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Electrocatalytic Reduction of Carbon Dioxide by the Binuclear Copper Complex [Cu_2(6-(diphenylphosphino)-2,2′-bipyridyl)$_2$(MeCN)$_2$][PF_6]$_2$

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The dicopper complex [Cu_2(μ-PPh_2bipy)$_2$(MeCN)$_2$][PF_6]$_2$, **1** (PPh_2bipy = 6-(diphenylphosphino)-2,2′-bipyridyl), and its pyridine analog [Cu_2(μ-PPh_2bipy)$_2$(py)$_2$][PF_6]$_2$, **2**, are electrocatalysts for the reduction of carbon dioxide. Two sequential single-electron transfers to **1** are observed at $E_{1/2}(2+/+) = -1.35$ V vs SCE and at $E_{1/2}(+/0) = -1.53$ V vs SCE in MeCN. Both are required to effect CO_2 reduction. A ^{13}C-labeling study shows that $^{13}CO_2$ is selectively reductively disproportionated to ^{13}CO and $^{13}CO_3^{2-}$. Cyclic and rotating disk voltammetry, chronoamperometry, and computer simulation of cyclic voltammetry have been applied to characterize the heterogeneous electron transfers and homogeneous chemical kinetics of catalysis by the dicopper complexes. Infrared spectroelectrochemical measurements were used to observe products formed during electrocatalysis. On the basis of these kinetic and spectroscopic studies, a mechanism for the catalytic reduction of CO_2 is proposed.

Introduction

With ever-increasing quantities of atmospheric carbon dioxide, the development of new catalysts that would allow utilization of this abundant carbon source is of increasing importance. Some potential uses include development of alternative fuel sources, as well as use as a C_1 feedstock in the production of chemicals. The single-electron reduction of carbon dioxide is the most elementary step in its conversion to other organic products. The CO_2 molecule is reducible at a very cathodic potential, $E° = -2.16$ V vs SCE, with the formation of the highly energetic $CO_2^{\bullet -}$ species.[1] In practice, large overpotentials for the electron transfer process make this reduction even less favorable. Net two-electron reductions of carbon dioxide can usually be achieved at more accessible potentials by coupling CO_2 reduction with the formation of other stable products, as in the reductions of CO_2 to CO and H_2O, $C_2O_4^{2-}$, or CO and CO_3^{2-}. A number of electrocatalysts for the reduction of carbon dioxide have been reported,[2−19] including systems based on polypyridyl[20−36] or phosphine ligands.[37,38] A series of triangular nickel clusters which were synthesized recently in the Kubiak laboratories display electrocatalytic and photochemical activity toward the reduction of CO_2.[39,40]

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We report here that the recently synthesized dicopper complex $[Cu_2(\mu\text{-}PPh_2bipy)_2(MeCN)_2][PF_6]_2$, **1** ($PPh_2bipy$ = 6-(diphenylphosphino)-2,2′-bipyridyl), is an effective and novel electrocatalyst for the reduction of carbon dioxide. The synthesis and characterization of this complex were recently reported.[41] Significantly, complex **1** is a *two*-electron electrocatalyst, capable of catalyzing the net two-electron reduction of carbon dioxide at −1.6 V vs SCE. A unique feature of the μ-phosphinobipyridyl complex, **1**, is that coordinated bipyridyl and bridging phosphine ligands are present. Both of these types of ligand systems are prominently featured among known electrocatalysts for CO_2 reduction, as cited above.[20−38] The reductions appear to be ligand-based, with the electrons localized in the π^* orbitals of the bipyridyl fragment. Thus, the bipyridyl-based ligand acts as an electron reservoir for these systems. As part of these studies, we have also characterized the pyridine substituted derivative $[Cu_2(\mu\text{-}PPh_2bipy)_2(py)_2][PF_6]_2$, **2**, as an electrocatalyst for carbon dioxide reduction. Cyclic and rotating disk voltammetry, chronoamperometry, and computer simulation of cyclic voltammetry have been applied to characterize the heterogeneous electron transfers and homogeneous chemical kinetics of catalysis by the dicopper complexes. Infrared spectroelectrochemical measurements were used to observe products formed during electrocatalysis. On the basis of these kinetic and spectroscopic studies, a mechanism for the catalytic reduction of CO_2 is proposed.

