# Orientation of Cyano-Substituted Bipyridine Re(I) *fac*-Tricarbonyl Electrocatalysts Bound to Conducting Au Surfaces

Melissa L. Clark,<sup>†</sup> Benjamin Rudshteyn,<sup>‡</sup> Aimin Ge,<sup>§</sup> Steven A. Chabolla,<sup>†</sup> Charles W. Machan,<sup>†</sup> Brian T. Psciuk,<sup>‡</sup> Jia Song,<sup>§</sup> Gabriele Canzi,<sup>†</sup> Tianquan Lian,<sup>§</sup> Victor S. Batista,<sup>‡</sup> and Clifford P. Kubiak<sup>\*,†</sup>

<sup>†</sup>Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Dr. MC 0358, La Jolla, California 92093-0358, United States

<sup>‡</sup>Department of Chemistry, Yale University, 225 Prospect St., New Haven, Connecticut 06520, United States <sup>§</sup>Department of Chemistry, Emory University, 1515 Dickey Drive, NE, Atlanta, Georgia 30322, United States

**S** Supporting Information

**ABSTRACT:** Sum frequency generation spectroscopy (SFG) and calculations of SFG spectra based on density functional theory are combined to elucidate the orientation of two Re(R-2,2'-bipyridine)(CO)<sub>3</sub>Cl (R = 4-cyano or 4,4'-dicyano) electrocatalysts when adsorbed on conductive gold surfaces. We find that the electrocatalysts lean on the Au surface to orient the plane of the bipyridine ligand at 63° relative to the surface normal. While the weak binding of the complexes to the gold surface precluded the ability to perform surface immobilized catalysis, homogeneous electrochemical experiments show that



the molecular catalysts are active toward the reduction of  $CO_2$  to CO and carbonate in the triply reduced state (TOF of 13.3 and 7.2 s<sup>-1</sup> for the doubly and singly substituted complexes, respectively). These findings demonstrate the capabilities of the approach of including rigorous spectroscopic and theoretical methods for revealing the conformation and orientation of  $CO_2$  reduction catalysts bound to electrode surfaces, which are critical considerations for redox state transitions and catalytic turnover.

## INTRODUCTION

As global anthropogenic carbon dioxide  $(CO_2)$  emissions continue to rise, there is a need not only to reduce production of  $CO_2$  but also to use it as a substrate for value-added products. One solution would be to utilize this  $CO_2$  to synthesize liquid fuels, which would help create a carbon neutral cycle.<sup>1</sup> The first step of the cycle can be done by electrocatalytically reducing  $CO_2$ , and both heterogeneous<sup>2,3</sup> and homogeneous<sup>4,5</sup> systems have been employed for this purpose.<sup>6–8</sup> While homogeneous systems are favored for their selectivity and tunability, heterogeneous catalysts have the advantages of stability, low catalyst loading, and straightforward product separation. Linking molecular catalysts to conductive surfaces provides an opportunity to combine the advantages of both systems.<sup>9</sup>

It is important to understand the nature of catalyst-to-surface binding as orientation can greatly affect electron transfer and substrate access to the active site.<sup>10</sup> In recent years, infraredvisible sum frequency generation (SFG) spectroscopy has emerged as a useful tool for determining the average molecular orientation at surfaces and interfaces.<sup>11–14</sup> As a second-order nonlinear technique, it is only allowed at interfaces that lack an inversion symmetry and is therefore a useful technique for probing complexes adsorbed to solid surfaces. Previously, we have investigated the molecular orientation and vibrational relaxation dynamics of a series of fac-Re(dcbpy)(CO)<sub>3</sub>Cl (dcbpy = 4,4'-dicarboxy-2,2'-bipyridine) CO<sub>2</sub> reduction catalysts on single crystal TiO<sub>2</sub> and gold surfaces.<sup>15–17</sup> These studies indicated that the catalytically active site of the rhenium favorably oriented outward from the surface and that longer alkyl anchoring chains increased the tilt angle of the catalyst toward the TiO<sub>2</sub> surface.

Considering the great potential and interest in attaching molecular catalysts to electrode surfaces, more attachment strategies need to be investigated. Rebpy-based catalysts are excellent model systems because of their high activity for CO<sub>2</sub> reduction, the wealth of mechanistic information known, and the easy synthetic tunability of the bpy ligand.<sup>18,19</sup> A noncovalent attachment of a Rebpy catalyst to graphitic carbon demonstrated that strong binding was not necessary for immobilizing an active catalyst,<sup>20</sup> and this attachment strategy was successfully employed toward other molecular catalysts as well.<sup>21</sup> However, little is known about how these types of noncovalent attachment strategies affect the orientation of the complexes. This can be investigated using Au electrodes, as Au is well-known for its ability to form air-stable self-assembled monolayers (SAMs)<sup>22</sup> with multiple substituents of differing binding strengths.<sup>23</sup> Au is furthermore ideal for our purposes as

Received:November 6, 2015Revised:December 22, 2015Published:January 5, 2016

a commonly used metal surface for SFG spectroscopy.<sup>24</sup> Herein we report spectroscopic and molecular electrochemical studies of  $\text{Re}(\text{R-bpy})(\text{CO})_3\text{Cl}$  (R-bpy = 4,4'-dicyano-2,2'-bipyridine (1), 4-cyano-2,2'-bipyridine (2)) and characterization of their adsorption onto an Au surface by SFG spectroscopy coupled with DFT simulations.

## **EXPERIMENTAL SECTION**

**General Experimental Considerations.** <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 298 K on a Varian 500 MHz spectrometer. <sup>1</sup>H chemical shifts are reported relative to TMS ( $\delta = 0$ ) by referencing to deuterated solvent shifts. FT-IR spectra were performed on a Thermo Scientific Nicolet 6700, and UV–vis–NIR data were collected on a Shimadzu UV 3600 spectrophotometer using Starna Standard open top 10 mm path length cuvettes. Microanalyses were performed by NuMega Resonance Laboratories, San Diego, CA, for C, H, and N.

Reagents. Solvents were obtained from Fisher Scientific (and used as received) unless otherwise noted, and deuterated solvents and <sup>13</sup>CO<sub>2</sub>(g) were obtained from Cambridge Isotope Laboratories. Electrochemistry and spectroscopy solvents were degassed with argon, dried over alumina, and dispensed by a custom-made solvent dispensing system. Reagents were obtained from commercially available sources: pentacarbonylchlororhenium(I) from Sigma-Aldrich, 2-pyridylzinc bromide solution 0.5 M in THF from Acros Organics, tetrakis(triphenylphosphine)palladium(0) from Strem Chemicals, 4,4'-dicyano-2,2'-bipyridine from Carbosynth Limited, and 2-bromoisonicotinonitrile from Matrix Scientific. Tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>, Aldrich, 98%) was recrystallized twice from methanol and dried at 90 °C overnight before use in electrochemistry experiments. The ligand 4-cyano-2,2'bipyridine was synthesized according to literature procedure.<sup>25</sup>

Synthesis of Re(bpy-R) (CO)<sub>3</sub>Cl Complexes. Analogous to similar previously reported complexes,<sup>26</sup> an oven-dried round-bottom flask was charged with equal molar equivalents of Re(CO)<sub>5</sub>Cl and bipyridine ligand. Dry toluene (20 mL) was then added, and the solution was heated to reflux for 3 h under a nitrogen atmosphere. The mixture was cooled in the freezer before filtering and washing with cold pentane to collect the desired solid product, which was dried overnight in a vacuum oven at ~80 °C.

