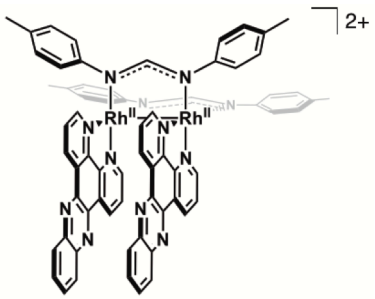
Final Report

Project Title: Multimetallic Systems for the Photocatalytic Production of Fuels from Abundant Sources

The reported findings herein are a result of a collaboration between the groups of

Claudia Turro at The Ohio State University (DE-SC0010542) and
Kim R. Dunbar at Texas A&M University (DE-SC0010721).

The Turro and Dunbar groups jointly discovered that cationic d^7–d^7 $Rh_2(II,II)$ complexes bridged by electron-donating formamidinate (form) ligands possess redox-active excited states that are relatively long-lived and can engage in charge transfer reactions. One example of the $[Rh_2(DTolF)_2(L)_2]^{2+}$ series (L = phen (**1**), dpq (**2**), dppz (**3**), dppn (**4**); DTolF = *p*-tolylformamidinate) is shown in Figure 1, and results are similar to those for the corresponding series featuring the F-form (*p*-fluoroformamidinate) bridging ligand.[1]



$[Rh_2(\mu\text{-DtolF})_2(dppz)_2]^{2+}$

Figure 1. Structure of **3**.

As part of the present grant we designed new complexes that exhibit strong absorption from the UV to ~800 nm.[2] Two new complexes, $[Rh_2(DTolF)_2(np)_2]^{2+}$ (**5**, np = 1,8-naphthyridine) and $[Rh_2(DTolF)_2(dap)_2]^{2+}$ (**6**, dap = 1,12-diazaperylene) exhibit significantly red-shifted absorption maxima relative to those in the related series **1** – **4** (Figure 2) that we previously reported.[1] Both complexes were easily prepared from the partially solvated precursor *cis*-$[Rh_2(DTolF)_2(CH_3CN)_6]^{2+}$ with excess diimine ligand (Figure 2a). In contrast to the chelating diimine ligands in **1**–**4** and **6**, complex **5** bears two bridging neutral ligands. In light of these findings, we began pursuing related complexes as potential LAs.

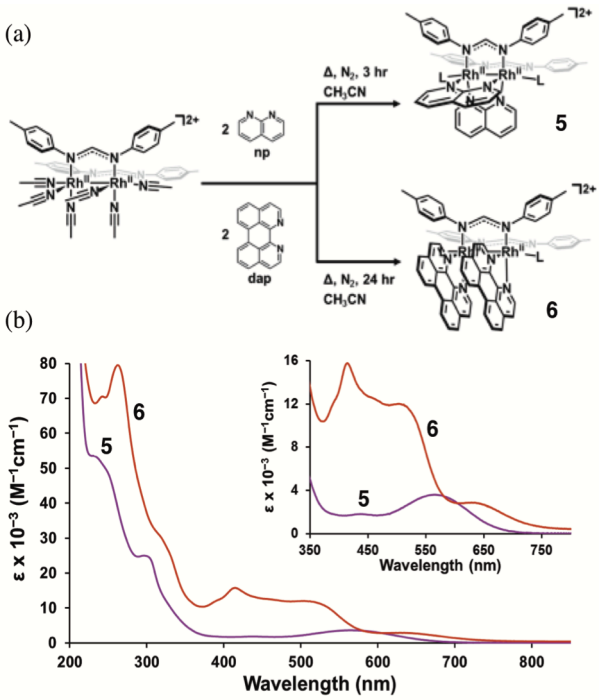


Figure 2. (a) Preparation and structures of **5** and **6** and (b) their corresponding absorption spectra.