Experimental Section

Electrochemical Measurements. For all electrochemical experiments, a Princeton Applied Research 173 potentiostat equipped with a Model 176 current follower was used. In all cyclic voltammetry and chronoamperometry experiments, a simple one-compartment cell was used, with a glassy carbon working electrode (GCE), Pt counter electrode, and SCE reference. A Pine Instruments, Inc., Model ASR2 electrode rotator was employed for the rotating disk experiments. A glassy carbon Teflon-shrouded rotating disk electrode (RDE) was used, as well as a Pt counter electrode and SCE reference. The electrochemical cell containing the 0.1 M $TBAP/CH_3CN$ solution was purged prior to all experiments with either nitrogen or argon. Tetrabutylammonium hexafluorophosphate (TBAP) was the supporting electrolyte in all experiments. The TBAP was dried by heating under vacuum at 140 °C for 24 h and stored under N_2 prior to use. HPLC grade acetonitrile was distilled from CaH_2 and degassed with nitrogen prior to use.

Bulk electrolysis experiments were carried out in a three-compartment sealed cell, with the compartments separated by high-porosity glass frits. A platinum foil working electrode was used, along with a platinum wire auxiliary electrode and an SCE reference. The bulk reductions were carried out in a 0.1 M $TBAP/CH_3CN$ solution, which was purged with argon for 20 min prior to electrolysis. A constant argon purge was maintained over the solution throughout the experiment. A background electrolysis of the blank solution was performed, and the current was found to be <1% of the current produced by electrolysis of **1**. Gas analyses for bulk electrolysis experiments were performed by GC using a Carle Series S-158 instrument with headspace sampler, thermal conductivity detector, and Hewlett-Packard Model 3396 integrator. Cell leakage was minimal on the time scale of the experiment. Gas samples (10 μL) were taken by gastight syringe directly from the electrolysis cell.

Determination of $[CO_2]$. Experiments to determine the concentration of CO_2 in CH_3CN were performed using the gas chromatographic method of Vianello and co-workers.[42] They reported that, in a CO_2-saturated solution of CH_3CN, $[CO_2] = 0.279 \pm 0.008$ M. 1,4-Dioxane was used as a standard. The concentration of CO_2 in 1,4-dioxane has been reported by several groups[42,43] to be 0.259 M at room temperature. A set of seven gas chromatograms were run for both CO_2-saturated 1,4-dioxane and CO_2-saturated CH_3CN, and the peak areas were compared to determine the concentration of CO_2 in a saturated solution of CH_3CN. In addition, a series of sealed flasks were prepared containing solutions of CO_2-saturated CH_3CN. These were mixed volumetrically with N_2-saturated CH_3CN to cover a range of CO_2 concentrations. The amount of CO_2 present was then determined both by solution GC and by solution IR. In addition, the amount of CO_2 in several of the solutions containing added 0.1 M TBAP was determined by solution IR. For the IR experiments, the absorbance of the band at 2342 cm^{-1} was used. Gas chromatograms for the $[CO_2]$ determination studies were run using a Hewlett Packard 5890 GC with a thermal conductivity detector. A GS-Q 30 meter column with an inner diameter of 0.53 mm was used. Injection volumes of 10 μL were used for all runs. For the IR experiments, a Perkin-Elmer 1710 FTIR with an IRDM data station was used. A solution IR cell with a path length of 0.024 cm was used in all of the CO_2 concentration experiments.

Cyclic Voltammetry Simulations. Computer simulations of the cyclic voltammograms of **1** under a variety of CO_2 concentrations were performed using the method described by Meyer et al. and Kochi et al.[27,44,45] Cyclic voltammograms of 1.33 mM solutions of **1** with a variety of CO_2 concentrations were taken at scan rates of 200, 100, 50, and 20 mV/s. A glassy carbon working electrode, platinum auxiliary electrode, and SCE reference electrode were used, with the working electrode polished between runs. Saturated CH_3CN solutions of N_2 and CO_2 were prepared by purging the solutions in sealed cells for at least 20 min. Varying amounts of these solutions were added to the electrochemical cell, as described above, giving a range of CO_2 concentrations in the 0.1 M $TBAP/CH_3CN$ solvent. Values for i(diff), or the current in the absence of CO_2, were found by averaging the currents for five runs at each of the scan rates listed above.

The simulations used were based on the method of finite differences,[46−49] with the equations for two sequential redox couples taken from a paper by Feldberg.[50] Two possible mechanisms were proposed, and their differential forms were translated into their finite difference forms. A program written in QBasic was used to calculate the $i(\text{diff})/i(CO_2)$ values for a range of CO_2 concentrations and rate constants for the first- and second-order in $[CO_2]$ mechanisms. The simulated data were then compared to the experimental data to determine the overall order of the reaction, as well as the homogeneous rate constant for the reaction between the doubly-reduced dimer and CO_2. The concentration-dependent terms $\log(RT[CO_2]^n/Fv)$ (where n = 1 or 2) are based on Saveant's adimensional λ function,[51] where $\lambda = k_{rds}[RT/Fv][CO_2]$ or $k_{rds}[RT/Fv][CO_2]^2$, depending on the reaction order in CO_2.[44]