Re(4,4'-dicyano-2,2'-bipyridine) (CO)<sub>3</sub>Cl (1). Reaction of Re(CO)<sub>5</sub>Cl (177 mg, 0.489 mmol) with 4,4'-dicyano-2,2'bipyridine (101 mg, 0.489 mmol) to yield a bright red-orange powder (236 mg, 94% yield). <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  = 9.22 (sh d, J = 6, 2H), 8.76 (sh s, 2H), 7.95 (sh d, J = 6, 2H). <sup>13</sup>C{H} NMR (CD<sub>3</sub>CN): 156.54, 155.18, 130.82, 128.17, 124.36, 116.15. IR (ACN):  $\nu$ (CO) 2027, 1927, and 1911 cm<sup>-1</sup>. IR (KBr pellet):  $\nu$ (CO) 2027, 1926, and 1889 cm<sup>-1</sup>;  $\nu$ (CN) 2245 cm<sup>-1</sup>. UV–vis (ACN):  $\lambda_{max}/nm = 221, 246, 312, 435$ . ESI-MS (m/z) [M - H]<sup>-</sup>: calcd: 511.0; found: 511.1. Elemental analysis for complex with one DCM molecule C16H8Cl3N4O3Re calcd: C 32.20, H 1.35, N 9.39; found: C 32.16; H 1.55; N 9.48. Single crystals suitable for X-ray diffraction were grown by slow evaporation of a supersaturated solution of 1 in dichloromethane. Faradaic efficiency during bulk electrolysis for CO was  $18 \pm 5\%$  over three runs.

*Re*(4-cyano-2,2'-bipyridine) (CO)<sub>3</sub>Cl (2). Reaction of Re-(CO)<sub>5</sub>Cl (260 mg, 0.719 mmol) with 4-cyano-2,2'-bipyridine (130 mg, 0.719 mmol) to yield a bright orange powder (257 mg, 73% yield). <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  = 9.19 (d, 1H), 9.04 (d, 1H), 8.77 (s, 1H), 8.45 (d, 1H), 8.25 (t, 1H), 7.89 (d, 1H), 7.69 (t, 1H). <sup>13</sup>C{H} NMR (CD<sub>3</sub>CN): 157.84, 155.13, 154.81, 154.17, 141.16, 129.87, 129.27, 127.54, 125.53, 124.02, 116.24. IR (ACN):  $\nu$ (CO) 2025, 1922, and 1905 cm<sup>-1</sup>. IR (KBr pellet):  $\nu$ (CO) 2024, 1913, and 1894 cm<sup>-1</sup>;  $\nu$ (CN) 2240 cm<sup>-1</sup>. UV–vis (ACN):  $\lambda_{max}/nm = 243$ , 305, 403. ESI-MS (m/z) [M – H]<sup>-</sup>: calcd: 486.0; found: 486.1. Elemental analysis for C<sub>14</sub>H<sub>7</sub>ClN<sub>3</sub>O<sub>3</sub>Re calcd: C 34.54, H 1.45, N 8.63; found: C 34.47, H 1.50, N 8.53. Single crystals suitable for X-ray diffraction were grown from vapor diffusion of diethyl ether into a saturated solution of **2** in dichloromethane. Faradaic efficiency during bulk electrolysis for CO was 41 ± 2% over three runs.

**X-ray Crystallography.** Single crystal X-ray diffraction studies were carried out on a Bruker Kappa APEX-II CCD diffractometer equipped with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) or a Bruker Kappa APEX CCD diffractometer equipped with Cu K $\alpha$  radiation ( $\lambda = 1.54184$  Å). The crystals were mounted on a Cryoloop with Paratone oil, and data were collected under a nitrogen gas stream at 100(2) K using  $\omega$  and  $\phi$  scans. Data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXS) produced a complete phasing model consistent with the proposed structure. All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-97).<sup>27</sup>

Homogeneous Electrochemistry. Electrochemical experiments were performed on a BASi Epsilon potentiostat. A single compartment cell was used consisting of a 1 mm glassy carbon electrode or 1 mm gold electrode, Pt wire counter electrode, and an Ag/AgCl reference electrode (separated from the solution by a CoralPor tip). Cyclic voltammograms were performed at room temperature using a 5 mL acetonitrile solution of 1 mM of the complex, 0.1 M TBAPF<sub>6</sub> as the electrolyte, and 1 mM ferrocene as the internal reference. The solutions were purged with dried Ar or CO<sub>2</sub> and stirred before each experiment. Cyclic voltammograms are reported at a scan rate of 100 mV/s and referenced to ferrocene unless otherwise noted. Uncompensated resistance between the working and reference electrodes was corrected by using *iR* compensation on the potentiostat. Scan-rate dependence studies for each complex were carried out to ensure the homogeneity of the system (see Supporting Information). To determine  $i_{cat}/i_{p}$ , the  $i_{\rm p}$  is determined as the peak current under Ar of a reversible electron transfer, which in this case is the first reduction. The peak catalytic current  $(i_{cat})$  is determined by the highest point of the catalytic wave (under CO<sub>2</sub> atmosphere).

Bulk Electrolysis. Bulk electrolysis was performed in a custom threaded 60 mL single-compartment cell with a custom airtight Teflon top. The setup consists of a carbon rod working electrode, coiled Pt wire counter electrode (protected from the bulk solution by fritted glass), and an Ag/AgCl pseudoreference electrode (separated from solution by a CoralPor tip). The ACN solution (~40 mL) consisted of 0.1 M TBAPF<sub>6</sub> and 1 mM complex, sparged with either Ar or CO<sub>2</sub> Solutions were constantly stirred and protected from light during the experiment. The voltage chosen for electrolysis was that of slightly past the third reduction in cyclic voltammetry. Experiments were set to have the catalyst undergo four turnovers, each passing roughly 33 coulombs. Gas analysis was performed by sampling 1 mL of the headspace of the cell at the end of each experiment and injecting on a Hewlett-Packard 7890A series gas chromatograph with two molsieve columns

(30 m × 0.53 mm i.d. × 25  $\mu$ m film). The 1 mL injection was split between two columns, one with N<sub>2</sub> carrier gas and the other He to quantify both CO and H<sub>2</sub>, respectively. Instrument specific calibration curves were used to determine amount of each gas produced.

Infrared Spectroelectrochemistry (IR-SEC). IR-SEC experiments were carried out in a custom-made cell<sup>28</sup> with a glassy carbon working, platinum counter, and pseudoreference silver electrode. A N<sub>2</sub> sparged solution of 0.3 mM complex in 0.1 M TBAPF<sub>6</sub> in ACN was used, and a blank solution of 0.1 M TBAPF<sub>6</sub> in ACN was used for the FTIR solvent subtractions. For experiments under CO<sub>2</sub> or <sup>13</sup>CO<sub>2</sub>, the solution was saturated with the gas (~0.28 M) directly before use. A Pine Instrument Company model AFCBP1 bipotentiostat was used to apply potential to the system.

**Preparation of Au Slides and Surface Attachment.** Optically flat Au substrates consisting of a layer of Cr (1–4 nm) and Au (200–300 nm) evaporated onto borosilicate glass slides were used. For surface attachment of the catalysts, all Au substrates were cleaned using a Bunsen burner method.<sup>29</sup> The Au slide was then cooled under a stream of N<sub>2</sub> before being immediately submersed in a 1 mM solution of 1 or 2 in chloroform and stored in the dark for 1–3 days. The slide was then removed from solution, washed with pentane, and dried under N<sub>2</sub> before immediate use. The samples were stored overnight in the dark before SFG measurements.