Because of the ease in the synthesis, two np-containing complexes pendant –COOH groups were prepared that we envisioned could be used to couple them to catalysts or semiconductor supports to sensitize charge transfer reactions. Our initial studies focused on the complexes shown in Figure 3a, $[Rh_2(DTolF)_2(R\text{-}np)_2]^{2+}$, where the np ligand is substituted with R = 2-COOH (**7**), 2-$COOCH_3$ (**8**), 4-COOH (**9**), and 4-$COOCH_3$ (**10**). The electronic absorption spectra of **9** and **10** are red-sifted as compared to the 2-substituted analogs (Figure 3b).

For **5** and **7**, ultrafast and nanosecond transient absorption (TA) spectroscopy reveal a ^{1}MLLCT (metal/ligand-to-ligand charge transfer) excited state with τ = 70 ps for **5** (λ_{exc} = 595 nm) and 20 ps for **7** (λ_{exc} = 700 nm) in DMSO (fwhm = 170 fs). These states decay to form a triplet excited state with τ ~ 50 ns for **7** (Figure 4a, λ_{exc} = 532 nm, fwhm = 8 ns) in DMSO. Complex **7** is able to reduce MV^{2+} and the reduced $MV^{+\bullet}$ species with characteristic maxima at 395 nm and 605 nm was observed in the transient absorption spectrum (Figure 4b).[3] The ns TA spectrum of **7** shown in Figure 6a is consistent with the bleach of the ground state in the 550–700 nm range and positive absorption features that correspond to the reduced np ligand and oxidized DTolF/Rh_2, as determined by spectro-electrochemistry. Unlike complexes **1**–**4**, which feature ^{3}MC (metal-centered) lowest energy states, it appears that the lowest energy triplet state in **7** is ^{3}MLLCT. It should be noted that steady-state photolysis experiments with **7** in the presence of MV^{2+} and triethanolamine (TEOA) as a sacrificial donor in 1:4 DMF:H2O also resulted in the generation of the reduced acceptor, $MV^{+\bullet}$, based on the formation of the well known blue product with absorption maxima at 395 nm and 605 nm. It should be noted that this photochemistry is accessible with irradiation wavelengths throughout UV-vis, including with the use of a cut-off filter that results in $\lambda_{irr} \geq 645$ nm, consistent with the absorption spectrum of **7** (Figure 5b), with significant absorption in this range.

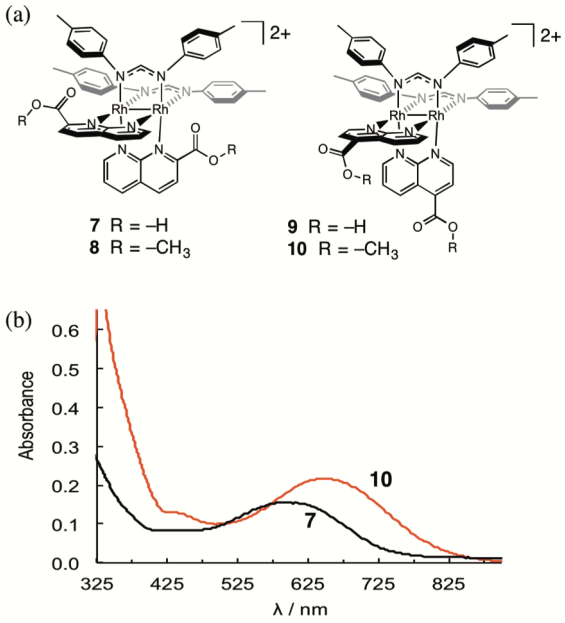


Figure 3. (a) Structures of **7**–**10** and (b) absorption spectra of **7** and **10** in DMSO.

