Electrochemical Reduction of CO2 Catalyzed by a Dinuclear Palladium Complex Containing a Bridging Hexaphosphine Ligand: Evidence for Cooperativity

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The complexes \([\text{Pd}_2(\text{CH}_3\text{CN})_2(eHTP)](\text{BF}_4)_4\) and \([\text{Pd}_2(\text{PET}_3)_2(eHTP)](\text{BF}_4)_4\) (where eHTP is bis(bis(diethylphosphino)ethylphosphino)methane, \(\text{Et}_2\text{PCH}_2\text{CH}_2\text{PCH}_2\text{P}((\text{CH}_2\text{CH}_2\text{PET}_3)_2\)) were prepared and characterized. \([\text{Pd}_2(\text{CH}_3\text{CN})_2(eHTP)](\text{BF}_4)_4\) catalyzes the electrochemical reduction of CO2 to CO in acidic dimethylformamide solutions. The rate of this reaction exhibits a biphasic dependence on acid, with a first-order dependence at low acid concentrations and zero-order dependence at acid concentrations greater than 0.06 M. At high acid concentrations the rate-limiting step is first order in catalyst and first order in CO2. When compared to the kinetic properties of previously studied mononuclear complexes, these data suggest both palladium atoms are involved in CO2 reduction. The closely related complex \([\text{Pd}_2(\text{PET}_3)_2(eHTP)](\text{BF}_4)_4\) undergoes two reversible two-electron reductions. The mixed-valence intermediate resulting from the first two-electron reduction is unstable and undergoes rapid decomposition.

Introduction

Structural and spectroscopic studies have shown that CO2 binding can be enhanced by cooperative effects between two metals and between a metal and its ligand. The two metals involved may be a transition metal and an alkali metal, two transition metals, or a transition metal is recycled in a catalytic fashion. The magnesium ions act as stoichiometric reagents. Catalytic reactions observed for Ni(cyclam)+ (where cyclam is 1,4,8,11-tetraazacyclotetradecane) adsorbed on Hg may also proceed through bimetallic intermediates, but no direct evidence has been presented, and dinuclear complexes on Ni(cyclam)+ have shown no cooperative effects. Bimetallic copper complexes and trinuclear nickel clusters have been reported to catalyze the electrochemical reduction of CO2. Mechanistic studies of these bimetallic complexes are consistent with a transition state containing one CO2 per two copper sites which may indicate a possible cooperative interaction. Unfortunately, no analogous mononuclear complexes exhibiting catalytic activity are available for comparison with these dinuclear complexes. Recent examples of bimetallic activation of other substrates include C-H activation of methane, phosphorylation and phosphate ester hydrolysis, and hydroformylation of olefins.

Structural studies and van der Waals energy calculations carried out by Stanley and co-workers on di-palladium complexes of the bridging hexaphosphine ligand eHTP ([Et2PCH2CH2PCH2P(CH2CH2PET3)_2] have shown that the preferred structure is a conformation with the palladium atoms nearly eclipsed as shown in
Figure 1. Calculated (bottom) and experimental (top) $^{31}$P NMR spectra for [Pd$_2$(PET$_3$)$_2$eHTP](BF$_4$)$_4$. Parameters used in the simulation are listed in the Experimental Section.

structure 1.20 Work from our laboratory has demon-

strated that the closely related [Pd(triphosphine)(CH$_3$-

CN)](BF$_4$)$_2$ complexes catalyze the electrochemical re-

duction of CO$_2$ to CO in acidic dimethylformamide or

acetonitrile solutions.21 These catalysts exhibit second

order rate constants as high as 300 M$^{-1}$ s$^{-1}$ and can be

very selective with current efficiencies exceeding 95%

for the production of CO. Our results and those of

Stanley and co-workers suggested that the complex

[Pd$_2$(CH$_3$CN)$_2$(eHTP)](BF$_4$)$_4$, 2, in which the chloride

ligands of 1 are replaced with acetonitrile, might exhibit

cooperative effects for CO$_2$ reduction by forming inter-

mediates containing a bridging CO$_2$ ligand. This paper

describes studies of 2 as a catalyst for electrochemical

CO$_2$ reduction.

Results

Synthesis and Characterization of Complexes.

