163 mg, 52%. ¹H NMR (d₂-CD₂Cl₂, 400 MHz): δ 8.68 (br m, 2H, Ar*H*), 8.32 (br m, 2H, Ar*H*), 7.53 (br m, 2H, Ar*H*), 6.99 (s, 4H, Ar*H*), 3.10 (s, 3H, -CH₃), 2.34 (s, 6H, -CH₃), 2.06 (s, 12H, -CH₃). ¹³C{¹H} NMR (d₂-CD₂Cl₂, 500 MHz): δ 189.07, 186.65, 185.04, 177.67, 177.55, 177.30, 158.36, 145.52, 136.72, 129.53, 123.57, 121.34, 115.98, 21.67, 20.84. IR (CH₂Cl₂) v_{CO}: 2134, 2127, and 2059 cm⁻¹; v_{OCO} 1611,

1606 cm⁻¹. ESI-MS (m/z) [M–Cl]⁺: Calcd. 609.13. Found: 609.26. Elemental Analysis for C₃₂H₃₁ClN₂O₄Ru · 0.5 CH₂Cl₂ Calc'd: C 56.85, H 4.70, N 4.08; Found: C 56.54, H 4.45, N 4.14. Ru(6,6'-dimesityl-2,2'-bipyridyl)(CO)₂(H)Cl. A round-bottom flask was charged with mesbpy (0.193 g, 0.49 mmol) and dichlorotricarbonylruthenium (II) dimer (0.250 g, 0.49 mmol) in dry methyl formate (10 mL) under N₂ atmosphere. The mixture was stirred at reflux for 30 minutes in the dark. After this time the solution was condensed under reduced pressure loaded onto neutral alumina with CH_2Cl_2 . Running a column on silica gel with ethyl acetate (100%) recovered a single fraction containing **mesbpy** ligand. Switching to CH₂Cl₂ as the eluent with a MeOH gradient (0 to 10%) recovered a single fraction, which was condensed under reduced pressure and found to contain Ru(mesbpy)(CO)₂(H)Cl as a tan powder. Yield (recovered) 75 mg, 26%. ¹H NMR (d₂-CD₂Cl₂, 500 MHz): δ 8.27 (m, 2H, ArH), 8.10 (m, 2H, ArH), 7.44 (m, 2H, ArH), 6.97 (m, 4H, ArH), 2.33 (d, 6H, -CH₃), 2.18 (d, 6H, -CH₃), 1.94 (d, 6H, -CH₃), -11.69 (s, 1H, Ru–H). ${}^{13}C{}^{1}H$ NMR (d₂-CD₂Cl₂, 500 MHz): δ 198.14, 196.55, 165.22, 163.55, 158.53, 156.81, 141.44, 140.06, 139.81, 139.59, 139.44, 137.28, 136.98, 135.71, 135.13, 129.20, 128.83, 128.47, 127.91, 127.84, 122.41, 122.32, 21.84, 21.54, 20.81, 20.53. IR (CH₂Cl₂) v_{CO}: 2032, 1951 cm⁻¹. ESI-MS (m/z) [M–Cl]⁺: Calcd. 551.13. Found: 551.19. Elemental Analysis for C₃₀H₂₉ClN₂O₄Ru Calc'd: C 61.48, H 4.99, N 4.78; Found: C 61.18, H 4.91, N 4.63.

Electrochemistry. Electrochemical experiments were carried out using a BAS Epsilon potentiostat. For all experiments, a single compartment cell was used with dry stir bar and a dry needle was connected to control the atmosphere. A 3 mm diameter glassy carbon electrode from BASi was employed as the working electrode. The counter electrode was a platinum (Pt) wire and the pseudo-reference electrode was a silver/silver chloride (Ag/AgCl) electrode separated from solution by a Vycor tip. Experiments were run with and without an added internal reference

of ferrocene. All solutions were in dry MeCN and contained 1 mM of catalyst and 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte, unless otherwise noted. Scan rates were 100 mV/s unless otherwise indicated. Experiments were purged with N_2 or CO_2 (to saturation at 0.28 M) before CVs were taken and stirred in between successive experiments. All experiments were reported referenced an internal ferrocene standard except for the bulk electrolysis experiments, which used the pseudo-reference electrode Ag/AgCl behind a Vycor tip.

Infrared Spectroelectrochemistry. The experimental setup and design of the IR-SEC cell has been published previously by our lab.^{33,34} A Pine Instrument Company model AFCBP1 bipotentiostat was employed. As the potential was scanned, thin layer bulk electrolysis was monitored by Fourier-Transform Reflectance IR off the electrode surface. All experiments were conducted in 0.1 M TBAPF₆/MeCN solutions with catalyst concentrations of ~5 mM (unless otherwise noted) prepared under a nitrogen atmosphere. For IR-SEC experiments under catalytic conditions, air-free samples were sparged briefly with ¹²CO₂ (10-20 seconds). The IR-SEC cells used (working electrode/counter electrode/reference electrode) were either glassy carbon/Ag/Pt or Pt/Ag/Pt, meaning that all potentials were in reference to a pseudo-RE, Ag/Ag+ (~+200 mV from the Fc/Fc+ couple).