Infrared Spectroelectrochemistry. All spectroelectrochemical experiments were carried out in 0.1 M $TBAP/CH_3CN$ solutions. The CH_3CN was purchased from Aldrich and distilled over CaH_2 under nitrogen. All electrolyte solutions were dried prior to use by passage down a column of activated alumina. Infrared spectral changes accompanying thin-layer bulk electrolyses were measured using a flow-through spectroelectrochemical thin-layer specular reflectance mode cell, as described elsewhere.[52] Electrochemical potentials were con-

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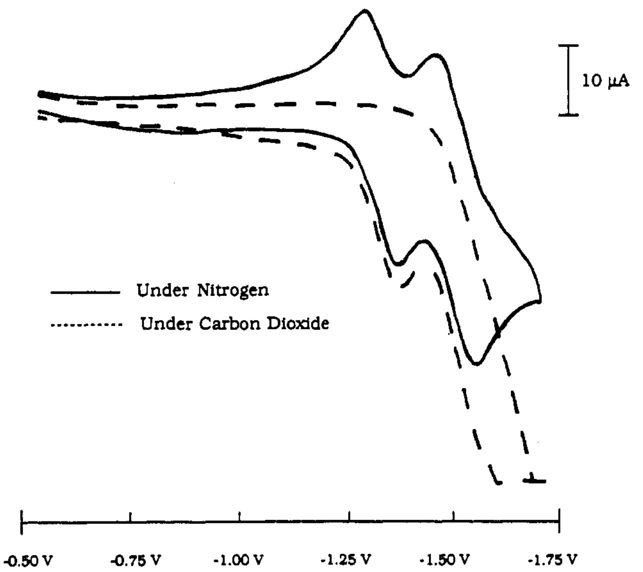

Figure 1. Cyclic voltammograms of 1 mM [Cu_2(μ-PPh_2bipy)$_2$(MeCN)$_2$][PF_6]$_2$ (**1**) under nitrogen (—) and under $CO_{2(g)}$ (- - -) recorded at a glassy carbon electrode (GCE) in MeCN solvent with 0.1 M TBAP at a scan rate of 100 mV/s. Potentials are referenced to SCE. Reductions occur at $E_{1/2} = -1.35$ V and $E_{1/2} = -1.53$ V.

trolled via a BAS 100 electrochemical analyzer. IR spectral measurements were collected on a Mattson Galaxy 6070 FTIR spectrometer. For the CO_2(g) experiments, CO_2 was bubbled through the catalyst solution for 15 min prior to injection into the spectroelectrochemical cell. For the $^{13}CO_2$ experiments, 10 mL of the gas was transferred via a gastight syringe into 5 mL of a 10 mM solution of **1**. The intensity of the band at 2280 cm^{-1} was used to obtain the approximate concentration of the gas in solution using $\epsilon(CO_2) = 1280$ L mol^{-1} cm^{-1}.

Results and Discussion

In kinetics studies of the electrocatalytic reduction of carbon dioxide, knowledge of the concentration of CO_2 in solution is essential. There has been some discrepancy in reported values of [CO_2] in 0.1 M TBAP supporting electrolyte acetonitrile solutions at 25 °C and 1 atm.[42–44] We have therefore redetermined [CO_2] in 0.1 M TBAP supporting electrolyte acetonitrile solutions at 25 °C at various partial pressures. We also determined $\epsilon(CO_2)$ by infrared spectroscopy in the same medium to facilitate rapid quantitative *in situ* determination of [CO_2] in the electrochemical cell. Using 1,4-dioxane as a standard, the concentration of CO_2 in a saturated solution of CH_3CN was found to be 0.28 ± 0.01 M by GC. This confirms the value reported earlier by Vianello.[42] In 0.1 M TBAP supporting electrolyte acetonitrile solutions at 25 °C, the IR absorbance of the CO_2 band at 2342 cm^{-1} shows a linear relationship with [CO_2] over the concentration range 0.0–0.11 M. From a plot of the absorbance at 2342 cm^{-1} versus [CO_2], the molar absorptivity, $\epsilon(CO_2)$, was determined to be 1280 L mol^{-1} cm^{-1}, using a cell with a path length of 0.024 cm. Of course, a linear relationship also exists between the concentration of CO_2 and the GC peak area for CO_2. However, we find that the *in situ* IR method is particularly useful for the determination of [CO_2] when supporting electrolyte and/or organometallic compounds are also necessarily present. The concentration of CO_2 in the electrochemical cell was controlled by the addition of varying amounts of the CO_2-saturated and N_2-saturated CH_3CN solutions.