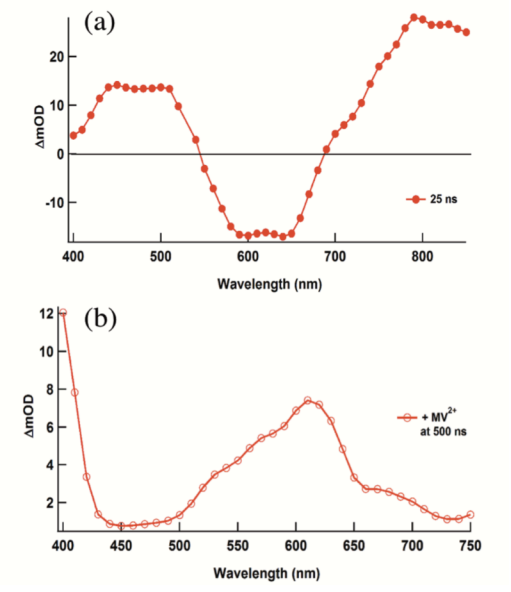


Figure 4. TA spectra of 0.2 mM **7** in the (a) absence (25 ns) and (b) presence of 2.6 mM MV^{2+} (500 ns) in DMSO (λ_{exc} = 532 nm, fwhm = 8 ns).

These Rh_2(II,II) complexes are not emissive at room temperature or 77K, such that estimation of the excited state energy, E_{00}, from the onset of the luminescence was not possible. Knowledge of the E00 value for the triplet states is necessary to estimate the excited state oxidation potential of the triplet state, E^{3*}_{ox}, since we believed this state must be involved in the bimolecular electron transfer we observed with MV^{2+}. In addition, we also observed electron transfer from **7** to the catalyst Co(dmg)Cl, where the formation of the Co(II) species was observed directly by transient absorption spectroscopy.

In order to determine the E^*_{ox} values of

7 and of the other Rh_2(II,II) complexes, we embarked on detailed energy transfer studies to first arrive at an estimate of E_{00}^T for each complex. Since the Rh_2(II,II) complexes are not emissive, the quenching of the lifetime of the long-lived $^3\pi\pi^*$ excited states of a series of organic molecules with known E_{00}^T energies, ranging from 1.93 eV (anthracene) to 1.15 eV (rubrene) and 0.78 eV (β-carotene), by each Rh_2(II,II) complex was examined using transient absorption measurements. Stern-Volmer plots of the τ_o/τ of the $^3\pi\pi^*$ state of each organic donor as a function of Rh_2(II,II) quencher resulted in quenching rate constants, k_q, that ranged from ~10^9 $M^{-1}s^{-1}$ for anthracene for all complexes and decreased with E($^3\pi\pi^*$) of the donor until no quenching was observed. None of the complexes quenched the $^3\pi\pi^*$ state of β-carotene (0.78 eV), but k_q values of 2.16×10^9 $M^{-1}s^{-1}$ and 2.03×10^8 $M^{-1}s^{-1}$ were measured for the quenching of anthracene and rubrene by **7**, respectively. Excited state oxidation or reduction is uphill in all cases with the exception of one series, and the values of k_q for the latter do not follow the expected trend with ΔG, such that if charge transfer is taking place, it must be a minor component of the observed quenching. Therefore, we believe that the quenching of the organic $^3\pi\pi^*$ state in these systems can be attributed to collisional energy transfer from the $^3\pi\pi^*$ state to the Rh_2(II,II) ^{3}MLLCT state.

In this manner, we were able to establish that the E_{00}^T of **7** must lie at ~1.1 eV, whereas those of **1**–**4** all lie at higher energies, ~1.7 eV for **1** and ~1.2 eV for **2**–**4**. Given these values, it appears that in **7** the ^{3}MLLCT state is positioned below the ^{3}MC state. The first oxidation and reduction waves in **7**–**10** occur at approximately +0.6 V and –0.6 V vs Ag/AgCl (CH_3CN, 0.1 M Bu_4NPF_6), respectively, resulting in E^*_{ox} ~ –0.5 V and E^*_{red} ~ +0.5 V vs Ag/AgCl from the ^{3}MLLCT states. Based on these estimates, and the reduction potential of MV^{2+} in CH_3CN, –0.40 V vs Ag/AgCl,[4] the electron transfer from the ^{3}MLLCT state of **7** is expected to be slightly favorable. It should be noted that the corresponding ^{1}MLLCT states of **7** and **10** are estimated to lie at ~3,000 cm^{-1} (~0.4 eV) above the ^{3}MLLCT state, making the singlet state more reducing and more oxidizing than the triplet by ~0.4 V.

