The bis(triphosphine) ligand C₈H₄[P(CH₃CN)₂P(CH₂CH₂P(C₆H₁₁)₂)₂], m-(triphos); (1), is synthesized by the reaction of m-bis(phosphino)benzene with 4 equiv of vinylidicyclohexylphosphine. Reaction of 1 with 2 equiv of [Pd(CH₂CN)₂][BF₄]₂ results in the formation of the bimetallic complex {m-(triphos)}₂[Pd(CH₂CN)₂][BF₄]₂ (2). A structural study of 2 confirms the presence of two [Pd(triphosphine)-(CH₂CN)]²⁺ substituents at the meta positions of a benzene ring. Complex 2 catalyzes the electrochemical reduction of CO₂ to CO in acidic dimethylformamide solutions. The kinetics of this reaction have been studied, and it is 0.5 order in catalyst and first order in CO₂. This catalyst exhibits catalyic rates comparable to that of its monometallic analogues. Significantly higher turnover numbers are observed for 2 than observed previously for monometallic, bimetallic, and dendritic complexes of this class of catalysts.

### Introduction

Electrochemical concentration and reduction of CO₂ provides a potential renewable route to carbon-based fuels and chemicals in addition to biomass. Recently, electrochemical separation and pumping of CO₂ from 0.5% CO₂ feed streams to nearly 100% in addition to biomass. Recently, electrochemical separation and reduction of CO₂ from 0.5% CO₂ feed streams to nearly 100% in addition to biomass. The laboratory has developed and studied the use of [Pd(triphosphine)-(CH₂CN)]²⁺ complexes as catalysts for the electrochemical reduction of CO₂ to CO catalyzed by a bimetallic palladium complex.

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**Electrochemical Concentration and Reduction of CO₂ to CO Catalyzed by a Bimetallic Palladium Complex**

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reduction of CO₂ to CO. These catalysts exhibit high catalytic rates (10–300 M⁻¹ s⁻¹), high selectivities (>90%), and low overpotentials (100–300 mV). Even higher catalytic rates (>10⁶ M⁻¹ s⁻¹) were obtained using bimetallic palladium complexes in which two triphosphine units were bridged by a methylene group. However, turnover numbers for these monometallic and bimetallic catalysts have been low, typically 10–100 for the production of CO. In this paper, we describe efforts to develop bimetallic palladium complexes with greater stability.

Experimental Section

General Comments. All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Dichloromethane and acetonitrile were distilled from calcium hydride under nitrogen. Dimethylformamide (Burndick and Jackson) was stored under nitrogen. H¹ and [³¹P(¹H)] NMR spectra were recorded on a Varian Unity 300 MHz spectrometer at 299.75 and 121.42 MHz, respectively. H¹ chemical shifts are reported relative to tetramethylsilane using residual solvent protons as a secondary reference. [³¹P] chemical shifts are reported relative to external phosphoric acid. Elemental analyses were performed by Galbraith Laboratories, Inc. [Pd(NCCH₃)₄][BF₄]₂, was prepared using the literature procedure.

Syntheses. C₂H₄ [P(CH₂CH₂P(CH₃)₂)₂]₂, m-(triphos) (1). A sealed Schlenk flask containing a mixture of 1,3-bis(phosphino)-benzene (0.50 g, 0.0035 mol), vinyldicyclohexylphosphine (3.35 g, 0.015 mol), and 2,2’-azobis-(2-methylpropiionitrile) (AIBN, 0.1 g) was placed inside a Rayonet photoreactor and irradiated at 254 nm for 3 h. The product was heated to 100°C for 3 h in a dynamic vacuum to remove volatile materials. After cooling, the resulting white solid (3.50 g, 96%) was recrystallized from dichloromethane/ethanol in approximately 70% yield. [³¹P][¹H] NMR (toluene-d₈): 1.55 ppm (d, J₁P₂ = 25 Hz, P(C₆H₄)), -14.38 ppm (t, C₆H₄P). H¹ NMR (toluene-d₈): 8.03 ppm (t, 6.9 Hz, Ar-H); 7.50 ppm (t, 6.0 Hz, Ar-H); 7.17 ppm (t, 7.5 Hz, Ar-H); 1.1–2.2 ppm (m, cyclohexyl and methylene protons).