Under nitrogen, the cyclic voltammetry of [Cu_2(μ-PPh_2bipy)$_2$(MeCN)$_2$][PF_6]$_2$, **1**, in acetonitrile shows two reductions at $E_{1/2}(2+/+) = -1.35$ V vs SCE and at $E_{1/2}(+/0) = -1.53$ V vs SCE. The first reduction is reversible, with a peak to peak separation, ΔE_{pp}, of 65 mV. The second reduction is somewhat less reversible, with $\Delta E_{pp} = 75$ mV. A bulk electrolysis of **1** was performed by stepping the potential to -1.7 V vs SCE, which is just cathodic of the second reductive couple for this dimer. On the basis of the number of coulombs passed, $n = 1.8 \pm 0.2$ for this system. To calculate the diffusion coefficient for **1** in CH_3CN, chronoamperometry experiments were carried out by stepping the potential to -1.45 and -1.7 V vs SCE. The D_0 value was calculated to be 2.2×10^{-6} cm^2/s, which is in good agreement with the value of 4.0×10^{-6} cm^2/s reported for the [Ru(terpy)(bipy)(H_2O)]$^{2+}$ dication.[54]

The cyclic voltammograms of **1** in the presence and absence of CO_2 are presented in Figure 1. The cyclic voltammogram of complex **1** appears dramatically different under an atmosphere of CO_2. The first reduction at $E_{1/2}(2+/+) = -1.35$ V vs SCE

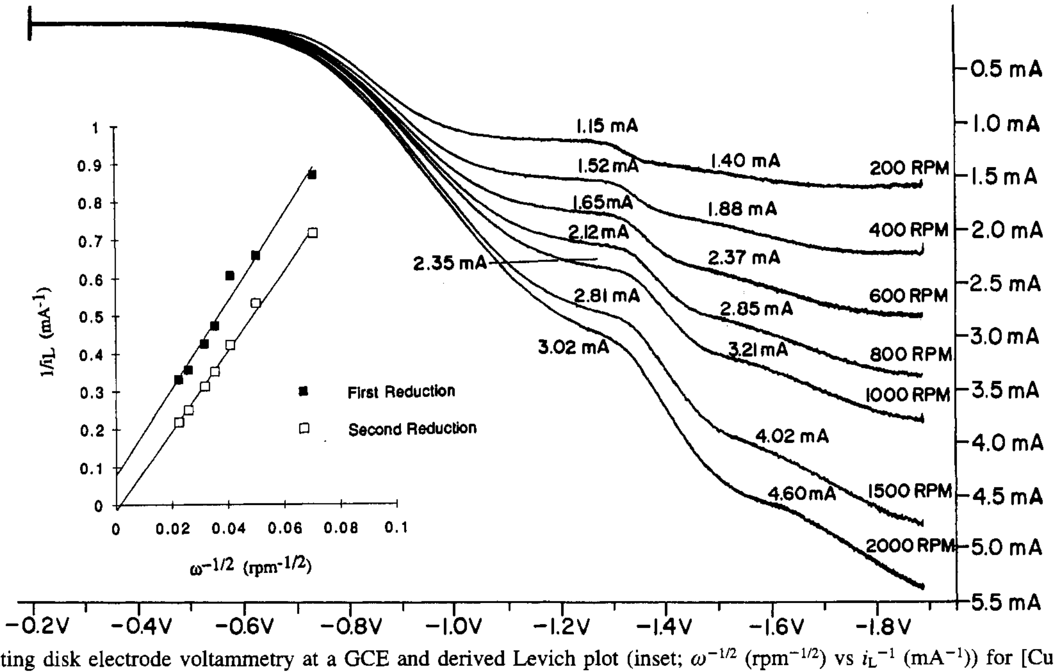

Figure 2. Rotating disk electrode voltammetry at a GCE and derived Levich plot (inset; $\omega^{-1/2}$ ($rpm^{-1/2}$) vs i_L^{-1} (mA^{-1})) for [Cu_2(μ-PPh_2bipy)$_2$(py)$_2$][PF_6]$_2$ (**2**) in 0.1 M TBAP/MeCN. Limiting currents, i_L, for the first reduction at $E_{1/2}(\mathbf{1}^{2+/+}) = -1.38$ V vs SCE and for the second reduction at $E_{1/2}(\mathbf{1}^{+/0}) = -1.58$ V vs SCE were recorded at electrode rotation rates, ω, of 200, 400, 600, 800, 1000, 1500, and 2000 rpm under argon.