In order to ascertain that the Rh_2(II,II) light absorber **7** could be used as the excited state electron in LA-CAT assemblies for H_2 production, we began by monitoring the bimolecular electron transfer from the triplet excited state of **7**, ^{3*}**7**, to a well-characterized cobaloxime catalyst for H_2 production. The Co(III) complex Co(dmgH)(py)Cl (dmgH = dimethylglyoximate) is a well known electrocatalyst for H_2 production. Pulse radiolysis experiments with Co(dmgH)(py)Cl resulted in an absorption maximum of the one-electron reduced Co(II) complex at ~460 nm, and for the two-electron Co(I) product at ~540 nm and ~630 nm.[5] The CoIII/II irreversible reduction was reported at E_p = –0.61 vs Ag/AgCl in DMF, followed by the CoII/I reduction at E_p = –0.98 V vs Ag/AgCl; the onset of the catalytic H_2 production wave was observed at –0.9 V vs Ag/AgCl in the presence of acid.[Error! Bookmark not defined.] Based on our results with complex **7**, with $E_{1/2}(Rh_2^{II,III/II,II})$ = +0.50 V vs Ag/AgCl in DMF and E_{00}^T ~1.15 eV, a value of E^*_{ox} ~ –0.65 V vs Ag/AgCl can be estimated. It was therefore expected that the excited state electron transfer from **7** to Co(dmgH)(py)Cl should be slightly exothermic, with ΔG ~ –0.05 V, to generate the Co(II) species.

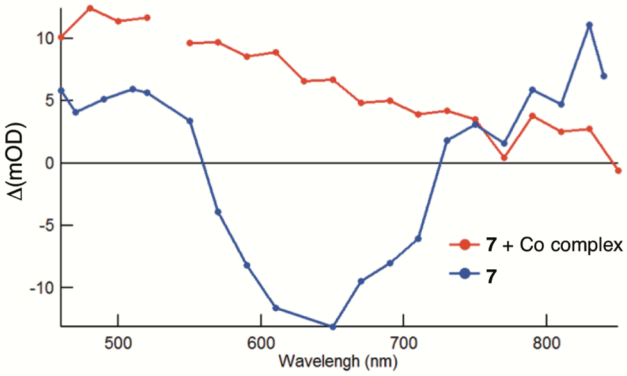


Figure 5. Transient absorption spectra of **7** alone (25 ns) and upon the addition of Co(dmgH)(py)Cl (100 ns) in CH_3CN (λ_{exc} = 532 nm, fwhm ~ 8 ns).

The transient absorption spectrum of 0.12 mM **7** shown in Figure 5 in deoxygenated CH_3CN reveals the spectral features of the ^{3}*MLLCT excited state and bleach of the complex collected ~25 ns after the laser pulse (λ_{exc} = 532 nm, fwhm ~ 8 ns) with τ ~ 40 ns. Upon addition of 5 mM Co(dmgH)(py)Cl, the lifetime of the observed transient increases to 250 ns with a spectrum that absorbs throughout the visible range and with a broad peak that maximizes at ~470 nm, collected 100 ns after the laser pulse (Figure 5). This new transient is attributed to electron transfer from **7** to the Co(III) complex, generating the Co(II) species, followed by charge recombination to regenerate the starting materials since the steady-state absorption spectrum of the solution remains unchanged after the transient absorption experiment.