The ligand eHTP was prepared as described in the

literature.22 Reaction of 1 equiv of eHTP with 2 equivs

of [Pd(CH$_3$CN)$_2$](BF$_4$)$_2$ resulted in formation of [Pd$_2$(CH$_3$-

CN)$_2$(eHTP)](BF$_4$)$_4$, 2. The $^{31}$P NMR spectrum of 2

consists of two singlets at 63.8 and 110.2 ppm assigned

to the terminal, $P_T$, and central, $P_C$, phosphorus atoms,

respectively, of the coordinated hexaphosphine ligand.

These assignments are based on the relative intensities of

these resonances and on the similarity of the chemical

shifts to those observed for monomeric analogues.21 The

presence of coordinated acetonitrile is indicated by CN

stretching and combination bands at 2295 and 2323

cm$^{-1}$ in the infrared spectrum.23

The labile acetonitrile of 2 is readily replaced by

triethylphosphine forming [Pd$_2$(PET$_3$)$_2$(eHTP)](BF$_4$)$_4$, 3.

The $^{31}$P NMR spectrum of 3 is complex as shown by the
top trace in Figure 1. This spectrum has been analyzed

as an AA'XX'M$_2$M$_2'$ spin system using the parameters

listed in the Experimental Section. This analysis

indicates a 47 Hz coupling between the two central

phosphorus atoms, $P_X$ and $P_X$, and a 9 Hz coupling

between $P_A$ and $P_X$. Similar four-bond coupling con-

stants have been observed in phosphido-bridged dimers

of Pd and Pt.24 The other coupling constants and

chemical shift values of 3 are close to those observed

for other square planar [Pd(triphosphine)(PET$_3$)](BF$_4$)$_2$

complexes.21 On the basis of their spectroscopic data

both 2 and 3 are assigned the bridged square-planar

structures shown above.

Electrochemical Studies. Cyclic voltammograms of 2 under different conditions are shown in Figure 2. Cyclic voltammogram a is of the complex under a nitrogen atmosphere. With the exception of the cathodic peak observed at $-1.94$ V, only a featureless cathodic current is observed with an onset potential of approximately $-1.1$ V. These same features are observed for all scan rates between 0.05 and 100 V/s. A similar cyclic voltammogram is observed in the presence of CO$_2$ as shown by trace b. Under an atmosphere of CO$_2$, the current onset of the first wave and the cathodic peak at $-1.95$ V are shifted to more positive potentials.

Controlled potential electrolysis of dimethylformamide solutions of 2 at $-1.3$ V under N$_2$, CO$_2$, and CO atmospheres resulted in the passage of 2.0 $\pm$ 0.2 Faradays/mol of 2 or 1.0 Faraday/mol of palladium. The product was the same in all cases. The $^{31}$P NMR

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Figure 2. Cyclic voltammograms of a 1.3 × 10⁻³ M solution of [Pd₂(CH₂CN)₆H₂TP]BF₄₂⁻ in dimethylformamide: (a) under nitrogen (solid line), (b) saturated with CO₂ at 620 mmHg (dashed line), (c) saturated with CO at 620 mmHg (++). Cyclic voltammograms of same solution containing 0.076 M HBF₄ (d) under nitrogen (solid line) and (e) saturated with CO₂ (dashed line). The supporting electrolyte was 0.3 M NEt₄BF₄, all scan rates were 0.1 V/s, and the working electrode was glassy carbon.

Figure 3. Peak current as a function of acid concentration for solutions saturated with CO₂ (open circles) and nitrogen (solid circles). The dashed line represents the best fit curve using eq 1 (k₁ = 31 M⁻¹ s⁻¹ and k₂ = 5.9 × 10⁴ M⁻² s⁻¹), and the solid line represents the best fit curve using eq 2 (k₁ = 45 M⁻¹ s⁻¹ and k₂ = 380 M⁻² s⁻¹). As discussed in the text, the values obtained for k₁ and k₂ should not be interpreted as true rate constants.

Figure 4. Plots showing the dependence of the catalytic current on CO₂ (top graph) and catalyst concentrations (bottom graph).

Cyclic voltammograms d and e of Figure 2 are of 2 in the presence of 0.076 M HBF₄ under nitrogen and CO₂ atmospheres, respectively. An increase in the cathodic current is observed in the presence of CO₂ compared to nitrogen. This increase is attributed to the reduction of CO₂ to CO. Electrolysis at −1.3 V of a dimethylformamide solution of 2 containing 0.1 M HBF₄ and 0.18 M CO₂ produced CO with a current efficiency of 85%. The other product formed during electrolysis is hydrogen, which accounts for the remaining charge consumed. A turnover number of 8 was calculated based on the moles of CO produced per mol of catalyst. The catalyst was considered deactivated when the current had decayed to 10% of its original value.