Table 1. Cyclic Voltammetry Data for Complex **1** in 0.1 M TBAP/CH_3CN with a Variety of CO_2 Concentrations, Where the Concentration of $[Cu_2(\mu\text{-}PPh_2bipy)_2(MeCN)_2][PF_6]_2$ Is 1.33 mM. *i*(d) Is the Peak Current Obtained in the Absence of CO_2, and *i*(CO_2) Is the Peak Current in the Presence of CO_2 (Peak Currents Corrected for Background)

run no.	[CO_2], M	scan rate, mV/s	*i*(d)/*i*(CO_2)
1	0.28	200	0.54
2	0.28	100	0.53
3	0.28	50	0.44
4	0.28	20	0.47
5	0.186	200	0.64
6	0.186	100	0.54
7	0.186	50	0.49
8	0.186	20	0.47
9	0.14	200	0.64
10	0.14	100	0.56
11	0.14	50	0.51
12	0.14	20	0.48
13	0.094	200	0.69
14	0.094	100	0.62
15	0.094	50	0.54
16	0.094	20	0.52
17	0.078	200	0.74
18	0.078	100	0.71
19	0.078	50	0.67
20	0.078	20	0.63
21	0.056	200	0.69
22	0.056	100	0.63
23	0.056	50	0.56
24	0.056	20	0.54
25	0.028	200	0.94
26	0.028	100	0.91
27	0.028	50	0.82
28	0.028	20	0.70
29	0.024	100	0.97
30	0.024	50	0.93
31	0.024	20	0.81
32	0.0186	100	1.0
33	0.0186	50	0.76
34	0.0186	20	0.62
35	0.0176	200	1.0
36	0.0176	100	1.0
37	0.0176	50	0.90
38	0.0176	20	0.80
39	0.0074	200	1.0
40	0.0074	100	1.0
41	0.0074	50	0.95
42	0.0074	200	0.86
43	0.0056	100	1.0
44	0.0056	50	1.0
45	0.0056	20	0.94
46	0.0012	200	1.0
47	0.0012	100	1.0
48	0.0012	50	0.99
49	0.0012	20	0.91

remains unaffected whether under CO_2 or nitrogen, but the second reduction at $E_{1/2}(+/0) = -1.53$ V vs SCE shows a very pronounced enhancement of cathodic current (more than double that observed in the absence of CO_2). In addition, both return anodic waves essentially disappear, indicating that the reduced form of **1** is consumed by reaction with CO_2. The large cathodic current enhancement indicates electrocatalysis. The original features of the cyclic voltammogram are restored by purging with nitrogen for several minutes. The electrochemical behavior of the pyridine derivative $[Cu_2(\mu\text{-}PPh_2bipy)_2(py)_2][PF_6]_2$, **2**, exhibits features which are similar to those of **1** in all respects, except that the enhancement of cathodic current in the presence of CO_2 is significantly less.

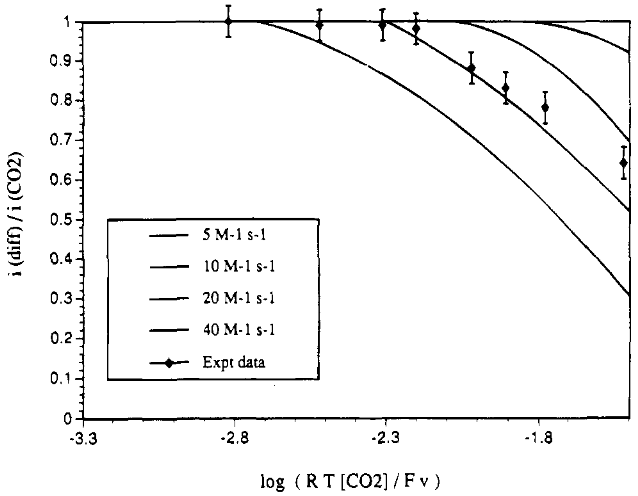

Figure 3. Plot of the *i*(diff)/*i*(CO_2) ratios found in Table 1 vs the concentration-dependent term, log(*RT*[CO_2]/*Fv*), for the first-order-in-CO_2 case. *R* = gas constant, *T* = temperature, *F* = Faraday's constant, and *v* = scan rate. Error bars of ±0.04 are based on the error of the best line fit for the experimental data. Rates of 10, 20, 40, and 80 M^{-1} s^{-1} were used in the simulations.