SFG Spectroscopy. The broadband vibrational SFG setup is based on a 1 kHz Spitfire Ti:sapphire regenerative amplifier system (Spectra-Physics) producing 150 fs pulses at 800 nm  $(12500 \text{ cm}^{-1})$  with a pulse energy of 4 mJ. Half of the fundamental was used to pump a TOPAS-COPA (Light Conversion) producing tunable IR pulses, centered near 2000 cm<sup>-1</sup>, with energies of ~10–15  $\mu$ J and a bandwidth of ~150 cm<sup>-1</sup>. The remaining 2 mJ of 800 nm output was spectrally narrowed to  $\sim 10 \text{ cm}^{-1}$  by using a home-built pulse shaper. The visible pulses were filtered to 2  $\mu$ J and combined with the IR at the sample surface. The angles of incidence of visible and IR are  $65^{\circ}$  and  $50^{\circ}$  with respect to the surface normal, respectively. The reflected sum frequency signal was collimated and filtered to remove any residual IR and fundamental visible photons before being refocused onto the slit of an 300 mm monochromator (Acton Spectra-Pro 300i) and detected with an liquid nitrogen-cooled CCD (Princeton Instruments, PyLoN, 1340  $\times$  100 pixels) operating at -120 °C. All spectra were collected under PPP polarization combination (Ppolarized SFG, P-polarized visible, P-polarized IR). The SFG intensity  $I_{SFG,N}$  can be expressed as<sup>30-</sup>

$$I_{\rm SFG} \propto |\chi_{\rm NR}^{(2)} + \chi_{\rm R}^{(2)}|^2 I_{\rm IR} I_{\rm vis}$$
$$= \left| A_{\rm NR}^{(2)} e^{i\delta} + \sum_{q} A_{q,\rm eff}^{(2)} \frac{1}{\omega_{\rm IR} - \omega_{q} + i\Gamma_{q}} \right|^2 I_{\rm IR} I_{\rm vis}$$
(1)

. (2)

(2).2

where  $\chi_{\rm R}^{(2)}$  and  $\chi_{\rm NR}^{(2)}$  are the effective resonant and nonresonant nonlinear susceptibility tensors, respectively,  $I_{\rm IR}$  ( $I_{\rm vis}$ ) is the intensity of IR (visible) beam,  $\delta$  and  $A_{\rm NR}$  are the phase and amplitude of the nonresonant signal,  $A_{q}$ ,  $\omega_{q}$ , and  $\Gamma_{q}$  are the amplitude of effective resonant susceptibility, frequency, and damping constant of the *q*th vibrational mode, respectively, and  $\omega_{\rm IR}$  is the frequency of the incident tunable infrared beam. To remove the contribution of frequency dependence of the incident beam, we have defined a normalized SFG spectra ( $S_{\rm SFG}$ ) according to eq 2, in which the sample SFG spectra was normalized by the SFG spectra of a bare gold thin film  $(I_{Au})$  measured under the same condition.

$$S_{\rm SFG} = \frac{I_{\rm SFG}}{I_{\rm Au}} = \frac{\left| A_{\rm NR}^{(2)} e^{i\delta} + \sum_{q} A_{q,\rm eff}^{(2)} \frac{1}{\omega_{\rm IR} - \omega_{q} + i\Gamma_{q}} \right|^{2}}{|A_{\rm NR}^{(2)}|^{2}}$$
(2)

It was observed that the nonresonant signals from gold thin films decrease with complexes 1 or 2 adsorbed on the surfaces. The reason for this change is unclear; we speculate that it likely reflects an adsorption-induced change of the surface electronic density of states in gold. For convenience, the intensity of SFG spectra of bare gold has been rescaled to yield a normalized SFG signal such that the normalized  $S_{SFG} = 1$  when the signal is dominated by nonresonant Au response. In the discussion below, only these normalized SFG spectra are shown and analyzed.

**DFT Geometry Optimization.** Density functional theory (DFT) calculations were carried out with the local PW91<sup>33–37</sup> functional using the Gaussian 2009 software package<sup>38</sup> and its default integration grid and optimization criteria. The 6-31G(d) basis set<sup>39,40</sup> was used on nonmetal atoms, i.e., *C*, *H*, *N*, *Cl*, and O. The LANL2DZ<sup>41–43</sup> pseudopotential and basis set were used on metal atoms, i.e., Re and Au. Automated density fitting<sup>44,45</sup> was used to quicken the calculations. The system was treated as a restricted neutral singlet with Re(I) and an even number of Au atoms. Images for these calculations were generated using Avogadro 1.1.1.<sup>46</sup>

The Au(111) surface, an approximate model for the bulk Au used in the experiments, was prepared as follows using the gradient-corrected PBE level of theory with a single- $\zeta$  quality basis set within the plane-wave pseudopotential scheme as implemented in the SIESTA software package. As a first step, bulk Au was optimized starting with a four-atom bulk Au cell and calculating minimum energy lattice parameters and fractal atomic coordinates. The optimized bulk cell parameters were used to construct a supercell containing an Au(111) slab with four layers of Au atoms in a  $4 \times 6$  (11.8 Å  $\times$  17.8 Å) supercell. Periodic boundary constraints were used with Gamma point sampling corresponding to a single k-point for the supercell. Plane waves were given a kinetic energy cutoff of 200 Ry. Geometry optimization was done with a force tolerance of 0.004 eV/Å while freezing all Au atoms. This slab was then carved into a cluster of 32 atoms (27 below the complex and 5 more below that) ensuring that the axial ligand can face the surface without passing the edge of the cluster.

For the geometry optimizations, all gold atoms were frozen to closer approximate surface conditions. Additionally, the N atom of the cyano N–Au bond was arbitrarily frozen around 2.134 Å (complex 1) or 2.083 Å (complex 2) from the Au atom for monodentate binding. Similarly, two N atoms were frozen around 2.134 and 2.165 Å from the Au atoms for bidentate binding. These restrictions were needed to prevent unrealistic edge effects from occurring due to the small size of the cluster.

**Theoretical Simulation of SFG.** The macroscopic secondorder susceptibility can be separated into specific tensor components for each normal mode, q, with corresponding Fresnel factors as shown in eq 3.

$$\chi_{\text{ppp}}^{(2)} = \sum_{q} \left( -L_{xxx} \chi_{xxz,q}^{(2)} - L_{xzx} \chi_{xzx,q}^{(2)} + L_{zxx} \chi_{zxx,q}^{(2)} + L_{zzz} \chi_{zzz,q}^{(2)} \right)$$
(3)

Here,  $L_{ijk} + (i, j, k = x, y, z)$  are products of the Fresnel factors of the IR, visible, and SFG beam at the experimental incident angles, which can be calculated from the known complex reflective index of Au (see Table S6).

The microscopic molecular tensor components are determined by eq 4

$$\chi_{ijk,q}^{(2)} = \sum_{l,m,n} \langle R_{il} R_{jm} R_{kn} \rangle A_{lmn,q}$$
(4)

where  $A_{lmn,q}$  is the molecular hyperpolarizability tensor element for each normal mode, q, and  $\langle R_{il}R_{jm}R_{kn}\rangle$  is the average product of the Euler transformation matrix components. Molecular reference frame Cartesian axes (l, m, n) for 1 and 2 are depicted in Figure 3A,B. Molecular rotation is performed via the  $Z_{\phi}Y_{\theta}Z_{\psi}$ rotation matrix, where the  $\theta$  angle is the tilt angle, the  $\psi$  angle is the twist angle, and the  $\phi$  angle is the final spin angle. Complexes in a laboratory setting are assumed to be distributed isotropically on the surface of Au; therefore,  $\chi$  is averaged of all  $\phi$  angles 0°-359° in increments of 5° in the simulated SFG polarized spectra.