{m-(triphos)}[P(CH₂CN)₃][BF₄]₂ (4). A solution of [P(CH₂CN)₃][BF₄]₂ (0.45 g, 0.001 mol) in acetonitrile (30 mL) was added to a solution of I in toluene (1.65 mL of a 0.3 M stock solution, 0.0005 mol), and the resulting solution was stirred at room temperature overnight. Removal of the solvent with a vacuum yielded a yellow powder (0.80 g, 95%). This product is pure by NMR spectroscopy. It can be recrystallized from a mixture of dichloromethane and ethanol. Anal. Calcd for C₆₆H₁₁₄B₄F₁₆N₂P₆Pd₂: C, 47.14; H, 6.83. Found: C, 46.76; H, 6.92. [³¹P][¹H] NMR (CD₃CN): 119.4 ppm (t, J₃P₄ = 4 Hz, C₆H₄P), 76.6 ppm (d, P(⁴C)); ³¹H NMR (CD₃CN): 7.7–8.2 ppm (m, s-C₆H₆), 1.1–3.2 ppm (m, cyclohexyl and methylene protons).

Kinetics of CO₂ Reduction. Cyclic voltammetry experiments were used to determine the kinetics of the catalytic reaction. In all cases, 2.0 mL of a 0.3 M solution of Et₄NBF₄ in dimethylformamide was used, and ferrocene was added as an internal reference. The working electrode was a glassy carbon disk, the counter electrode was a glassy carbon rod, and an electrode consisting of a platinum wire inserted into a 1:1 solution (1 M each) of decamethylferrocene/decamethylferrocenium in acetonitrile was used as a pseudo-reference electrode.

Order with Respect to Acid. This was determined by titration with tetrafluoroboric acid. To a dimethylformamide solution was added catalyst to make the solution 2 mM in catalyst. The solution was purged with N₂, and an initial cyclic voltammogram was recorded. After a 15 min CO₂ purge to saturate the solution, aliquots of aqueous 7.5 M HBF₄ solution were added and the cyclic voltammograms were recorded to determine the catalytic currents. A plot of i₁/i₀ versus [H⁺] was used to determine the order with respect to H⁺. The peak current observed under 1 atm of N₂ in the absence of acid is i₁, and the peak or plateau current observed in the presence of various amounts of acid and 62.0 mmHg of CO₂ is i₀.

Order with Respect to CO₂. A stock solution of 0.120 M catalyst in DMF containing electrolyte was prepared. Acid was added to the solution in the cell to make it 0.1 M HBF₄, and it was purged with CO₂. Then aliquots of the catalyst solution were added, and cyclic voltammograms were recorded. A plot of peak or plateau current versus the catalyst concentration was used to determine the order.

Catalytic Coupling. A three-necked flask with a stopcock having a total volume of 120 mL was used for bulk electrolysis experiments. One neck was a 24/40 joint that accepted a stainless steel 24/40 fitting with an insulated copper wire running through it. To this was attached a cylinder of reticulated vitreous carbon as a working electrode. The other two necks of the flask were 14/20 joints. Both were fitted with glass compartments with Vycor frits on the bottom. One was used as the reference electrode; it was filled with a solution of decamethylferrocene/decamethylferrocenium in acetonitrile, and a Pt wire was inserted. The other was used as the counter electrode, and it contained a saturated solution of ferrocene in 0.3 M Et₄NBF₄ in DMF and a tungsten wire. Gas was introduced into the sealed flask through the stopcock. The cell was typically filled with 15 mL of a 0.3 M Et₄NBF₄ solution in dimethylformamide. Acid (0.1 M) and catalyst (1 mM) were added to the solution, which was then purged with CO₂ for 15 min. Controlled potential coulometry was performed in 1 h increments at -1.0 to -1.1 V versus the decamethylferrocene/decamethylferrocenium/acetonitrile reference.