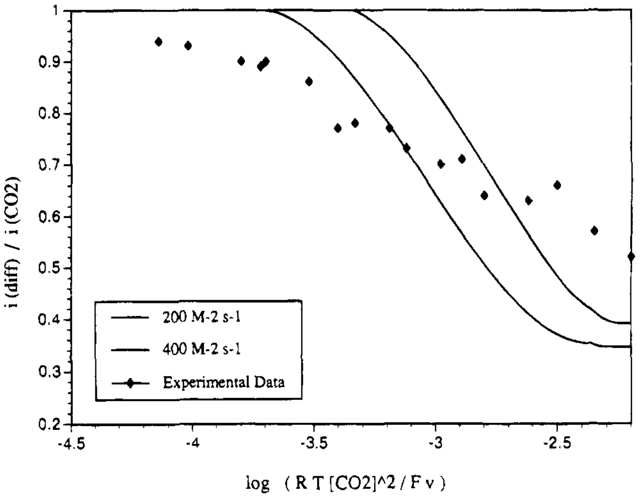

Figure 4. Plot of the *i*(diff)/*i*(CO_2) ratios found in Table 1 vs the concentration-dependent term, log(*RT*[CO_2]^2/*Fv*), for the second-order-in-CO_2 case. Rates of 200 and 400 M^{-2} s^{-1} were used in the simulations. The constants are the same as those defined in Figure 3.

In order to determine the products of CO_2 reduction, a bulk electrolysis of a 0.3 mM solution of **1** in the presence of CO_2 was carried out in acetonitrile using a Pt gauze working electrode. The solution was saturated with CO_2 in a sealed electrochemical cell for 10 min before stepping the potential to −1.7 V vs Ag/AgCl (slightly cathodic of the second reduction of **1**). The only gaseous product was found to be CO, as determined by GC. Analyses for CO_2(g) and CO(g) were performed before, during, and after electrolysis. On the basis of the amount of CO(g) produced, a turnover frequency of >2 h^{-1} was maintained over the course of a 24 h experiment, and the catalyst itself was still active at the end of this experiment. The current efficiency for CO production, $\eta_{CO} = N_{CO}/N_{e^-}$, is 0.5, consistent with the reductive disproportionation of CO_2: $2CO_2 + 2e^- = CO + CO_3^{2-}$. An IR spectrum of the solid product isolated following electrolysis showed that complex **1** was still present in its original form, at near-quantitative recoveries. There were also spectroscopic evidence of CO_3^{2-} as the other reduction product and no evidence of other carbonyl or carboxyl products (*vide infra*).

The heterogeneous electron transfer kinetics for the two

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discrete reductions of the electrocatalyst **1** were studied by rotating-disk voltammetry. The rotating disk electrode voltammetry results obtained for complex **1** in acetonitrile are shown in Figure 2. By using rotating disk electrode methods to examine the limiting currents, i_L, as a function of the electrode rotation rate (ω), linear Levich plots ($\omega^{-1/2}$ (rpm$^{-1/2}$) vs i_L^{-1} (mA^{-1})) were obtained for both reductions. These are shown in the inset of Figure 2. From the intercept of the Levich plots, the "kinetically-controlled current", which is independent of hydrodynamic transport, were obtained. The kinetically-controlled current is proportional to the rate of heterogeneous electron transfer. For the first reduction ($1^{2+/+}$), $k_e = 0.40$ cm/s. The second reduction ($1^{+/0}$) is too rapid to measure by this technique. The very fast rate of the second electron transfer is likely due to the complex already having diffused to the electrode surface. This is significant, since it is clear from the cyclic voltammograms that reduction of CO_2 occurs only from the doubly-reduced state of the electrocatalyst.

The homogeneous electron transfer kinetics for the reduction of CO_2 by complex **1** were studied using computer simulations of the cyclic voltammograms at various CO_2 concentrations and scan rates. The current ratios obtained by varying the concentration of **1** remained constant, indicating a reaction that is first order with respect to [**1**]. Two possible routes for the reaction between the doubly-reduced dimer and CO_2 are outlined in (1)–(3). The current ratios for the peak current obtained in the absence of CO_2 versus the peak currents at various CO_2 concentrations, over the range 0.0–0.28 M, can be found in Table 1. These values were plotted against the concentration-dependent terms, $\log(RT[CO_2]/Fv)$ for the first-order case and $\log(RT[CO_2]^2/Fv)$ for the second-order case, as shown in Figures 3 and 4. The overall order of the reaction, as well as an approximation of the homogeneous rate constant, can thus be determined. For this system, we found the overall reaction to be first order with respect to [**1**] and [CO_2], in agreement with eqs 1, 2, and 3A. The homogeneous rate constant, k_{rds}, was found to be 18 ± 4 M^{-1} s^{-1}.

$$[Cu_2(PPh_2bipy)_2(CH_3CN)_2]^{2+} + e^- \rightleftharpoons [Cu_2(PPh_2bipy)_2(CH_3CN)_2]^{+} \quad (1)$$

$$[Cu_2(PPh_2bipy)_2(CH_3CN)_2]^{+} + e^- \rightleftharpoons [Cu_2(PPh_2bipy)_2(CH_3CN)_2]^{0} \quad (2)$$

$$[Cu_2(PPh_2bipy)_2(CH_3CN)_2]^{0} + CO_2 \xrightarrow{k_{rds}} \text{products} \quad (3A)$$

$$[Cu_2(PPh_2bipy)_2(CH_3CN)_2]^{0} + 2CO_2 \xrightarrow{k_{rds}} \text{products} \quad (3B)$$