Molecular hyperpolarizability tensor elements are determined by the partial derivatives of the polarizabilities  $\alpha_{lm}$  and dipole moments  $\mu_n$  with respect to the coordinate, Q, of a given normal mode, q, as shown in eq 5.

$$A_{lmn,q} = \frac{\partial \alpha_{lm}}{\partial Q_q} \frac{\partial \mu_n}{\partial Q_q} \tag{5}$$

Polarizability derivatives and dipole moment derivatives with respect to normal mode coordinates were obtained from *ab initio* molecular orbital calculations. Geometry optimization, energy minimization, and vibrational normal-mode analysis were performed for gas phase complexes using DFT. These were carried out with the hybrid  $B3LYP^{47-50}$  functional using Gaussian 2009<sup>38</sup> and its default integration grid and optimization criteria. The 6-311+G(d) basis set<sup>39,40</sup> was used on nonmetal atoms, i.e., C, H, N, Cl, and O. The SDD pseudopotential and basis set<sup>51</sup> was used on the Re atom. Images for these calculations were generated using Gauss-View.<sup>52</sup> Theoretical frequencies were scaled by 0.975.

The SFG spectra of the sample have been fitted according to eqs 2–4 with theoretically derived amplitudes  $(A_{lmn,q})$  from the PW91 cluster geometries.  $A_{\text{NR}}$ ,  $\Gamma_{q^{\prime}}$  and orientation angles ( $\theta$ and  $\psi$ ) are fitting parameters.  $\Gamma_q$  determines the width of the resonant peaks.  $A_{\text{NR}}$  is used as a scaling factor to ensure that the overall amplitude of computed SFG spectra match the experimental values. The relative SFG amplitudes of the three CO stretching modes are determined by the relative values of computed  $A_{lmn,q}$  and orientation angles ( $\theta$  and  $\psi$ ). The angular dependence enables us to determine molecular orientation by comparing the measured and computed SFG spectra.

The fitting parameters listed in Table S4 were obtained allowing frequencies to relax (Figure 4) while parameters obtained for fixed frequencies are listed in Table S3 (Figure S14). For complex 2, the frequencies relaxed within  $\pm 20$  cm<sup>-1</sup>. The nonresonant amplitudes were restricted to be positive, and the damping constants were restricted to be between 0 and 25.

## RESULTS AND DISCUSSION

**Synthesis and Characterization of Molecular Catalysis.** The ligand 4-cyano-2,2'-bipyridine (CN-bpy) was synthesized as previously reported by the Negishi coupling of 2-pyridylzinc bromide and 2-bromo-4-cyanopyridine.<sup>25</sup> The two complexes Re(diCN-bpy) (CO)<sub>3</sub>Cl (1) and Re(CN-bpy) (CO)<sub>3</sub>Cl (2) (Figure 1) were synthesized similarly to



Figure 1.  $Re(diCN-bpy)(CO)_3Cl(1)$  and  $Re(CN-bpy)(CO)_3Cl(2)$ .

analogous compounds<sup>26</sup> and characterized by NMR, FTIR, UV–vis, and elemental analysis. Single crystals suitable for X-ray diffraction studies were grown by slow evaporation of a supersaturated solution of 1 or 2 in dichloromethane (Figure S1). A crystallographic data summary and key bond lengths and angles are presented in Tables S1 and S2, respectively. Previous studies of the Re(bpy)(CO)<sub>3</sub>Cl catalysts suggest that electron-withdrawing groups on the bipyridine ligands generally lower the activity of CO<sub>2</sub> reduction for catalysis.<sup>53</sup> Thus, we note that 1 and 2 were not expected to be optimal catalysts, but they do represent two of the very few options for catalyst attachment to Au surfaces, namely cyanide,<sup>54</sup> isocyanide,<sup>55</sup> and thiol<sup>56,57</sup> linkages.

Electrochemical experiments in acetonitrile (ACN) solution were conducted to probe the catalytic activity of the unsupported complexes. The cyclic voltammograms (CV) of both 1 and 2 show three one-electron reductive features (Figure 2): a quasi-reversible wave followed by two irreversible reductions. At higher scan rates, the second reduction becomes more reversible for 1 (-1.63 V; all potentials vs  $Fc/Fc^+$ ) indicative of a slow chemical step on the CV time scale. The second reduction for 2(-1.87 V) as well as the third reductive wave for both complexes (1: -2.43 V; 2: -2.80 V) remain irreversible even at high scan rates (Figures S2 and S3). Under saturated CO<sub>2</sub> conditions (~0.28 M in ACN), current enhancement is observed only at the third reduction. This is in contrast to most previous reported Rebpy-based catalysts, which are catalytically active in their doubly reduced state,<sup>26</sup> although not unprecedented when electron-withdrawing substituents are employed.<sup>58</sup> This underscores the importance of considering the interplay between the donor-acceptor properties of the groups used to attach catalysts to surfaces and their effect on the  $\pi$ -system of the bpy ligand. Comparing the peak current under Ar and CO<sub>2</sub> saturated conditions, 1 is more active than 2 with  $i_{cat}/i_p$  values of 8.3 and 6.1 and turnover frequencies (TOF)<sup>59</sup> of 13.3 and 7.2 s<sup>-1</sup> for 1 and 2, respectively.

Controlled potential electrolysis (CPE) with sampling of the headspace for gas chromatography identified the production of CO. Gaseous products were not detected in CPE experiments under inert gas, indicating CO is a product of catalysis. An FTIR spectrum was taken of the CPE solution after the experiment, which in addition to showing stretches akin to an intermediate species of the catalyst (as compared to IR-SEC spectra, *vide infra*), a peak at 1684 cm<sup>-1</sup> was also observed (Figure S5). This can be assigned to a carboxyamide stretch, which is most likely a decomposition product from the hydrolysis of the cyano groups. This has also been observed for Re(4-methyl-4'-cyano-2,2'-bipyridine)(CO)<sub>3</sub>Cl.<sup>60</sup>

Infrared spectroelectrochemistry (IR-SEC) experiments<sup>28</sup> were performed to further characterize the products of catalysis.



**Figure 2.** Cyclic voltammograms of 1 (A) and 2 (B) under argon (black) and  $CO_2$  (red). Reductive waves for 1 occur at -1.20, -1.63, and -2.43 V vs Fc/Fc<sup>+</sup> and for 2 at -1.41, -1.87, and -2.80 V vs Fc/Fc<sup>+</sup>. Conditions: 1 mM analyte, 0.1 M TBAPF<sub>6</sub> in ACN with a glassy carbon working, Pt counter, and Ag/AgCl pseudo reference electrodes at 100 mV/s with 1 mM ferrocene added as an internal reference. The current increase of the third reduction under  $CO_2$  is indicative of catalysis.