and CO generated. After 15 h, 190 mole of CO were produced per of the flask were removed every 20 min via a gastight syringe and rocenium reference electrode. Samples of the gas in the headspace remained.

color, habit orange plate

cryst dimens 0.28 x 0.26 x 0.12 mm
temperature –138(2) °C
λ 0.71073 Å
μ 0.650 mm–1
density (calcd) 1.432 g cm–3
no. of reflns collected 42 928
no. of indep reflns 11 339 (R(int) = 0.0845)
no. of params 909
R1(whole) = 0.0823
wr2(R = 2 F2) = 0.2383
goodness of fit* 1.056

*a = (Σ[w(Fo2 - Fc2)]2/Σ[w(Fc2)]2)1/2, w = 1/[σ2(Fo2) + (0.1325P)+ 9.6648P]; P = F2 + 2 F2/3. Goof = S = (Σ[w(Fo2 - Fc2)]2/(n–p))1/2, n = number of reflections, p = number of parameters.

crystalline reference electrode. Samples of the gas in the headspace of the flask were removed every 20 min via a gastight syringe and analyzed by gas chromatography to determine the amount of H2 and CO generated. After 15 h, 190 mole of CO were produced per mole of catalyst. A sample of the catalytic solution was analyzed by 31P NMR spectroscopy, and 82% of the original catalyst remained.

Gas Chromatography. GC was performed using a Perkin-Elmer AutoSystem gas chromatograph. Gas samples were collected with a 0.1 mL gas syringe. Chromatograms were obtained and analyzed using Perkin-Elmer Turbochrom Workstation software. The GC was calibrated for H2 and CO by injecting known quantities of pure gas into the bulk electrolysis cell and then analyzing a 0.1 mL sample of the headspace. A calibration curve was generated for both hydrogen and carbon monoxide.

X-ray Crystallography. Crystals were examined under light hydrocarbon oil. The datum crystal was mounted to the tip of a thin glass fiber affixed to a tapered copper mounting pin and placed into the goniometer of a Siemens SMART CCD diffractometer equipped with an LT-2A low-temperature apparatus operating at 135 K. Cell dimensions were determined after harvesting reflections from three orthogonal sets of 20 0.3° ω scans and were refined using 8483 reflections harvested from the entire data collection. An arbitrary hemisphere of data was collected to 0.68 Å resolution using 0.3° ω scans, each measured for 30 s. The data were truncated at 0.92 Å during refinement because of weak diffraction and poor agreement between equivalents at higher angles. All data were corrected for Lorentz and polarizability effects, as well as for absorption.

Structure solution via direct methods in centrosymmetric space group P21/n revealed most of the cation structure and several of the anions. Cycles of least-squares refinement followed by difference Fourier map calculation uncovered the missing atoms and showed disorder in three cyclohexyl groups. In addition, a region of electron density was discovered. This was modeled as three heavily disordered molecules of acetonitrile using the routine SQUEEZE from the package PLATON (Speck, University of Utrecht, 2004). All non-hydrogen atoms were refined using parameters for anisotropic thermal motion. Hydrogens were placed at calculated geometries and allowed to ride on the position of the parent atom. Hydrogen thermal motion was modeled isotropically using U equal to 1.2× the equivalent isotropic U of the parent atom (1.5× for methyl hydrogens). Crystal and refinement data are listed in Table 1.