The k_{rds} values for complexes **1** and **2** were also studied using potential-step experiments. For electrocatalytic systems, the steady-state current at long times is proportional to the rate of substrate reduction.[48] Stepping the potential of a GCE from 0.0 to −1.7 V vs SCE, the rate of reaction of the doubly-reduced dimer with CO_2 was found to be an order of magnitude less for the pyridine adduct, **2**, than for the acetonitrile adduct, **1**. These data suggest that substitution of the labile acetonitrile and pyridine ligands of **1** and **2**, respectively, may be required for CO_2 reduction. These data further suggest that CO_2 binding to the reduced form of the copper complex is a key step in its reduction.

We were also interested in probing the reaction intermediates and products upon reduction of **1** in the presence of CO_2. To do this, IR spectroelectrochemistry of the copper dimer, **1**, was studied under an atmosphere of CO_2. The design of the reflectance IR spectroelectrochemical cell employed or closely followed the cell design of Mann and co-workers.[52,53] In the region of interest (1500–1800 cm^{-1}), this complex shows no IR bands and shows no observable changes upon reduction under nitrogen. However, under CO_2 (Figure 5) several bands appeared over the course of the experiment, the strongest of which was a band at 1642 cm^{-1} which grew in as the cluster was reduced. A steady-state current significantly larger than the background current was maintained throughout the course of the experiment, indicative of a catalytic reaction. The IR band at 1642 cm^{-1} closely matches that observed when **1** is deliberately combined with Na_2CO_3 in MeCN solution. The isolation and structural characterization of this apparent carbonate intermediate has not yet been possible. Importantly, when the electrocatalytic reduction of $^{13}CO_2$ is accomplished under similar conditions, the strongest IR absorbance grows in at 1604 cm^{-1}, establishing the origin of the carbonate absorbance as CO_2 (under rigorously anhydrous conditions). The $^{13}CO_2$ spectroelectrochemical experiment also leads to the direct observation of ^{13}CO at 2115 cm^{-1}. Significantly, no other carbonyl absorbances are observed, indicating that CO_2 is selectively disproportionated to CO and CO_3^{2-}.

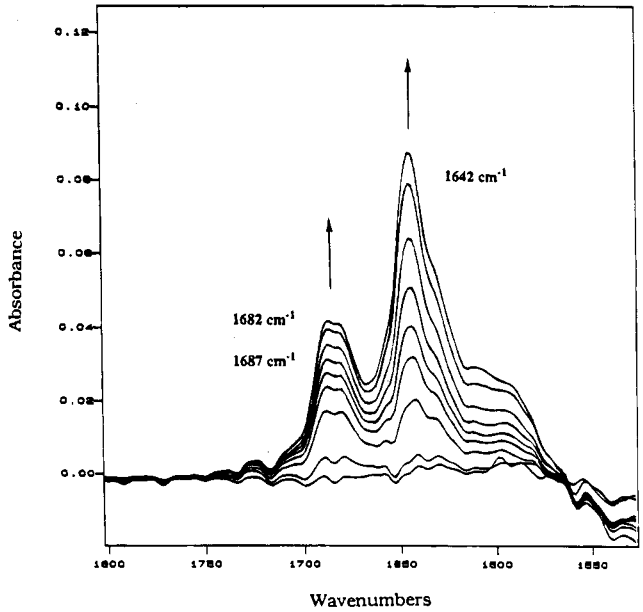

Figure 5. Plot of the IR spectral changes observed during the spectroelectrochemical reduction of 3 mM $[Cu_2(PPh_2bipy)_2(CH_3CN)_2]$-$[PF_6]_2$ in a 0.1 M TBAP/CH_3CN solution saturated with CO_2(g). Potential held at −1.9 V vs a Ag wire reference.

Conclusions

Complex **1** is a two-electron electrocatalyst for the reduction of carbon dioxide. The two-electron redox cycle of **1** appears to lead to at least an order of magnitude increase of the catalytic currents for CO_2 reduction over a recently reported nickel cluster electrocatalyst which operates via a single electron redox cycle.[40] The reductions of the dinuclear complexes **1** and **2** are most likely ligand-based. The PPh_2bipy ligand offers the dual advantages of coordinated bipyridine as well as bridging phosphines. In the present study, the π^* unsaturation of the bipy component of the PPh_2bipy ligand also provides the ability to shuttle electrons in and out of a closed-shell d^{10}–d^{10} binuclear complex. The proposed catalytic cycle for **1** is presented in Figure 6. Two sequential heterogeneous electron tranfers, one fast and the other immeasurably fast by RDE voltammetry, are required to load the system for reduction of CO_2. The rate-