The dependence of the catalytic current on substrate and catalyst concentrations are shown in Figures 3 and 4. A plot of the catalytic current versus acid concentration (Figure 3, open circles) is biphasic. The catalytic current initially increases with acid concentration and
then becomes independent of it. As discussed in more detail later, this behavior is consistent with a first-order dependence of the catalytic rate on acid at low acid concentrations and a zero-order dependence at high acid concentrations. The solid circles in Figure 3 show the currents observed for solutions of different acid concentrations in the absence of CO₂. At all acid concentrations a significant current enhancement is observed for solutions purged with CO₂ compared to those purged with N₂. Plots of the catalytic current versus the square root of the CO₂ concentration and versus the catalyst concentration are shown in Figure 4. The square root dependence of the catalytic current on CO₂ concentration is consistent with a rate-determining step that is first order in CO₂. The linear dependence of the current on catalyst concentration implies a first order dependence on the catalyst concentration as well.

The catalytic current was decreased by approximately 20% when the CO₂ pressure was held constant at 1 atm and the partial pressure of CO was increased to 0.5 atm (scan rate 0.1 V/s). This indicates that the product, CO, inhibits the reaction. Reaction of CO with 2 in undried dimethylformamide-d₆ produces H₂, CO, and 4 over a period of 1-2 days with no detectable intermediates as shown in eq 1. The production of 4 was monitored by ¹³P NMR spectroscopy, and the formation of H₂ and CO₂ was measured by gas chromatography. Reaction 1 is promoted by addition of water, and it is retarded in the presence of 0.07 M HBF₄. Although reaction 1 occurs in acidic DMF solutions under conditions identical to those for catalytic reactions, the rate is slow with less than 1 equiv of H₂ produced in 24 h. These results suggest that hydrogen produced during the electrochemical reduction does not arise from the water gas shift reaction and that the formation of 4 is competitive with hydrogen production.

Ideally the catalytic current should be independent of the scan rate. However, the catalytic current exhibited a square root dependence on the scan rate for scan rates between 0.05 and 100 V/s at room temperature as shown in Figure 5. The catalytic current also remained scan rate dependent for solutions cooled to -50 °C.

Cyclic voltammograms of 3 at two different scan rates are shown in Figure 6. At 10 V/s (voltammogram a), two reversible two-electron reductions are observed at -1.12 and -1.44 V. These two waves are assigned to the two Pd(II/O) couples expected for the tetrakis(diphenylphosphino)benzene 

\[
\begin{align*}
\text{CO} + 2 + H₂O &\rightarrow CO₂ + 4 + H₂ 
\end{align*}
\]  

(1)
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The rate determining step in the decomposition of the possibility of a reversible loss of triethylphoshine being excess triethylphosphine cyclic voltammogram observed. The labile acetonitrile ligand of triethylphosphine ligand and the central phosphorus atom of the second square-planar unit suggests a two-electron reduction of complex 3.

Discussion

[Pd₂(μ₃-CH₃CN)(μ-3HTP)(BF₄)₄], 2, is readily prepared from 3HTP and [Pd(CH₃CN)₄](BF₄)₂. Substitution of the labile acetonitrile ligand of 2 with triethylphosphine produces [Pd₂(μ₃-PEt₃)(μ-3HTP)(BF₄)₄], 3. The coupling observed by ³¹P NMR between the two central phosphorus atoms of 3, ¹Jₚₚ = 43 Hz, and between the triethylphosphine ligand and the central phosphorus atom of the second square-planar unit, ⁴Jₚₚ = 9 Hz, suggests a significant interaction between the two square-planar units. The 300 mV difference between the two Pd(II/0) couples observed by cyclic voltammetry for 3 is also consistent with a strong interaction between the two palladium sites.