X-ray Crystallography. Single crystal X-ray diffraction studies reported herein were carried out on a Bruker Kappa APEX-II CCS diffractometer equipped with MoK α radiation ($\lambda = 0.71073$ Å). The crystals were mounted on a Cryoloop while in Paratone oil. The data was collected under a stream of N₂ gas at 100(2) K using ω and ϕ scans. Data were integrated using the Bruker SAINT software program and scaled using SADABS software. A complete phasing model consistent with the molecular structure was produced by SHELXS direct methods. Non-

Page 21 of 24

hydrogen atoms were reined anisotropically by full matrix least squares (SHELXL-97).⁶⁵ All hydrogen atoms were determined using a riding model with positions constrained to their parent atom using the appropriate FHIX command. Crystallographic data is in supplementary information (**Tables S1**).

Calculations. Complexes were geometry-optimized using the BP86 functional with TZ2P basis sets. The resulting structures were confirmed as minima through analytical frequency calculations at the same level of theory. Kohn-Sham orbital representations were generated using the ADF GUI. All calculations were performed with the ADF 2012.01 software suite in collaboration with the research group of Prof. Joshua S. Figueroa.

ASSOCIATED CONTENT

Supporting Information. A selection of cyclic voltammograms, X-ray crystallographic information tables, IR-SEC plots, and chemical reductions are available online at http://pubs.acs.org.

Corresponding Author

*ckubiak@ucsd.edu

Author Contributions

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

Funding Sources

AFOSR Basic Research Initiative (BRI) Grant (FA9550-12-1-0414).

ACKNOWLEDGMENT

We acknowledge support for this work from the AFOSR through a Basic Research Initiative (BRI) grant (FA9550-12-1-0414) and the UCSD Department of Chemistry and Biochemistry for analytical instrumentation. We also acknowledge the assistance of Dr. Curtis Moore in obtaining and solving the molecular structure presented here through single crystal X-ray diffraction studies. We acknowledge the UCSD Chemistry and Biochemistry Molecular MS facility for use of their facilities and Steven A. Chabolla for his assistance with ESI-MS. All calculations were performed in collaboration with Prof. Joshua S. Figueroa.

Bibliography

- (1) Benson, E. E.; Kubiak, C. P.; Sathrum, A. J.; Smieja, J. M. Chem. Soc. Rev. 2009, 38, 89.
- (2) Finn, C.; Schnittger, S.; Yellowlees, L. J.; Love, J. B. *Chem. Commun.* **2012**, *48*, 1392.
- (3) Inglis, J. L.; MacLean, B. J.; Pryce, M. T.; Vos, J. G. Coord. Chem. Rev. 2012, 256, 2571.
- (4) Grice, K. A.; Kubiak, C. P. In *Advances in Inorganic Chemistry*; Aresta, M., van Eldik, R., Eds.; Academic Press: San Diego, USA, 2014.
- (5) Qiao, J.; Liu, Y.; Hong, F.; Zhang, J. Chem. Soc. Rev. **2014**, 43, 631.
- Appel, A. M.; Bercaw, J. E.; Bocarsly, A. B.; Dobbek, H.; DuBois, D. L.; Dupuis, M.; Ferry, J. G.;
 Fujita, E.; Hille, R.; Kenis, P. J. A.; Kerfeld, C. A.; Morris, R. H.; Peden, C. H. F.; Portis, A. R.;
 Ragsdale, S. W.; Rauchfuss, T. B.; Reek, J. N. H.; Seefeldt, L. C.; Thauer, R. K.; Waldrop, G. L.
 Chem. Rev. 2013, 113, 6621.
- (7) Costentin, C.; Passard, G.; Robert, M.; Savéant, J.-M. Proc. Natl. Acad. Sci. USA 2014, 111, 14990.
- (8) Costentin, C.; Savéant, J.-M. ChemElectroChem 2014, 1, 1226.
- (9) Costentin, C.; Passard, G.; Savéant, J.-M. J. Am. Chem. Soc. **2015**, 137, 5461.
- (10) Costentin, C.; Robert, M.; Saveant, J.-M. *Chem. Soc. Rev.* **2013**, *42*, 2423.
- (11) Costentin, C.; Drouet, S.; Robert, M.; Savéant, J.-M. Science 2012, 338, 90.
- (12) Froehlich, J. D.; Kubiak, C. P. J. Am. Chem. Soc. 2015, 137, 3565.
- (13) Sampson, M. D.; Nguyen, A. D.; Grice, K. A.; Moore, C. E.; Rheingold, A. L.; Kubiak, C. P. J. Am. *Chem. Soc.* **2014**, *136*, 5460.
- (14) Smieja, J. M.; Benson, E. E.; Kumar, B.; Grice, K. A.; Seu, C. S.; Miller, A. J. M.; Mayer, J. M.; Kubiak, C. P. *P. Natl. Acad. Sci. USA* **2012**, *109*, 15646.
- (15) Savéant, J.-M. Chem. Rev. 2008, 108, 2348.
- (16) Ishida, H.; Fujiki, K.; Ohba, T.; Ohkubo, K.; Tanaka, K.; Terada, T.; Tanaka, T. *J. Chem. Soc., Dalton Trans.* **1990**, 2155.
- (17) Chardon-Noblat, S.; Deronzier, A.; Ziessel, R.; Zsoldos, D. Inorg. Chem. 1997, 36, 5384.
- (18) Collomb-Dunand-Sauthier, M.-N.; Deronzier, A.; Ziessel, R. Inorg. Chem. 1994, 33, 2961.
- (19) Chardon-Noblat, S.; Cripps, G. H.; Deronzier, A.; Field, J. S.; Gouws, S.; Haines, R. J.; Southway, F. *Organometallics* **2001**, *20*, 1668.
- (20) Kuramochi, Y.; Itabashi, J.; Fukaya, K.; Enomoto, A.; Yoshida, M.; Ishida, H. *Chem. Sci.* **2015**, *6*, 3063.
- (21) Schmittel, M.; Ganz, A.; Schenk, W. A.; Hagel, M. Z. Naturforsch. **1999**, 54b, 559.