Under inert  $(N_2)$  and catalytic conditions  $(CO_2 \text{ saturation})$ , similar reduced states were observed through the carbonyl and cyano region of the IR spectra for both complexes (Figures S6-S8). New bands however were observed at 1672 and 1282 cm<sup>-1</sup>, which correspond with the formation of carbonate  $(CO_3^{2-})$ . To confirm the production of  $CO_3^{2-}$  as a product of catalysis, the experiment was repeated with <sup>13</sup>CO<sub>2</sub>. In the IR-SEC of 2 under these conditions (Figure S9) the carbonate bands shifted to lower in energy by 41 and 17 cm<sup>-1</sup>, respectively, which is close to the shift expected by the harmonic oscillator model (~15 cm<sup>-1</sup> per bond).<sup>61,62</sup> This indicates  $CO_3^{2-}$  is being formed from  $CO_2$  and not labile carbonyl ligands. Because of the weak strength of the expected CO(g) stretch and its possibility to overlap with that of the cyano group ( $\nu$ (CO) 2137 cm<sup>-1</sup>), carbon monoxide was not definitively detected in these measurements. These results from CPE and IR-SEC experiments indicate the reaction catalyzed is the disproportionation of two equivalents of gaseous CO<sub>2</sub> to CO and  $CO_3^{2-.63}$  To the best of our knowledge, the thermodynamic potential for the reaction of  $2CO_2 + 2e^- \rightarrow$  $CO + CO_3^{2-}$  has not been determined in ACN, most likely due to the unavailable free energy thermodynamic values for carbonate in ACN. The closest approximation for a thermodynamic potential would be for the reaction of  $2CO_2$ + 2H<sub>2</sub>O + 2e<sup>-</sup>  $\rightarrow$  CO + H<sub>2</sub>O + HCO<sub>3</sub><sup>2-</sup> (where  $E^{\circ} = -0.65$  vs NHE or approximately -1.3 V vs Fc/Fc<sup>+</sup>),<sup>64</sup> which is likely occurring due to our electrochemical solutions inescapably having small amounts of H<sub>2</sub>O present. With this consideration and by using the half-wave potential method,<sup>65</sup> these complexes have overpotentials of -1.0 V for 1 and -1.3 V for 2. In part, these large overpotentials result from the fact that both CNbpy ligands produce Re catalysts that reduce CO2 at the potential of the most negative of three redox processes while typical Rebpy catalysts reduce CO2 at the potential of the second redox process.

Further electrochemical studies were performed to access the interactions of 1 and 2 with gold electrodes. As molecular (nonimmobilized) catalysts, 1 and 2 behave similarly using an Au electrode as they did using a glassy carbon electrode with almost identical reduction potentials (Figure S10); however, catalysis could not be observed due to the potential window of Au being more positive than the third reduction of the complexes (ca. -2.3 V vs Fc/Fc<sup>+</sup> under an atmosphere of CO<sub>2</sub>, Figure S11). Even at slow scan rates (25 mV/s) there was no discernible catalyst/surface interaction on the CV time scale.

These scans were repeated using a gold coated slide where the complex was adsorbed onto the surface as determined by SFG. No current response for either catalyst was observed in aqueous or organic solvents. This is most likely due to the weak nature of the Au–NC interaction and the large overpotential of the complexes, such that the adsorbed complexes dissociate from the Au surface before any redox features can be observed. We further probed the ability for the SAM to stay on the gold surface in different solvents by gently rinsing a coated slide with various solvents before taking surface measurements. It was found that ACN, ethanol, tetrahydrofuran, water, acetone, chloroform, and dichloromethane all removed the complexes from the surface; thus, no further electrochemical measurements were made.

**Catalyst Orientation on Au Surface by DFT Calculation.** Cyano groups have been found to bind weakly with gold;<sup>23</sup> thus, a particular geometry of the complexes 1 and 2 on gold surfaces could not be assumed. To determine the lowest energy binding modes to the surface, density functional theory (DFT) with the PW91 functional was used to find optimized geometries of the complexes on an Au(111) model cluster. Several possible binding orientations were investigated under restrictions of at least one cyano group bound to a gold atom.

The DFT-optimized geometries for complexes 1 and 2 are depicted in Figure 3. Orientation of the complex is described using angles corresponding to the tilt  $(\theta)$ , twist  $(\psi)$ , and rotation ( $\phi$ ) of the molecule relative to the Au surface (Figure 3A). Throughout, the tilt angles  $(\theta)$  are found to be close to 63°; however, the energetic analysis shows that there is no significant preference for which axial ligand faces the surface (CO or Cl) for either complex. This tilt angle is in agreement with previous reports of the preference of CN groups to orient parallel to metal surfaces.<sup>66</sup> In the case of complex 1, both mono- and bidentate (Figure S12) cyano binding modes were explored. Starting from the bidentate structure with only one cyano group bound to the surface, letting the N-Au bond relax leads to spontaneous dissociation of the second cyano group. This suggests that monodentate binding is more stable than bidentate binding even though the cyano groups span a similar distance to that between two Au atoms separated by 2 other Au atoms (8.6 Å). The preference for monodentate binding may be due to the added flexibility it offers in getting the axial CO ligand closer to the surface and thus interacting with the Au surface. In the monodentate structure of 1, the distance between the CO and the nearest Au atom is 3.3 Å while in the



**Figure 3.** (A) Schematic illustration of the orientation angles used to model the complex on the gold thin film surface. Axes *x*, *y*, and *z* represent the laboratory coordinates of the gold surface, while *a*, *b*, and *c* represents the molecular coordinates of the complex. Orientation angles  $\theta$ ,  $\psi$ , and  $\phi$  are the Euler transformation angles between the two Cartesian coordinates in the ZYZ rotation matrix formalism. (B) Molecular axis system for complex **1**. The same axis system is used for complex **2**. (C–F) DFT optimized monodentate geometries for **1** for either Cl facing the surface (C) or CO facing the surface (D). DFT optimized geometries for **2** with Cl facing the surface (E) and CO facing the surface (F). Values indicated are the tilt angle ( $\theta$ ), twist angle ( $\psi$ ), and the energy ( $\Delta E$ ) relative to the geometry labeled with " $\Delta E = 0$ " of that complex.

bidentate structure it is 3.5 Å, slightly farther. These are similar to recent results obtained of **2** using infrared reflection absorption spectroscopy (IRRAS).<sup>67</sup> In the monodentate structures of **1**, the unattached arm is found tilted about 10° from being in a bidentate configuration (Figure 3C,D). To compare to similar complexes that have carboxy linkages to  $TiO_{2}$ ,<sup>16</sup> orientations of **1** and **2** were simulated where the bpy ligand is perpendicular to the surface (Figure S13). These structures were found to be less stable than the CO facing monodentate structures (Figure 3B,D) by 9.64 and 7.56 kcal/ mol for **1** and **2**, respectively, indicating a strong relationship between the binding strength of the anchoring group and the molecular orientation of the complex on the surface.

Orientation Confirmation by SFG Spectroscopy. To determine which of the calculated orientations most likely exist on the surface, SFG measurements were performed to compare to simulated SFG spectra from the DFT optimized structures. The efficacy of using SFG to determine molecular orientation comes from the technique's capability to use the dependencies of the polarization of SFG signal on the vibrational transition moments of the adsorbed species.<sup>11-16</sup> That is, the SFG signal comes from the sum of a constant frequency visible beam and a tunable infrared beam (tunable to the vibrational resonance of the molecule) overlapping at the surface of the material. This creates an output beam-the sum frequency signal, which is the sum of these two input beams. A resonant SFG signal can only be obtained from vibrational modes that are both Raman- and IR-active, and the intensity of the resulting SFG signals of different normal modes can be used to determine molecular geometry by simulation. Self-assembled monolayers of complexes 1 and 2 were prepared by soaking a cleaned Aucoated glass slide in a 1 mM solution of the complex in chloroform for 3 days. The sample was then washed with pentane and dried under N2 before being used for SFG measurements.