Given the formation of the Co(II) species, we then attempted the same experiment but in the presence of excess sacrificial donor TEOA. The TEOA was expected to reduce **[7]$^+$** after it transferred an electron to the Co complex, thus regenerating **7** such that it could be excited again and reduce Co(II) to Co(I). Based on the position of the $Co^{II/I}$ wave at E_p = –0.98 V vs Ag/AgCl, ^{3}***7** would not be expected to reduce Co(II) to Co(I) in the Co(dmgH)(py)Cl complex. However, we did observe spectral changes and a new transient feature at ~900 ns after the 532 nm laser pulse. We are currently attempting to characterize the species formed under these conditions. It is possible that the redox potentials are shifted under the conditions of the experiment relative to those from the electrochemical measurements. It is also possible that, since back electron transfer is not possible in this experiment, the photogenerated Co(II)-Cl species may exchange chloride for the CH_3CN solvent, thus changing its reduction potential. Disproportionation of two Co(II) complexes to generate Co(I) and Co(III) starting material also needs to be considered as a possible reaction.

Extending the lifetime by blocking axial sites. The ligands 2-py-np [6] and 2-quinoxaline-np (2-q-np)[7] were used to block the axial positions (Figure 6), a property that we have now shown lengthens the excited state lifetime by several orders of magnitude. This increase in excited state lifetime is attributed to an increase in energy of the ^{3}MC state through strong interactions of the antisymmetric ligand combination of the axial ligands with with the Rh_2 d(σ*) orbital. In addition, solvent coordination at the axial sites is not be possible in these complexes, such that thermal deactivation through high frequency solvent vibrations will be inhibited.

Selected structures of this series of complexes, $[Rh_2(DTolF)_2(2\text{-py-np})_2]^{2+}$ and $[Rh_2(DTolF)_2(2\text{-q-np})(CH_3CN)_2]^{2+}$ and their crystal structures, are displayed in Figure 6a. The latter compound is important because it will serve as the precursor for mixed-ligand complexes, since the CH_3CN ligands

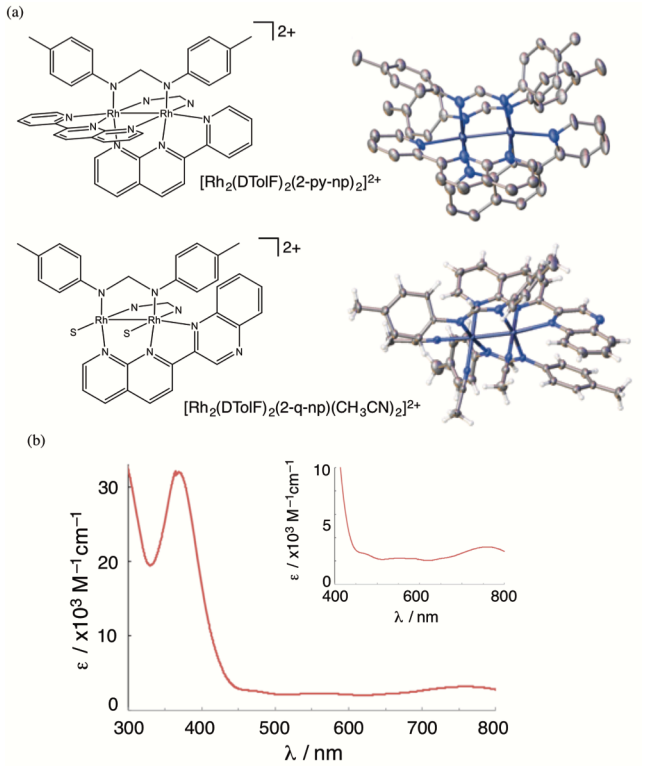


Figure 6. (a) Structures of new complexes with 2-py-np (top) and 2-q-np (bottom) ligands (S = CH_3CN) and corresponding X-ray crystal structures and (b) absorption spectrum of $[Rh_2(DTolF)_2(2\text{-q-np})_2](BF_4)_2$ in CH_3CN.