ge 23 of 24	Journal of the American Chemical Society
	23
(22)	Cleare, M. J.; Griffith, W. P. <i>J. Chem. Soc. A</i> 1969 . 372.
(23)	Gagne, R. R.; Allison, J. L.; Ingle, D. M. <i>Inorg. Chem.</i> 1979 , <i>18</i> , 2767.
(24)	Gagne, R. R.; Ingle, D. M. J. Am. Chem. Soc. 1980, 102, 1444.
(25)	Fujita, E.; Creutz, C.; Sutin, N.; Szalda, D. J. <i>J. Am. Chem. Soc.</i> 1991 , <i>113</i> , 343.
(26)	McCarthy, B. D.; Martin, D. J.; Rountree, E. S.; Ullman, A. C.; Dempsey, J. L. Inorg. Chem. 2014, 53, 8350.
(27)	Chardon-Noblat, S.; Deronzier, A.; Ziessel, R.; Zsoldos, D. J. Electroanal. Chem. 1998, 444, 253.
(28) (29)	Horvath, S.; Fernandez, L. E.; Appel, A. M.; Hammes-Schiffer, S. <i>Inorg. Chem.</i> 2013 , <i>52</i> , 3643. Raamat, E.; Kaupmees, K.; Ovsjannikov, G.; Trummal, A.; Kütt, A.; Saame, J.; Koppel, I.; Kaljurand, I.; Lipping, L.; Rodima, T.; Pihl, V.; Koppel, I. A.; Leito, I. <i>J. Phys. Org. Chem.</i> 2013 , <i>26</i> , 162.
(30)	Solis, B. H.; Hammes-Schiffer, S. Inorg. Chem. 2014, 53, 6427.
(31)	Whittlesey, M. K.; Perutz, R. N.; Moore, M. H. Organometallics 1996, 15, 5166.
(32)	Salsman, J. C.; Kubiak, C. P. In <i>Spectroelectrochemistry</i> ; Kaim, W., Klein, A., Eds.; Royal Society of Chemistry: Cambridge, England, 2008.
(33)	Machan, C. W.; Sampson, M. D.; Chabolla, S. A.; Dang, T.; Kubiak, C. P. Organometallics 2014 , 33, 4550.
(34)	Zavarine, I. S.; Kubiak, C. P. J. Electroanal. Chem. 2001, 495, 106.
(35)	Haukka, M.; Kiviaho, J.; Ahlgren, M.; Pakkanen, T. A. Organometallics 1995 , 14, 825.
(36)	Haukka, M.; Hirva, P.; Luukkanen, S.; Kallinen, M.; Ahlgrén, M.; Pakkanen, T. A. <i>Inorg. Chem.</i> 1999 , <i>38</i> , 3182.
(37)	Eskelinen, E.; Haukka, M.; Venäläinen, T.; Pakkanen, T. A.; Wasberg, M.; Chardon-Noblat, S.; Deronzier, A. <i>Organometallics</i> 2000 , <i>19</i> , 163.
(38)	Luukkanen, S.; Homanen, P.; Haukka, M.; Pakkanen, T. A.; Deronzier, A.; Chardon-Noblat, S.; Zsoldos, D.; Ziessel, R. <i>Appl. Cat. A</i> 1999 , <i>185</i> , 157.
(39)	Gibson, D. H. <i>Coord. Chem. Rev.</i> 1999 , <i>185–186</i> , 335.
(40)	Gibson, D. H.; Ding, Y.; Miller, R. L.; Sleadd, B. A.; Mashuta, M. S.; Richardson, J. F. <i>Polyhedron</i> 1999 , <i>18</i> , 1189.
(41)	Sampson, M. D.; Froehlich, J. D.; Smieja, J. M.; Benson, E. E.; Sharp, I. D.; Kubiak, C. P. <i>Energy</i> <i>Environ. Sci.</i> 2013 , <i>6</i> , 3748.