The increased current observed in the presence of CO₂ for acidic solutions of 2 suggested that 2 catalyzes the electrochemical reduction of CO₂ (Figure 2 trace e). This was confirmed by controlled potential electrolysis experiments carried out at −1.3 V and identification of CO as the major reduction product by gas chromatography. The dependence of the catalytic current on acid concentration (Figure 3) is consistent with two different rate-determining steps. For monomeric [Pd₃(triphosphine)(CH₃CN)](BF₄)₃ complexes, two rate determining steps were also observed. In that case, a linear dependence of the catalytic current on acid concentration was observed for solutions with low acid concentrations. Because of the square root dependence of the catalytic current on substrate concentration, a linear dependence is consistent with a rate-determining step that is second order in acid, which implies a transition state involving two protons. The proposed rate-determining step at low acid concentrations is the cleavage of the C–O bond to form CO and water. At higher acid concentrations the current was independent of acid, first order in catalyst, and exhibited a square root dependence on the concentration of CO₂. This is consistent with a rate determining step that is first order in catalyst and CO₂. On the basis of this and other electrochemical data, the reaction of a Pd(I) species with CO₂ was proposed as the rate determining reaction at high acid concentrations. For the mononuclear complexes, the kinetic data were fit to eq 2, where η is the catalytic current, η_d is the peak current due to reversible reduction of the catalyst, υ is the scan rate, n is the number of electrons involved in catalyst reduction, k₁ and k₂ are rate constants for the two rate-determining steps discussed above, and σ is a factor which depends on whether the second electron transfer to the catalyst occurs at the electrode surface or in solution. Using eq 2, the best fit curve to the data shown in Figure 3 is shown by the dashed line. The observed data do not fit this model well. A better fit is obtained using eq 3,

\[
\frac{i_c}{i_d} = \frac{\sigma}{0.447} \sqrt{\frac{RT}{nFυν}} \sqrt{\frac{k_1 k_2 [CO₂][H^+]^2}{k_1 [CO₂] + k_2 [H^+]^2}}
\]

which assumes a first-order dependence on acid at low acid concentrations. The solid line shown in Figure 3 is the best curve obtained assuming a first-order dependence on acid. The data are clearly much more consistent with this model. The presence of only one proton in the activated complex of the dimeric catalyst suggests the possibility of a transition state with a bridging CO₂ molecule as shown in eq 4. In structure 5, one proton of the mononuclear transition state has been replaced by the second palladium atom of the dimer. This would account for the biphasic dependence of catalytic current of 2 on acid concentration and also for the difference in the acid dependence observed for monomeric catalysts and 2.

At high acid concentrations, the first-order dependence of the rate-limiting step on the concentrations of 2 and CO₂ is consistent with two palladium atoms and one CO₂ molecule in the transition state. This stoichiometry could reflect a cooperative binding as shown by structure 6 in eq 5, or it could simply be the result of deactivation of the second palladium due to reduction of the first. To distinguish between these two possibilities, an effort was made to measure the rate of this reaction. Determination of catalytic rate constants using eq 3 requires a reliable value for the peak current under noncatalytic conditions. As can be seen from cyclic voltammogram of a Figure 2, determination of an appropriate peak current for 2 is difficult because no peaks are observed. Complex 3 was prepared to provide a good estimate of this value. In previous work, [Pd₃(triphosphine)(PEt₃)](BF₄)₃ complexes have exhibited reversible two-electron reductions, and two reversible two-electron reductions are observed for 3. Dividing the peak currents observed for the two-electron reductions of 3 by 2.83 suggests that should provide a reasonably good estimate of the current expected for a reversible one electron


reduction of 2, because 2 and 3 are expected to have very similar diffusion coefficients. Using the value of \( i_d \) obtained in this manner, eq 2 can be used to fit the data shown in Figure 3. The solid curve shown is the fit obtained using values of 45 and 380 M\(^{-1}\) s\(^{-1}\) for \( k_1 \) and \( k_2 \). These values do not reflect true rate constants for this reaction because they are scan rate dependent. However, the dependence of the catalytic currents on substrate and catalyst concentrations is consistent with the proposed rate-determining steps.