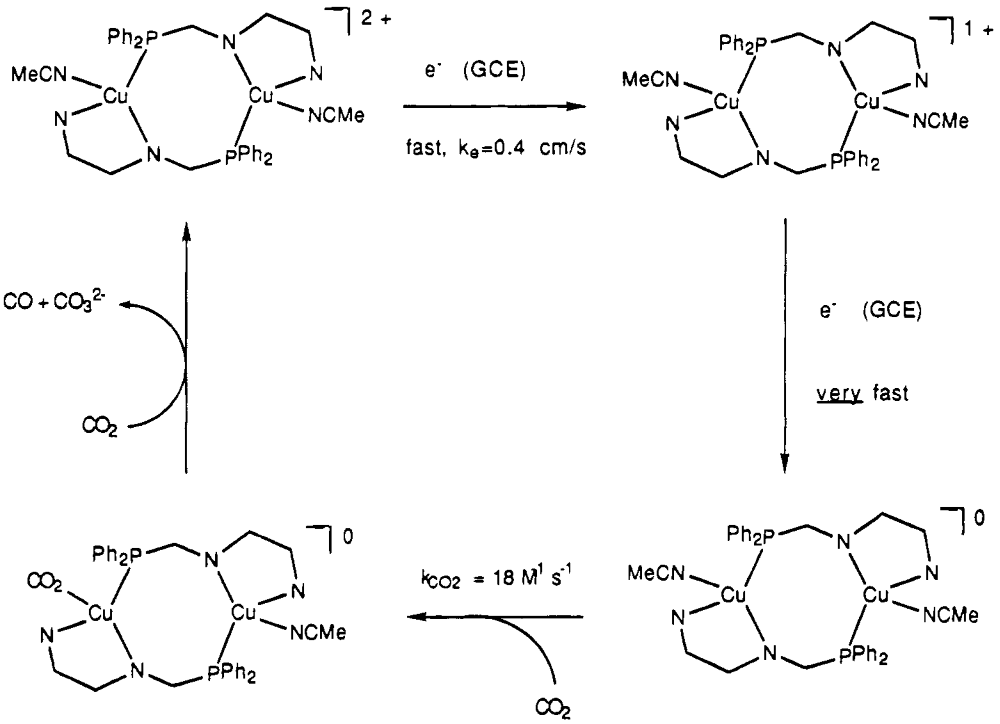

Figure 6. Proposed catalytic cycle for the reduction of carbon dioxide by complex **1**.

determining step for the reaction between the doubly-reduced dimer **1** and CO_2 is first order in both [**1**] and [CO_2]. Solvent dependence and significantly less catalytic current for the pyridine adduct **2** compared to **1** suggest that the reduction of CO_2 involves substitution of a solvent molecule by a CO_2 molecule.

The experiments performed on the copper dimer system suggest that a CO_3^{2-} complex is formed as an intermediate after reaction of the reduced dimer with 2 equiv of CO_2. The observed products of the reaction, CO and CO_3^{2-}, result from reductive disproportionation of two CO_2 molecules. The reductive disproportionation of CO_2 generally involves "head-to-tail" dimerization of two CO_2 molecules followed by collapse to CO and CO_3^{2-};[39,40] however, in the present system this process is too rapid to be observed directly. The complex $[Os(bipy)_2(CO)H]^+$ was recently reported to catalyze the reduction of CO_2 by a two-electron mechanism,[44] with a rate constant for the rate-determining step between the doubly reduced form of the complex and CO_2 of approximately the same value as that for complex **1**. We note that in this study the concentration of CO_2 in a saturated solution of 0.1 M TBAP/ CH_3CN was cited as 0.14 M, and hence reported second-order rate constants may be artificially high. Nonetheless, the overall similarity in the reactivity of the osmium system with CO_2 may be a reflection of the use of a bipyridyl-based ligand in both cases. Indeed, the reductive waves for the two systems appear quite similar.

The new dinuclear copper complex, **1**, has proven to be a selective electrocatalyst for the reduction of carbon dioxide to CO and CO_3^{2-}. As an air-stable compound, it is a potentially useful system for practical applications. Even after exposure of the catalyst to the atmosphere for several days, little degradation occurs. Ongoing studies are devoted to methods of polymerizing the new catalysts onto electrode surfaces. This is expected to increase activities of the catalysts by eliminating mass transport restrictions on the essential electron transfers and to create potentially more durable immobilized catalysts.

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Supplementary Material Available: For the measurements of [CO_2] in CH_3CN, calibration plots for the determinations made by gas chromatography and by solution IR (2 pages). Ordering information is given on any current masthead page.