Table 1. Crystal and Refinement Data for {m-(triphos)}2[Pd(CH3CN)]2][BF4]4, 2

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<tr>
<td>α</td>
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</tr>
<tr>
<td>β</td>
<td>92.821(5)°</td>
</tr>
<tr>
<td>γ</td>
<td>90°</td>
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<td>color, habit</td>
<td>orange plate</td>
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<tr>
<td>cryt dimens</td>
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<td>1.432 g cm–3</td>
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<tr>
<td>no. of reflns</td>
<td>42 928</td>
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<tr>
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<td>0.2383</td>
</tr>
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<td>goodness of fit*</td>
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</tbody>
</table>

using U equal to 1.2× the equivalent isotropic U of the parent atom (1.5× for methyl hydrogens). Crystal and refinement data are listed in Table 1.

Results

Catalyst Synthesis and Characterization. The bis(triphosphine) ligand C8H4[P(CH3CH2P(C6H11)2]2, m-(triphos)2 (1), can be prepared by the reaction of m-bis(phosphino)benzene with 4 equiv of vinylcyclohexylphosphine using AIBN as a free radical initiator, step 1 of reaction 1. The 31P NMR spectrum of the product consists of a doublet at 1.55 ppm assigned to the terminal cyclohexylphosphine group and a triplet at –14.38 ppm assigned to the central phosphorus atom of the triphenyl moiety. The observed three-bond phosphorus–phosphorus coupling of 25 Hz is typical for triphosphine ligands with two-carbon backbones, and the calculated chemical shifts of 0 and –16 ppm for the terminal and central phosphorus atoms are in good agreement with the experimental values (1.55 and –14.38 ppm, respectively).3,19

Figure 1. ORTEP drawing of {m-(triphos)}2[Pd(CH3CN)]2][BF4]4 cation showing 30% probability ellipsoids and the atom-numbering scheme.

Reaction of 1 with [Pd(CH3CN)]4+ results in the formation of {m-(triphos)}2[Pd(CH3CN)]2][BF4]4 (2), step 2 of reaction 1. The 31P NMR spectrum of 2 consists of a triplet at 119.4 ppm (JPP = 4 Hz) and a doublet at 76.6 ppm assigned to the central and terminal phosphorus atoms, respectively. These chemical shifts and the coupling constant are very similar to those of monomeric [Pd(etpC)(CH3CN)]2 [115.6 ppm (central P), 74.5 ppm (terminal P), and 7 Hz; where etpC is bis(dicyclohexylphosphinoethyl)phosphine].3,19 31P NMR spectral data and elemental analysis are also consistent with the formulation shown for 2 (see Experimental Section).

An X-ray diffraction study confirms the structure proposed for 2, although there is disorder in the cyclohexyl rings, anions, and solvent molecules. The crystals of 2[BF4]4 consist of {m-triphos}2[Pd(CH3CN)]2][BF4]4 cations, BF4– anions, and solvent

The N...caused by the restricted bite size of the triphosphine ligands. If this solution is saturated—exhibits a broad irreversible cathodic wave at 1.38 V versus the ferrocene/ferrocenium couple. At all potentials more irreversible waves are observed at about the two P...C bonds attaching them to the benzene ring (C33...P5 and C31...P2) so that unfavorable steric interactions are avoided. The observed Pd...P and Pd...N bond distances in the first coordination sphere are similar to those observed previously for [Pd(PCP)(CH3CN)]2+ (where MesetpE is bis(2-diethylphosphinoethyl)mesitylphosphine), which are shown in Table 2 for comparison. Pd...P bond angles associated with the five-membered rings are all acute (83°...85°). These acute angles are caused by the restricted bite size of the triphosphine ligands. The N...Pd...Padd angles are greater than 90° to compensate for acute P...Pd...P angles of the triphosphine ligand. The Pd...P bond distances for the central phosphorus atoms are at least 0.1 Å shorter than the Pd...P bond distances to terminal phosphorus atoms. The most likely cause of this difference is the stronger trans influence of phosphorus compared to nitrogen, but restricted vibrational amplitudes arising from incorporation into two rings may also contribute to the observed difference.