The normalized experimental SFG spectra and matching simulated DFT spectra of 1 and 2 are displayed in Figure 4. Both experimental spectra were collected under PPP polarization combination (P-polarized SFG, P-polarized visible, Ppolarized IR). The resonant signals of the complexes are greatly affected by the strong nonresonant signals from the Au surface, resulting in an "S-shaped" signal.<sup>32</sup> The overlap and differing amplitudes of the carbonyl stretches as well as interference with Au signal in the SFG prevent direct comparisons to the IR spectra, in both shape and band energy assignment. Simulated SFG spectra were found by using the B3LYP functional with the orientation angles from the optimized geometries. Plotting the simulated SFG spectrum (Figure S17) with the nonresonant contribution removed against the corresponding experimental IR spectrum shows that there is a significant loss of features in the simulated spectrum as well as a red-shift. Figure S18 shows that the SFG amplitudes are highly sensitive to these orientation angles, especially to  $\theta$ . For example, the symmetric a'(1) stretch loses half of its intensity in going from  $\theta = 0^{\circ}$  to  $\theta = 30^{\circ}$  ( $\psi$  fixed at  $80^{\circ}$ ). The same kind of loss would require  $\psi$  to change from 0° to 60° ( $\theta$  fixed at 65°).

The geometry that most closely related to the experimental SFG data was that of the CO ligand facing the surface for both complexes with monodentate binding (Figure S14 and Table



Figure 4. Representative PPP-polarized SFG spectra of (A) 1 and (B) 2 monolayers adsorbed onto gold thin films (black circles) with DFT simulations of the SFG spectra (red).

S3). In order to achieve a more accurate spectral fit, the calculated frequencies were allowed to relax by  $\pm 20$  cm<sup>-1</sup> (Figure 4, red line). This corresponds to a 1% error (20  $cm^{-1}$ relative to 2000 cm<sup>-1</sup>) in the calculated frequency while not changing the expected orientation. The fitted frequencies for complex 1 give an in-phase symmetric a'(1) stretch around  $2028 \text{ cm}^{-1}$ , an antisymmetric a" stretch around 1948 cm $^{-1}$ , and an out-of-phase symmetric a'(2) stretch around 1946 cm<sup>-1</sup>. For complex 2 these stretches are around 2028, 1981, and 1931 cm<sup>-1</sup>, respectively (other fitting parameters are given in Table S4 and spectral data in Table S5). According to the spectral shape and the DFT simulations, the a'' and a'(1) modes have amplitudes opposite in sign relative to the a'(2) mode. The a''mode has an intensity about 3 times smaller compared to the other two modes; thus, the peak near 1960 cm<sup>-1</sup> originates mostly from the a'(2) mode. As a result, the contribution of the a" mode in the SFG spectra and the resulting fitted frequency is not as well-defined. We found that the nonresonant amplitude (and phase) was about 1.83  $(-6^{\circ})$  for complex 1 and 1.02  $(17^{\circ})$  for complex 2, indicating the two molecules interact slightly differently with the gold surface.

The calculated SFG spectra from the other optimized geometries had clear differences to rule them out as possible orientations (Figure S15). Those with the Cl facing toward the Au surface led to SFG spectra with a strong intensity a'(2) stretch and almost no intensity from the other two modes. Bidentate binding of complex 1 was ruled out based on the mismatched intensities. The SFG spectra also rule out bidentate binding as the nonzero value of the a" stretch indicates a twist relative to the surface that could not be achieved if both cyano groups adsorbed onto Au. The differences in the spectra in Figure 4 for 1 and 2 despite their similar binding modes are due to the sensitivity of SFG to slight differences in orientations. Figure S16 shows that using the orientation angles for 2 makes the SFG spectrum for 1 resemble that of 2.

It is important to note that in this calculation we have used the hyperpolarizability calculated for isolated molecules. If there exists strong intermolecular interaction due to close proximity of molecules on surface, the hyperpolarizability tensor elements may change, which would affect the orientations determined from fitting the SFG spectra. This possibility cannot be excluded, although it is not very likely according to the preferred binding geometry shown in Figure 3.

## CONCLUSIONS

We have determined the binding geometries of a pair of molecular electrocatalysts bound to Au(111) by combining SFG spectroscopy and DFT calculations of SFG spectra. The complexes Re(diCN-bpy)(CO)<sub>3</sub>Cl and Re(CN-bpy)(CO)<sub>3</sub>Cl were found to be catalytically active toward CO<sub>2</sub> in their triply reduced states, generating equimolar amounts of carbon monoxide and carbonate. No electrochemical behavior was observed from immobilized 1 or 2 on an Au surface, as the weak binding nature of the Au-NC interaction coupled with the large overpotential of the catalysts led to dissociation of the complexes from the surface before any redox features could be observed. Under no applied potential, both complexes orient into an adsorbed monolayer on Au surfaces as characterized by SFG. Based on DFT optimized geometries, the weak binding of the cyano groups to Au surfaces lends to a large tilt angle, orienting the bpy ligand more parallel to the surface with the axial chloride facing up, a favorable orientation for redox state transitions and catalysis. The similar binding orientation of both complexes and the lack of bidentate binding of  $\text{Re}(\text{diCN-byy})(\text{CO})_3\text{Cl}(1)$  demonstrates that only one anchoring group may be needed for the attachment of molecular catalysts to conductive surfaces. These conclusions highlight the strength in the methodology of coupling DFT with SFG spectroscopy to determine and verify the binding modes and orientations of transition metal electrocatalysts on metallic electrodes, demonstrating the careful balance between active molecular catalysts and attachment strategies, both of which are needed to create a deployable  $\text{CO}_2$  reduction system.

## ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b10912.

Crystallographic structures, select bond lengths, and refinement details (CCDC 1432450-1432451); molecular electrochemistry figures: scan rate dependence, bulk electrolysis, infrared spectroelectrochemistry, and CVs with an Au electrode; additional simulated binding geometries and SFG spectra; DFT refinement parameters; DFT theoretical coordinates (PDF) Structure of Re(diCN-bpy)(CO)<sub>3</sub>Cl (CIF) Structure of Re(CN-bpy)(CO)<sub>3</sub>Cl (CIF)

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*Tel (858) 822-2665; e-mail ckubiak@ucsd.edu (C.P.K.).

#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

This material is based upon work supported by AFOSR Grant #FA9550-13-1-0020. S.C. acknowledges support from a NSF GRFP award. B.R. acknowledges support from the National Science Foundation Graduate Research Fellowship under Grant DGE-1122492. V.S.B. acknowledges computer time from the supercomputing facilities at Yale as well as at NERSC. M.L.C. thanks Tram Dang for assistance with gold sample preparation. The authors also thank Dr. Arnold Rheingold and Dr. Curtis Moore for their assistance with X-ray crystallography, the UCSD Chemistry & Biochemistry Molecular MS Facility for mass spectrometry analyses, and Dr. Wendu Ding and Dr. Ke R. Yang for their advice on the calculations.

#### REFERENCES

(1) Whipple, D. T.; Kenis, P. J. A. Prospects of  $CO_2$  utilization via direct heterogeneous electrochemical reduction. *J. Phys. Chem. Lett.* **2010**, *1*, 3451–3458.

(2) Hori, Y.; Kikuchi, K.; Suzuki, S. Production of CO and  $CH_4$  in electrochemical reduction of  $CO_2$  at metal electrodes in aqueous hydrogencarbonate solution. *Chem. Lett.* **1985**, 1695–1698.