Ideally the catalytic current should not depend on the scan rate. However, because of the square root dependence observed for the catalytic current (Figure 5), the apparent rate constants calculated using eq 3 exhibit a linear dependence on the scan rate as shown in Figure 7 for \( k_1 \). This linear dependence could arise from (1) a slow catalytic reaction, (2) depletion of the substrates, (3) rapid decomposition of the catalyst, or (4) inhibition by the product CO. A slow catalytic reaction can be ruled out on the basis of the large catalytic currents observed and the fact that enhanced currents are observed in the presence of CO\(_2\) even at scan rates as high as 100 V/s. A diffusion-controlled wave with small or no current enhancement in the presence of CO\(_2\) is expected for a slow catalytic reaction at high scan rates. Depletion of substrates can be discounted because other monomeric catalysts show much larger currents that are scan rate independent under identical conditions. The third possibility, decomposition of the catalyst, is a reasonable possibility. Controlled potential electrolysis experiments indicate the turnover number for 2 is low, 8, and on the basis of \(^{31}\)P NMR spectra of the spent reaction mixture, the major decomposition product is the tetrameric or oligomeric compound 4 discussed above. The formation of 4 must occur very rapidly, because the reduction wave assigned to this product is observed at scan rates as high as 100 V/s under CO\(_2\) and N\(_2\) atmospheres. Finally, the peak current of cyclic voltammograms simulated assuming a decomposition reaction with a rate competitive with the catalytic reaction has a square root dependence on scan rate as shown in Figure 5. The calculated peak currents are the results of simulations assuming a rate constant for \( k_1 \) (eq 2) of \( 1 \times 10^6 \) M\(^{-1}\) s\(^{-1}\) and a first-order rate constant for the decomposition of the catalyst of \( 3 \times 10^4 \) s\(^{-1}\). These values are not unique in fitting the data but only serve to illustrate that the assumption of a competing decomposition reaction is consistent with the observed behavior of the catalytic current on scan rate.\(^{30}\)

Carbon monoxide inhibits the catalytic current as discussed above. This product inhibition could also contribute to the nonideal behavior of the catalytic current. Although CO and H\(_2\)O react with 2 to form 4, H\(_2\), and CO\(_2\), reaction 1 is slow and unlikely to contribute to the observed current inhibition. The reaction of reduced forms of 2 with CO appears to be more rapid as indicated by the shift in the first reduction wave of 2 to more positive potentials in the presence of CO as shown by trace c of Figure 2. It is therefore concluded that it is a reduced form of 2 which binds CO sufficiently rapidly to produce inhibition. However, any CO complexes which form are not stable since reduction of 2 in the presence of CO produces 4.

Attempts to slow the decomposition reaction by lowering the temperature to \(-50^\circ\text{C}\) and reducing the catalyst concentration were unsuccessful, because the catalytic current still exhibited a scan rate dependence under these conditions. In principle, at sufficiently high scan rates the decomposition of the catalyst should become insignificant and a true catalytic current could be measured. However, this does not occur for scan rates as high as 100 V/s as shown in Figure 7. Consequently a true rate constant cannot be determined, but a lower limit of at least \( 25 \times 10^3 \) M\(^{-1}\) s\(^{-1}\) can be inferred for \( k_1 \) from this data. This rate constant is 3 orders of magnitude larger than the 25 M\(^{-1}\) s\(^{-1}\) value expected for a mononuclear [Pd(triphosphine)(CH\(_3\)CN)](BF\(_4\))\(_2\) complex with a redox potential of \(-1.18 \text{ V}\). This result supports a cooperative effect between the two metal sites of 2 during the electrochemical reduction of CO\(_2\) to CO.

**Summary and Conclusions**

Complex 2 catalyzes the reduction of CO\(_2\) to CO in acidic DMF solutions. Three observations suggest a cooperative interaction between the two palladium sites and CO\(_2\) during the catalytic cycle. (1) At low acid concentrations, the first-order dependence of the catalytic rate on acid concentration observed for 2 compared to a second-order dependence for mononuclear complexes is consistent with the second palladium atom of 2 binding to an oxygen atom of CO\(_2\) as shown in structure 5. (2) At high acid concentrations, the dependence of the catalytic current on the concentrations of CO\(_2\) and catalyst is consistent with two palladium atoms per CO\(_2\). (3) The catalytic rate of CO\(_2\) reduction for 2 is at least 3 orders of magnitude greater than that expected for a mononuclear [Pd(triphosphine)(CH\(_3\)CN)](BF\(_4\))\(_2\) complex having the same potential. These observations suggest that dinuclear complexes such as 2 can provide a useful approach for dramatically enhancing catalytic rates of CO\(_2\) reduction. On the other hand, the very high rate of decomposition of these catalysts must be overcome before advantage can be taken of these higher catalytic rates. Research is in progress to address this issue.

**Experimental Section**

**Materials and Physical Methods.** Reagent-grade diethyl ether and toluene were purified by distillation from sodium.
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benzophenone ketyl. Acetonitrile was distilled from CaH₂ under nitrogen. Reagent-grade dimethylformamide from Bur- 
dick and Jackson was deoxygenated by purging with nitrogen and stored in an inert-atmosphere glovebox. Acetonitrile (0.4 mL) was 
dried over 4-A molecular sieves, vacuum transferred, and stored in a glovebox. Triethylamine was obtained from Strem Chemicals, Inc. and used without further purification. The ligand eHTP and [Pd(CH₂CN)₄][BF₄]₂ were prepared by literature methods.²²

NMR spectra were obtained on a Varian Unity 300 MHz NMR spectrometer operating at 299.95, 121.42, and 75.43 MHz for 1H, 31P, and 13C nuclei, respectively. Chemical shifts for 1H NMR spectra are reported in ppm relative to tetramethylsilane using solvent peaks as secondary references. 31P NMR chemical shifts are referenced to external 85% H₃PO₄. Infrared spectra were obtained using a Nicolet 510 P spectrometer on samples prepared as Nujol mulls or dichloromethane solutions. Couloicmetric measurements were carried out at 25–30 °C using a Princeton Applied Research Model 173 potentiostat equipped with a Model 179 digital coulometer and a Model 175 universal programmer. The working electrode was constructed from a reticulated vitreous carbon rod with a 1-cm diameter and a 5-mm diameter. Measurements of current efficiencies for gas production were carried out in a sealed flask (120 mL). In a typical experiment, a 1.0 × 10⁻³ M solution of 2 in dimethylformamide (10.0 mL) was saturated with CO₂ (0.18 M at 620 mmHg) by purging the solution for approximately 30 min. The solution was then added via syringe and the solution electrolyzed at −1.5 V. The electrolysis was considered complete when the current had decayed to approximately 5–10% of the initial value. During the course of the electrolysis, gas aliquots were withdrawn for gas chromatographic analysis. The gases were analyzed at 200 °C using a 1/8 in. × 15 ft stainless steel column packed with 60/80 carboxen 1000 support (Supelco). Cyclic voltammetry and chronoamperometry experiments were carried out using a Cypress Systems computer-aided electrolysis system. The working electrode was a glassy carbon disk of approximately 1-mm diameter. The counter electrode was a glassy carbon rod, and the reference electrode was a Pt wire immersed in a permethylferrocene/permethylferrocenium solution. Ferrocene was used as an internal standard, and all potentials are reported vs the ferrocene/ferrocenium couple. All solutions for cyclic voltammetry and couloicmetric experiments were 0.3 N NEt₄BF₄ in dimethylformamide.

Synthesis. [Pd₂(CH₂CN)₄(eHTP)][BF₄]₄. 2. A solution of eHTP (1.00 g, 1.84 mmol) in toluene (20 mL) was added to a solution of [Pd(CH₂CN)₄][BF₄]₂ (1.63 g, 3.68 mmol) in acetonitrile (50 mL), and the orange reaction mixture was stirred for 1 h. The solvent was removed with a vacuum to produce a yellow solid which was washed with ether and dried. The product was recrystallized from a mixture of acetonitrile and ether (yield 1.8 g, 83%). Anal. Calcd for C₄₂H₇₀F₁₆N₈P₈Pd₂: C, 35.96; H, 6.47; P, 17.66. Found: C, 37.11; H, 6.47; P, 15.96.

Synthesis. [Pd₂(P₂Et₆)₄(eHTP)][BF₄]₄. 3. A solution of eHTP (0.25 g, 0.46 mmol) in toluene (5 mL) was added to a solution of [Pd(CH₂CN)₄][BF₄]₂ (0.41 g, 0.92 mmol) in acetonitrile (25 mL), and the orange reaction mixture was stirred for 1 h. Triethylphosphine (0.11 g, 0.95 mmol) was added to the reaction mixture, which was stirred for an additional 2 h. The solvent was removed in a vacuum, and the orange solid which resulted was washed repeatedly with ether and dried (0.34 g, 55%). Anal. Calcd for C₄₂H₇₀F₁₆N₈P₈Pd₂: C, 35.96; H, 6.47; P, 15.96. Found: C, 37.11; H, 6.47; P, 15.96.

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