**Catalytic Studies.** Cyclic voltammograms recorded on complex 2 in dimethylformamide under four different conditions are shown in Figures 2 and 3. The black trace in Figure 2 is the cyclic voltammogram of 2 under nitrogen atmosphere. It exhibits a broad irreversible cathodic wave at −1.38 V versus the ferrocene/ferrocenium couple. If this solution is saturated with CO2 at 1 atm pressure, the cyclic voltammogram shown by the red trace in Figure 2 is obtained. Under CO2 three irreversible waves are observed at −1.41, −1.51, and −1.75 V. The first two of these are strongly overlapping, which leads to a single broad wave with two humps. At all potentials more negative than the onset potential of the first reduction wave, the current is higher in the presence of CO2 than in the absence of CO2. This suggests that catalysis is occurring even in the absence of an added proton source. Presumably CO2 acts as an acceptor for O2− to form carbonate. In the presence of both HBF4 and CO2, the green trace in Figure 3, a large catalytic wave is observed for the reduction of CO2. In the absence of HBF4, but no CO2, the blue trace in Figure 3 is obtained. In this case a broad, poorly defined reduction wave is observed that corresponds to the catalytic reduction of protons to H2. These cyclic voltammety results suggest, but do not prove, that 2 is a catalyst for CO2 reduction. For example, cyclic voltammograms of the complex [Pd(PCP)(CH3CN)]2+ [where PCP is 2,6-bis(diphenylphosphinomethyl)phenyl] also show enhanced current in the presence of CO2, but the product formed in the presence of acid and CO2 is hydrogen and not CO. For [Pd(PCP)(CH3CN)]2+, CO2 acts as a cocatalyst for hydrogen generation.

Catalytic reduction of CO2 by 2 was confirmed by carrying out controlled-potential electrolysis experiments on the plateau of the catalytic wave (−1.7 V) for dimethylformamide solutions containing 0.1 M HBFOX and a large headspace of CO2 at 620 mmHg (see Experimental Section). The current efficiencies for CO and H2 production were determined to be 80% and 26%, respectively, by gas chromatography. Because this experiment and previous experiments for this class of catalysts were conducted in dimethylformamide, the formation of trace amounts of formate would be obscured by formate formation from solvent decomposition. After a total of 190 turnovers of the catalyst for CO production, a 31P NMR analysis of the solution indicated that 82% of the catalyst was unchanged.

**Kinetic Studies.** For a reversible electron-transfer reaction followed by a fast catalytic reaction at high substrate concentrations, the ratio between the catalytic current, ic, and the diffusion
The current observed for the reduction of the catalyst in the absence of substrates, \( i_d \), is given by eq 2.20

\[
\frac{i_c}{i_d} = \frac{\sigma}{0.447} \sqrt{\frac{RT}{nF}} \sqrt{\frac{kC^m}{\nu}}
\]

where \( n \) is the number of electrons involved in catalyst reduction (2 in this case), \( k \) is the rate constant, \( \nu \) is the scan rate, \( C \) is the concentration of the substrate (\( \text{CO}_2 \)), and \( m \) is an exponent corresponding to the reaction order of the substrate. The value of the factor designated by \( \sigma \) in eq 2 depends on whether the second electron transfer to the catalyst occurs in solution or at the electrode surface. If the second electron transfer occurs in solution—a SET mechanism—the value of \( \sigma \) is \( 2^{1/2} \). If the second electron transfer occurs at the electrode surface—an ECE mechanism—the value of \( \sigma \) is 2. In previous work, a value of 2 was used for this parameter, and this value is used in this study as well. From eq 2 it can be seen that a plot of the catalytic current versus the square root of the \( \text{CO}_2 \) concentration should be linear if the reaction is first order in \( \text{CO}_2 \). Such a plot is shown in the bottom graph of Figure 4. The catalytic current also shows a square root dependence on the catalyst concentration, top graph of Figure 4. In the case of the catalyst, the current shows a first-order dependence if the reaction is first order in catalyst, a second-order dependence if the reaction is second order, etc.20 Therefore a square root dependence on catalyst concentration indicates that only half of the bimetallic complex is required for catalysis. The transition state of a given catalytic cycle contains one palladium center and one \( \text{CO}_2 \). This indicates that the two palladium atoms act independently of each other.