(3) Hori, Y. Electrochemical  $CO_2$  reduction on metal electrodes. Mod. Asp. Electrochem. **2008**, 42, 89–189.

(4) Benson, E. E.; Kubiak, C. P.; Sathrum, A. J.; Smieja, J. M. Electrocatalytic and homogeneous approaches to conversion of  $CO_2$  to liquid fuels. *Chem. Soc. Rev.* **2009**, *38*, 89–99.

(5) Windle, C. D.; Perutz, R. N. Advances in molecular photocatalytic and electrocatalytic  $CO_2$  reduction. *Coord. Chem. Rev.* **2012**, 256, 2562–2570.

(6) Qiao, J.; Liu, Y.; Hong, F.; Zhang, J. A review of catalysts for the electroreduction of carbon dioxide to produce low-carbon fuels. *Chem. Soc. Rev.* **2014**, *43*, 631–675.

(7) Kumar, B.; Llorente, M.; Froehlich, J.; Dang, T.; Sathrum, A.; Kubiak, C. P. Photochemical and photoelectrochemical reduction of CO<sub>2</sub>. *Annu. Rev. Phys. Chem.* **2012**, *63*, 541–569.

(8) 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.; et al. Frontiers, opportunities, and challenges in biochemical and chemical catalysis of CO<sub>2</sub> fixation. *Chem. Rev.* **2013**, *113*, 6621–6658.

(9) Wrighton, M. S. Surface functionalization of electrodes with molecular reagents. *Science* **1986**, *231*, 32–37.

(10) Prezhdo, O. V.; Duncan, W. R.; Prezhdo, V. V. Dynamics of the photoexcited electron at the chromophore-semiconductor interface. *Acc. Chem. Res.* **2008**, *41*, 339–348.

(11) Chen, Z.; Shen, Y. R.; Somorjai, G. A. Studies of polymer surfaces by sum frequency generation vibrational spectroscopy. *Annu. Rev. Phys. Chem.* **2002**, *53*, 437–465.

(12) Shen, Y. R. Phase-sensitive sum-frequency spectroscopy. Annu. Rev. Phys. Chem. 2013, 64, 129–150.

(13) Johnson, C. M.; Baldelli, S. Vibrational sum frequency spectroscopy studies of the influence of solutes and phospholipids at vapor/water interfaces relevant to biological and environmental systems. *Chem. Rev.* **2014**, *114*, 8416–8446.

(14) Wang, H. F.; Velarde, L.; Gan, W.; Fu, L. Quantitative sumfrequency generation vibrational spectroscopy of molecular surfaces and interfaces: lineshape, polarization, and orientation. *Annu. Rev. Phys. Chem.* **2015**, *66*, 189–216.

(15) Anfuso, C. L.; Xiao, D. Q.; Ricks, A. M.; Negre, C. F. A.; Batista, V. S.; Lian, T. Q. Orientation of a series of  $CO_2$  reduction catalysts on single crystal TiO<sub>2</sub> probed by phase-sensitive vibrational sum frequency generation spectroscopy (PS-VSFG). *J. Phys. Chem. C* **2012**, *116*, 24107–24114.

(16) Anfuso, C. L.; Snoeberger, R. C., III; Ricks, A. M.; Liu, W.; Xiao, D.; Batista, V. S.; Lian, T. Covalent attachment of a rhenium bipyridyl  $CO_2$  reduction catalyst to rutile  $TiO_2$ . J. Am. Chem. Soc. **2011**, 133, 6922–6925.

(17) Anfuso, C. L.; Ricks, A. M.; Rodríguez-Córdoba, W.; Lian, T. Ultrafast vibrational relaxation dynamics of a rhenium bipyridyl CO<sub>2</sub>–reduction catalyst at a Au electrode surface probed by time-resolved vibrational sum frequency generation spectroscopy. *J. Phys. Chem. C* **2012**, *116*, 26377–26384.

(18) Grice, K. A.; Kubiak, C. P. In *Advances in Inorganic Chemistry*; Michele, A., Rudi van, E., Eds.; Academic Press: 2014; Vol. 66, Chapter 5, pp 163–188.

(19) Keith, J. A.; Grice, K. A.; Kubiak, C. P.; Carter, E. A. Elucidation of the selectivity of proton-dependent electrocatalytic  $CO_2$  reduction by *fac*-Re(bpy) (CO)<sub>3</sub>Cl. *J. Am. Chem. Soc.* **2013**, *135*, 15823–15829.

(20) Blakemore, J. D.; Gupta, A.; Warren, J. J.; Brunschwig, B. S.; Gray, H. B. Noncovalent immobilization of electrocatalysts on carbon electrodes for fuel production. *J. Am. Chem. Soc.* **2013**, *135*, 18288–18291.

(21) Kang, P.; Zhang, S.; Meyer, T. J.; Brookhart, M. Rapid selective electrocatalytic reduction of carbon dioxide to formate by an iridium pincer catalyst immobilized on carbon nanotube electrodes. *Angew. Chem., Int. Ed.* **2014**, *53*, 8709–8713.

(22) Dubois, L. H.; Nuzzo, R. G. Synthesis, structure, and properties of model organic surfaces. *Annu. Rev. Phys. Chem.* **1992**, 43, 437–463.

(23) Kiguchi, M.; Miura, S.; Hara, K.; Sawamura, M.; Murakoshi, K. Conductance of a single molecule anchored by an isocyanide substituent to gold electrodes. *Appl. Phys. Lett.* **2006**, *89*, 213104.

(24) Bain, C. D. Sum-frequency vibrational spectroscopy of the solid/liquid interface. J. Chem. Soc., Faraday Trans. **1995**, 91, 1281.

(25) Fang, Y.-Q.; Hanan, G. S. Rapid and efficient synthesis of functionalized bipyridines. *Synlett* **2003**, 2003, 0852–0854.

(26) Smieja, J. M.; Kubiak, C. P. Re(bipy-tBu)  $(CO)_3$ Cl-improved catalytic activity for reduction of carbon dioxide: IR-spectroelec-trochemical and mechanistic studies. *Inorg. Chem.* **2010**, *49*, 9283–9289.

(27) Sheldrick, G. A short history of SHELX. Acta Crystallogr., Sect. A: Found. Crystallogr. 2008, 64, 112–122.

(28) Machan, C. W.; Sampson, M. D.; Chabolla, S. A.; Dang, T.; Kubiak, C. P. Developing a mechanistic understanding of molecular electrocatalysts for  $CO_2$  reduction using infrared spectroelectrochemistry. *Organometallics* **2014**, *33*, 4550–4559.

(29) Nogues, C.; Wanunu, M. A rapid approach to reproducible, atomically flat gold films on mica. *Surf. Sci.* **2004**, *573*, L383–L389.

(30) Wang, H.-F.; Gan, W.; Lu, R.; Rao, Y.; Wu, B.-H. Quantitative spectral and orientational analysis in surface sum frequency generation vibrational spectroscopy (SFG-VS). *Int. Rev. Phys. Chem.* **2005**, *24*, 191–256.

(31) Zhuang, X.; Miranda, P.; Kim, D.; Shen, Y. Mapping molecular orientation and conformation at interfaces by surface nonlinear optics. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, *59*, 12632.

(32) Lambert, A. G.; Davies, P. B.; Neivandt, D. J. Implementing the theory of sum frequency generation vibrational spectroscopy: A tutorial review. *Appl. Spectrosc. Rev.* **2005**, *40*, 103–145.