are easily replaced for other bridging ligands upon refluxing, such as 4-COOH-np. The electronic absorption spectrum of $[Rh_2(DTolF)_2(2\text{-q-np})_2]^{2+}$, with both axial positions blocked is shown in Figure 6b. This complex exhibits ε = 3,160 $M^{-1}cm^{-1}$ at 785 nm and absorbs strongly throughout the UV and visible ranges (Figure 5b and inset). The excited state properties of these new complexes were investigated, and our recently accepted manuscript describes the effect of blocking the axial ligands on the lifetime of singlet and triplet excited states, redox properties, and the ability of the excited state(s) to reduce electron acceptors. Importantly, $[Rh_2(DTolF)_2(2\text{-py-np})_2]^{2+}$ was shown to be able to both transfer electrons to MV^{2+} in solution from its ^{3}ML-LCT state and also to oxidize the phenylene diamine. These properties show that this class of complexes will be able to inject holes into NiO and electrons into TiO_2.

Electrocatalysis.

The Rh_2(II,II) complexes **1**–**10** are poised to undergo catalytic reduction of substrates because they are robust to changes in metal oxidation state, the two metals and the two diimine ligands, together with the non-innocent formamidinate bridges, can be used to store redox equivalents, making these complexes capable of coupling one-electron events with multi-electron transformations.

We discovered of the electrocatalytic reduction of H^+ and CO_2 by complexes **1**–**4**.[8,9] These complexes are able to electrocatalytically reduce H^+ to H_2 with high turnover frequencies (TOFs) and overpotentials, η, of ~0.5 V,[8] as well as to reduce CO_2 to HCOOH.[9] We now have experimental evidence that both the production of H_2 from H^+ and HCOOH. The molecular catalysts are stable after the acid and/or CO_2 is consumed since electrocatalysis is restored at the same rate upon the addition of substrate to the cell.[8,9] Moreover, we showed that the catalysis is not a result of a decomposition product deposited on the electrode, since placing an electrode from an active electrocatalytic solution into one that does not contain catalyst completely shuts down the reactivity.[8,9]

The proposed mechanism involves the formation of a Rh_2(II,III)–H (hydride) intermediate, which when reduced by one electron, would react with either a H^+ or undergo CO_2 insertion to produce H_2 or HCOOH, respectively. We now have ample experimental evidence for the Rh_2(II,III)–H species, generated independently from the reaction of $[Rh_2(DTolF)_2(phen)_2]^{2+}$ (**1**) with H_2 or D_2 gas, producing **1–H** and **1–D**, respectively, as previously reported for related complexes.[10,11] The IR spectra of **1**, **1–H**, and **1–D** collected as solids are compared in Figure 9b, where a new peak is observed for **1–H** at 1965 cm^{-1}, in a position similar to those reported for other terminal rhodium-hydride complexes.[11] Based on the literature, we expected this peak to shift by ~587 cm^{-1} to ~1378 cm^{-1} in **1–D**, [11] and we do observe a small increase in intensity at 1398 cm^{-1} (not shown). It was evident from attempts to collect ^{1}H NMR spectra that **1–H** is paramagnetic. As such, we were able to collect its EPR spectrum at 100K in CH_2Cl_2, which is clearly different than that of the chemically oxidized complex, $\mathbf{1}^+$. The latter compares well with EPR spectra of other lantern Rh_2(II,III) complexes previously reported, including $[Rh_2(DTolF)_4]^+$.[12] The reaction of **1–H** with CO_2 results in a new product that we are now attempting to characterize, but this result is consistent with the insertion of CO_2 into the Rh–H bond as proposed in Figure 9a. We are currently exploring the reactivity of **1–H** in hydride transfer reactions with other substrates and in the presence of CO_2 and reducing agents, as well as attempting to grow single crystals for x-ray diffraction.