The dependence of the catalytic current on acid is shown by the red circles in Figure 5. These data are uncorrected for any background current that may be due to hydrogen production. The blue circles indicate data in which the current in the absence of \( \text{CO}_2 \), i.e., the current observed at different acid concentrations, is subtracted. Both of these data sets indicate that at low acid concentrations the current exhibits a strong dependence on the acid concentration, but at higher acid concentrations the current approaches a limiting value that is independent of the acid concentration. This behavior indicates the presence of two rate-determining steps depending on the reaction conditions.

In previous work on monomeric \([\text{Pd}(\text{triphosphine})-(\text{CH}_3\text{CN})]^+\) catalysts, eq 2 was modified to eq 3 to account for this behavior.9,10 In this equation, both the acid and \( \text{CO}_2 \)
concentrations are treated explicitly, and $k_1$ is the second-order rate constant for the reaction of CO$_2$ with the Pd(I) species formed on reduction of Pd(II). The rate constant $k_2$ is a composite constant and not a simple rate constant. It can be seen that depending on whether a background correction is made, the data can be fitted for either a first-order (red curve) or second-order (blue curve) acid dependence. Because of this, the correct order of the catalytic reaction with respect to the acid concentration is ambiguous, and two different rate constants for $k_1$ are obtained, 145 M$^{-1}$ s$^{-1}$ assuming a first-order dependence on [H$^+$] and 53 M$^{-1}$ s$^{-1}$ assuming a second-order dependence on [H$^+$]. However, there is no doubt that there is an acid dependence.

$$\frac{i_c}{i_d} = \frac{\sigma}{0.447 \sqrt{\frac{RT}{nF\nu}} \sqrt{k_1 k_2 [\text{CO}_2] [\text{H}^+]^m}} \sqrt{k_1 [\text{CO}_2] + k_2 [\text{H}^+]^m}$$

(3)

**Discussion**

In previous work, we have described the electrocatalytic reduction of CO$_2$ by monometallic [Pd(triphosphine)(CH$_3$CN)]$_2^{2+}$ complexes (3), the bimetallic complex [Pd$_2$(CH$_3$CN)$_2$eHTP)$_4^{4+}$ (4), and dendrimers 5 and 6. The monometallic complexes 3 are excellent catalysts for the reduction of CO$_2$ to CO. The reactant step in the catalytic cycle for these complexes is the reaction of the reduced Pd(I) catalyst with CO$_2$. Second-order rate constants for this reaction range from 5 to 300 M$^{-1}$ s$^{-1}$, making these catalysts some of the fastest CO$_2$ reduction catalysts known. They also operate at moderate overpotentials and can exhibit current efficiencies for CO production exceeding 90%. However, measured turnover numbers are less than 150. It was found that one of the major decomposition pathways for these monometallic palladium complexes was the formation of bimetallic Pd(II) dimers having structure 7. This decomposition pathway is retarded by the use of bulky substituents such as cyclohexyl groups on the terminal phosphorus atoms, but deactivation still occurs. One attempt to increase the stability of these complexes was to incorporate them into dendrimers such as 5 and 6. The premise underlying the study of these dendrimers was that the restricted positions of the [Pd(triphosphine)(CH$_3$CN)]$_2^{2+}$ units within the dendrimers would prevent Pd–Pd bond formation. However, the selectivity of these dendrimers for CO production was decreased and the turnover numbers were generally less than those of their monometallic analogues, 3. It was concluded from these studies that increased turnover numbers for dendrimers might be possible if the [Pd(triphosphine)(CH$_3$CN)]$_2^{2+}$ units were more isolated from each other.