(33) Burke, K.; Perdew, J. P.; Wang, Y. In *Electronic Density Functional Theory: Recent Progress and New Directions*; Dobson, J. F., Vignale, G., Das, M. P., Eds.; Plenum: Berlin, 1998; pp 11–20.

(34) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. Erratum: Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1993**, 48, 4978–4978.

(35) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1992**, *46*, 6671–6687.

(36) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple [Phys. Rev. Lett. 77, 3865 (1996)]. *Phys. Rev. Lett.* **1997**, *78*, 1396–1396.

(37) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(38) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *Gaussian 09*; Gaussian, Inc.: Wallingford, CT, 2009.

(39) McLean, A. D.; Chandler, G. S. Contracted Gaussian basis sets for molecular calculations. I. Second row atoms, Z = 11-18. *J. Chem. Phys.* **1980**, *72*, 5639–5648.

(40) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. Selfconsistent molecular orbital methods. XX. A basis set for correlated wave functions. *J. Chem. Phys.* **1980**, *72*, 650–654.

(41) Hay, P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. J. Chem. Phys. **1985**, 82, 270–283.

(42) Hay, P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. *J. Chem. Phys.* **1985**, *82*, 299–310.

(43) Wadt, W. R.; Hay, P. J. Ab initio effective core potentials for molecular calculations. Potentials for main group elements Na to Bi. J. Chem. Phys. **1985**, 82, 284–298.

(44) Dunlap, B. Fitting the Coulomb potential variationally in  $X\alpha$  molecular calculations. J. Chem. Phys. **1983**, 78, 3140–3142.

(45) Dunlap, B. Robust and variational fitting: Removing the fourcenter integrals from center stage in quantum chemistry. *J. Mol. Struct.: THEOCHEM* **2000**, 529, 37–40.

(46) Hanwell, M. D.; Curtis, D. E.; Lonie, D. C.; Vandermeersch, T.; Zurek, E.; Hutchison, G. R. Avogadro: An advanced semantic chemical editor, visualization, and analysis platform. *J. Cheminf.* **2012**, *4*, 17.

(47) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. Ab-initio calculation of vibrational absorption and circular-dichroism spectra using density-functional force-fields. *J. Phys. Chem.* **1994**, *98*, 11623–11627.

(48) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. J. Chem. Phys. **1993**, 98, 5648-5652.

(49) Lee, C. T.; Yang, W. T.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electrondensity. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785–789.

(50) Vosko, S. H.; Wilk, L.; Nusair, M. Accurate spin-dependent electron liquid correlation energies for local spin-density calculations - a critical analysis. *Can. J. Phys.* **1980**, *58*, 1200–1211.

(51) Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. Energy-adjusted abinitio pseudopotentials for the first row transition elements. *J. Chem. Phys.* **1987**, *86*, 866–872.

(52) Dennington, R.; Keith, T.; Millam, J. GaussView, Version 5; Semichem Inc.: Shawnee Mission, KS, 2009.

(53) Benson, E. E.; Grice, K. A.; Smieja, J. M.; Kubiak, C. P. Structural and spectroscopic studies of reduced [Re(bpy-R) (CO)3]–1 species relevant to  $CO_2$  reduction. *Polyhedron* **2013**, *58*, 229–234.

(54) Mishchenko, A.; Zotti, L. A.; Vonlanthen, D.; Burkle, M.; Pauly, F.; Cuevas, J. C.; Mayor, M.; Wandlowski, T. Single-molecule junctions based on nitrile-terminated biphenyls: a promising new anchoring group. *J. Am. Chem. Soc.* **2011**, *133*, 184–187.

(55) Angelici, R. J.; Lazar, M. Isocyanide ligands adsorbed on metal surfaces: applications in catalysis, nanochemistry, and molecular electronics. *Inorg. Chem.* **2008**, *47*, 9155–9165.

(56) de la Llave, E.; Herrera, S. E.; Méndez De Leo, L. P.; Williams, F. J. Molecular and electronic structure of self-assembled monolayers containing ruthenium(II) complexes on gold surfaces. *J. Phys. Chem. C* **2014**, *118*, 21420–21427.

(57) Ferrence, G. M.; Henderson, J. I.; Kurth, D. G.; Morgenstern, D. A.; Bein, T.; Kubiak, C. P. Covalent attachment of nickel clusters to gold electrode surfaces. Formation of rectifying molecular layers. *Langmuir* **1996**, *12*, 3075–3081.

(58) Cosnier, S.; Deronzier, A.; Moutet, J. C. Substitution effects on the electrochemical-behavior of the (2,2'-bipyridine) tricarbonylchlororhenium(I) complex in solution or in polymeric form and their relation to the catalytic reduction of carbon dioxide. *New J. Chem.* **1990**, *14*, 831–839.

(59) Smieja, J. M.; Sampson, M. D.; Grice, K. A.; Benson, E. E.; Froehlich, J. D.; Kubiak, C. P. Manganese as a Substitute for Rhenium in  $CO_2$  Reduction Catalysts: The Importance of Acids. *Inorg. Chem.* **2013**, 52, 2484–2491.

(60) Mecchia Ortiz, J. H.; Morán Vieyra, F. E.; Borsarelli, C. D.; Romero, I.; Fontrodona, X.; Parella, T.; Lis de Katz, N. D.; Fagalde, F.; Katz, N. E. Mono- and dinuclear complexes of tricarbonylrhenium(I) with 4-methyl-2,2'-bipyridine-4'-carbonitrile. *Eur. J. Inorg. Chem.* **2014**, 2014, 3359–3369.

(61) Machan, C. W.; Chabolla, S. A.; Yin, J.; Gilson, M. K.; Tezcan, F. A.; Kubiak, C. P. Supramolecular assembly promotes the electrocatalytic reduction of carbon dioxide by Re(I) bipyridine catalysts at a lower overpotential. *J. Am. Chem. Soc.* **2014**, *136*, 14598–14607.

(62) Simón-Manso, E.; Kubiak, C. P. Dinuclear nickel complexes as catalysts for electrochemical reduction of carbon dioxide. *Organometallics* **2005**, *24*, 96–102.

(63) Sullivan, B. P.; Bolinger, C. M.; Conrad, D.; Vining, W. J.; Meyer, T. J. One- and two-electron pathways in the electrocatalytic reduction of  $CO_2$  by *fac*-Re(bpy) (CO)<sub>3</sub>Cl (bpy = 2,2'-bipyridine). *J. Chem. Soc., Chem. Commun.* **1985**, 1414.

(64) Costentin, C.; Drouet, S.; Robert, M.; Saveant, J. M. A Local Proton Source Enhances  $CO_2$  Electroreduction to CO by a Molecular Fe Catalyst. *Science* **2012**, 338, 90–94.

(65) Appel, A. M.; Helm, M. L. Determining the Overpotential for a Molecular Electrocatalyst. *ACS Catal.* **2014**, *4*, 630–633.

(66) Parker, G. K.; Hope, G. A. A Spectroelectrochemical Investigation of the Interaction of Gold with Cyano-Containing Ligands. *ECS Trans.* **2010**, *28*, 223–235.

(67) Wang, J.; Clark, M. L.; Li, Y.; Kaslan, C. L.; Kubiak, C. P.; Xiong, W. Short-range catalyst-surface interactions revealed by heterodyne two-dimensional sum frequency generation spectroscopy. *J. Phys. Chem. Lett.* **2015**, *6*, 4204–4209.

1665