References

(1) Li, Z.; Leed, N. A.; Dickson-Karn, N. M.; Dunbar, K. R.; Turro, C. "Directional charge transfer and highly reducing and oxidizing excited states of new dirhodium(II,II) complexes: potential applications in solar energy conversion" *Chem. Sci.* **2014**, *5*, 727-737.

(2) White, T. A.; Dunbar, K. R.; Thummel, R. P.; Turro, C. "Electronic influences of bridging and chelating diimine ligand coordination in formamidinate-bridged Rh_2(II,II) dimers" *Polyhedron* **2016**, *103*, 172-177.

(3) Watanabe, T.; Honda, K. "Measurement of the Extinction Coefficient of the Methyl Viologen Cation Radical and the Efficiency of Its Formation by Semiconductor Photocatalysis" *J. Phys. Chem.* **1982**, *86*, 2617-2619.

(4) Jacobi, D.; Abraham, W.; Pischel, U.; Grubert, L.; Stösser, Schanbel, W. "Oxidation of aryl-substituted cycloheptatrienes by photoinduced electron transfer" *J. Chem. Soc. Perkin Trans.* **1999**, *2*, 1695-1702.

(5) Kumar, M.; Natrajan, E.; Neta, P. "Electron Transfer and Alkyl Transfer with Cobaloximes in Aqueous Solutions. Kinetic Studies by Pulse Radiolysis" *J. Phys. Chem.* **1994**, *98*, 8024-8029.

(6) Aguirre, J. D.; Lutterman, D. A.; Angeles-Boza, A. M.; Dunbar, K. R.; Turro, C. "Effect of Axial Coordination on the Electronic Structure an Biological Activiti of Dirhodium(II,II) Complexes" *Inorg. Chem.* **2007**, *46*, 7494-7502.

(7) Ashford, D. L.; Glasson, C. R. K.; Norris, M. R.; Conceptcion, J. J.; Keinan, S.; Brennaman, M. K.; Templeton, J. L.; Meyer, T. J. "Controlling Ground and Excited State Properties through Ligand Changes in Ruhenium Polypyridyl Complexes" *Inorg. Chem.* **2014**, *53*, 5637-5646.

(8) White, T. A.; Witt, S. E.; Li, Z.; Dunbar, K. R.; Turro, C. "New Rh_2(II,II) Architecture for the Catalytic Reduction of H^+" *Inorg. Chem.* **2015**, *54*, 10042-10048.

(9) Witt, S. E.; White, T. A.; Li, Z.; Dunbar, K. R.; Turro, C. "Cationic dirhodium(II,II) complexes for the electrocatalytic reduction of CO_2 to HCOOH" *Chem. Commun.* **2016**, *52*, 12175-12178.

(10) Complex **1** (20 mg) was dissolved in ~1 mL distilled MeOH and hydrogenated at room temperature for 3 hours. A black solid was precipitated with ether and collected by vacuum filtration.

(11) Kohrt, C.; Hansen, S.; Drexler, H.-J.; Rosenthal, U.; Schulz, A; Heller, D. "Molecular Vibration Spectroscopy Studies on Novel Trinuclear Rhodium-7-Hydride Complexes of the General Type $\{[Rh(PP^*)X]_3(\mu_2\text{-}X)3(\mu_3\text{-}X)\}(BF_4)_2$ (X = H,D)" *Inorg. Chem.* **2012**, 51, 7377−7383.

(12) Piraino, P.; Bruno, G.; Shiavo, S.; L.; Laschi, F.; Zanello, P. "Synthesis, x-ray crystal structure, and electrochemical properties of the dirhodium(4+) complex $Rh_2(form)_4$ (from = N,N'-di-p-tolylsformamidinate anion)" *Inorg. Chem.* **1987**, 26, 2205-2211.