A second reason for interest in dendrimers 5 and 6 was the possibility of cooperative interactions between metal sites during CO$_2$ reduction. There is considerable literature precedent that CO$_2$ binding can be stabilized by the interaction of two metals. In these systems one metal binds to a carbon atom and the second metal binds to oxygen. However, no evidence of cooperative interaction between the palladium atoms was observed for dendrimers 5 and 6. In contrast, kinetic studies of the bimetallic complex 4 indicated that the transition state formed by the reaction of the Pd(I) form of 4 with CO$_2$ involved both metal atoms and one proton. This is consistent with a cooperative interaction between metals for CO$_2$ reduction, and the rate constant appeared to be significantly higher (10$^4$ M$^{-1}$ s$^{-1}$). However, decomposition of this Pd(I) intermediate was also much faster and a turnover number of 8 was observed for 4.

The dipalladium complex 2 was prepared to determine if beneficial cooperative effects observed for 4 would be preserved if the distance between the central phosphorus atoms of the two triphosphine units was increased. A second objective was to determine if catalyst degradation could be retarded by incorporating cyclohexyl substituents on the terminal phosphorus atoms and increasing the intramolecular Pd–Pd distance relative to 4. The kinetic results described above for 2 demonstrate that the transition state that occurs during the catalytic reduction of CO$_2$ to CO involves only one palladium atom, one CO$_2$ molecule, and one or two protons. These results indicate that the cooperative interaction between two palladium atoms observed for complex 4 is not observed for 2 and that the two [Pd(triphosphine)(CH$_3$CN)]$_2^{2+}$ units act independently during the catalytic process. The catalytic rates of 2 (50–150 M$^{-1}$ s$^{-1}$) and its analogous monomeric complex [Pd(etpC)(CH$_3$CN)]$_2^{2+}$ (50 M$^{-1}$ s$^{-1}$) are also quite comparable. This also suggests that no cooperative interaction between the two palladium atoms occurs during the catalytic cycle of 2. Cooperative binding of CO$_2$ for 2 is apparently prevented by the bulkiness of the cyclohexyl substituents. However, the stability of 2 is greater than its monometallic analogue, [Pd(etpC)(CH$_3$CN)]$_2^{2+}$, and complexes 4–6. Complex 2 undergoes less than 20% degradation after nearly 200 turnovers. Previous turnover numbers of 130, 8, 15, and 5 for [Pd(etpC)(CH$_3$CN)]$_2^{2+}$, 4, 5, and 6, respectively, were determined when 10% or less of the original catalytic activity remained. Retention of 80% of 2 after nearly 200 turnovers indicates that the turnover numbers for this complex are at least 1–2 orders of magnitude greater than for

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The increased stability of 2 is attributed to a combination of the steric interactions of the cyclohexyl groups and an intramolecular restriction of the Pd–Pd distance in 2 that arises from the constraints of the m-benzene bridge. Both of these features should retard Pd–Pd bond formation.

In summary, the new bimetallic palladium complex 2 has been prepared and characterized by NMR spectroscopy and an X-ray diffraction study. Complex 2 is a catalyst for the electrochemical reduction of CO₂ to CO. Kinetic studies indicate that the transition state involves one palladium, one CO₂ molecule, and either one or two protons. Therefore the two palladium atoms of 2 act independently of each other during the catalytic cycle. However, because of the steric constraints of the cyclohexyl substituents and the bridging m-benzene backbone, 2 exhibits significantly higher turnover numbers than other members of this class of catalysts.

Acknowledgment. The support of the Director’s Discretionary Research and Development Program of the National Renewable Energy Laboratory is gratefully acknowledged.

Supporting Information Available: X-ray structural data including tables of crystal and refinement data, atomic positional and thermal parameters, and interatomic distances and angles for \{m-(triphos)₂[Pd(CH₃CN)]₂\}_₄(BF₄)₄ (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

OM060228G