(42)	Darensbourg, D. J.; Rokicki, A.; Darensbourg, M. Y. J. Am. Chem. Soc. 1981, 103, 3223.
(43)	Sullivan, B. P.; Meyer, T. J. Organometallics 1986 , <i>5</i> , 1500.
(44)	Lehn, JM.; Ziessel, R. <i>J. Organomet. Chem.</i> 1990 , <i>382</i> , 157.
(45)	Sahara, G.; Ishitani, O. Inorg. Chem. 2015 , 54, 5096.
(46)	Sekizawa, K.; Maeda, K.; Domen, K.; Koike, K.; Ishitani, O. J. Am. Chem. Soc. 2013, 135, 4596.
(47)	Sun, D.; Gao, Y.; Fu, J.; Zeng, X.; Chen, Z.; Li, Z. <i>Chem. Commun.</i> 2015 , <i>51</i> , 2645.
(48)	Coffey, R. S. <i>Chem. Commun.</i> 1967 , 923b.
(49)	Halpern, J.; Kemp, A. L. W. <i>J. Am. Chem. Soc.</i> 1966 , <i>88</i> , 5147.
(50)	Anderson, P. A.; Deacon, G. B.; Haarmann, K. H.; Keene, F. R.; Meyer, T. J.; Reitsma, D. A.; Skelton, B. W.; Strouse, G. F.; Thomas, N. C. <i>Inorg. Chem.</i> 1995 , <i>34</i> , 6145.
(51)	Matubayasi, N.; Nakahara, M. <i>J. Chem. Phys.</i> 2005 , <i>122</i> , 074509.
(52)	Riplinger, C.; Sampson, M. D.; Ritzmann, A. M.; Kubiak, C. P.; Carter, E. A. <i>J. Am. Chem. Soc.</i> 2014 , <i>136</i> , 16285.
(53)	Shimizu, K. <i>Bull. Chem. Soc. Jpn.</i> 1977 , 50, 2921.
(54)	Voyame, P.; Toghill, K. E.; Méndez, M. A.; Girault, H. H. Inorg. Chem. 2013 , 52, 10949.
(55)	Coalter, J. N.; Huffman, J. C.; Caulton, K. G. Organometallics 2000, 19, 3569.
(56)	Grills, D. C.; Farrington, J. A.; Layne, B. H.; Lymar, S. V.; Mello, B. A.; Preses, J. M.; Wishart, J. F. J. Am. Chem. Soc. 2014 , 136, 5563.
(57)	Fenwick, A. Q.; Luca, O. R. J. Photoch. Photobio. B, DOI: 10.1016/j.jphotobiol.2015.04.003.
(57)	Fenwick, A. Q.; Luca, O. R. <i>J. Photoch. Photobio. B</i> , DOI: 10.1016/j.jphotobiol.2015.04.003.

- (58) Musashi, Y.; Sakaki, S. J. Am. Chem. Soc. 2000, 122, 3867.
- (59) Komiya, S.; Yamamoto, A. J. Organomet. Chem. **1972**, 46, C58.
- (60) Kolomnikov, I. S.; Gusev, A. I.; Aleksandrov, G. G.; Lobeeva, T. S.; Struchkov, Y. T.; Vol'pin, M. E. J. Organomet. Chem. **1973**, *59*, 349.
- (61) Jessop, P. G.; Ikariya, T.; Noyori, R. *Nature* **1994**, *368*, 231.
- (62) Munshi, P.; Main, A. D.; Linehan, J. C.; Tai, C.-C.; Jessop, P. G. J. AM. Chem. Soc. **2002**, 124, 7963.
- (63) Urakawa, A.; Jutz, F.; Laurenczy, G.; Baiker, A. *Chem. Eur. J.* **2007**, *13*, 3886.
- (64) Jessop, P. G.; Hsiao, Y.; Ikariya, T.; Noyori, R. J. Am. Chem. Soc. 1996, 118, 344.
- (65) Sheldrick, G. Acta Crys. A 2008, 64, 112.

TOC Figure:

