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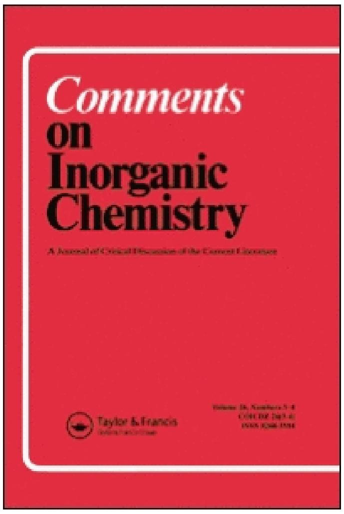

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# Development of Transition Metal Phosphine Complexes as Electrocatalysts for $CO_2$ and CO Reduction

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# Development of Transition Metal Phosphine Complexes as Electrocatalysts for $CO_2$ and CO Reduction

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[Pd(triphosphine)(solvent)]$(BF_4)_2$ complexes have been developed as catalysts for the electrochemical reduction of $CO_2$ to CO. A variety of structural features of these complexes have been varied to determine their effects on the mechanism, rates, and decomposition products of these catalysts. The structural features varied included substituents on the triphosphine ligand, the size of the chelate bite, and donor atoms of the tridentate ligand. Bimetallic catalysts containing two [Pd(triphosphine)(solvent)] units have been prepared and characterized that exhibit a cooperative interaction during $CO_2$ reduction with large rate enhancements compared to their monomeric analogs. As a first step in developing electrocatalysts capable of reducing CO, electrochemically generated hydrides of Ni and Pd have been shown to transfer their hydride ligands to coordinated CO to form formyl complexes.

**Key Words:** *carbon dioxide reduction, electrocatalysis, metal phosphine complexes, cooperative effects, formyl complexes*

## INTRODUCTION

### Rationale

Photosynthesis is the largest renewable energy reaction occurring on earth. It is estimated that each year photosynthesis converts 350 billion

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tons of $CO_2$ into biomass.[1] In its simplest form, photosynthesis can be broken down into two steps: (1) the adsorption of visible light to produce charge separation, and (2) the electrochemical reduction of $CO_2$ to produce biomass. This biomass can be used directly by man to generate fuels, or nature may process it over millions of years to produce the fossil fuels on which we are so heavily dependent for our energy supply today.

Of the major possible sources of renewable energy—photovoltaics, wind, geothermal, hydroelectric, and biomass—only biomass results in the production of fuels. The remaining renewable energy sources, and nuclear energy, all produce electricity as their primary product. Although biomass can produce some of the fuels which will be needed in the future, it is likely that increasing food demands will limit the land mass available for fuels production from biomass. This leads to the conclusion that, if renewable energy is to be used to produce fuel supplies in the future, electricity will need to be converted to fuels instead of the reverse process that is used today (in which fossil fuels are converted to electricity). Although fuels will likely be displaced by electricity in many markets in the future, the high energy density and storage properties of fuels will likely make them irreplaceable for many applications.

## Background

The efficient electrochemical reduction of $CO_2$ to a liquid fuel such as methanol, ethanol, or methane would provide a route to renewable fuels with high energy densities which will be important in insuring a balanced distribution of energy vectors in the future. This process will require major advances in the development of electrocatalysts for $CO_2$ reduction. Over the past 20 years, a number of electrocatalysts for $CO_2$ reduction have been reported.[2,3] These catalysts may be conveniently grouped into four major classes: (1) metal complexes with macrocyclic ligands, (2) metal complexes with bipyridine ligands, (3) metal complexes with phosphorus ligands, and (4) metal electrodes. Although a number of catalytic systems are known, many obstacles still need to be overcome before the direct electrochemical reduction of $CO_2$ to a fuel is feasible.

The first report of macrocyclic complexes catalyzing the reduction of $CO_2$ was by Meshitsuka and co-workers using cobalt and nickel phthalocyanines adsorbed on graphite electrodes.[4] This was followed by the work of Eisenberg, who demonstrated that discrete metal complexes of cobalt and nickel could catalyze the reduction of $CO_2$ to CO.[5] Many contributions to our mechanistic understanding of this class of catalysts have been made by a number of different research groups.[6] Perhaps the most promising catalysts for $CO_2$ reduction in this group are the nickel cyclam complexes first studied in detail by Sauvage and co-workers.[7] These complexes are very selective for the production of CO, and the turnover numbers appear to be high. Two major drawbacks to the Ni cyclam catalysts are that adsorption on Hg is required for high catalytic rates and high turnover numbers, and only a two-electron reduction of $CO_2$ is observed.

Catalysts based on bipyridine ligands were first reported by Lehn and co-workers in which a rhenium complex originally intended to serve as a photosensitizer was also found to function as a $CO_2$ reduction catalyst.[8] In this case, the product is CO as well. A number of bipyridine complexes containing Re, Ru, Rh, Os, and various first-row transition metal complexes have been reported.[9] One of the most intriguing results from this class of compounds is the observation that under certain condition four- and six-electron reductions can be observed.[10] However, the catalytic rates and/or the selectivity for these more highly reduced products are not high.

Only a few transition metal phosphine complexes have been reported that catalyze the reduction of $CO_2$, [11–20] although a large number of $CO_2$ complexes of this class are known. Wagenknecht and co-workers reported the first example of a catalyst belonging to this class, a rhodium diphosphine complex, but these complexes had large overpotentials, low catalytic rates, and low turnover numbers.[11] The most extensively studied metal phosphine complexes for $CO_2$ reduction are the [Pd(triphosphine)(solvent)]$^{2+}$ complexes reported by our research group.[13–20] Catalysts with high selectivity, high rates, and low overpotentials have been prepared and characterized, but again the major reduction product for these catalysts is CO, and turnover numbers are low.

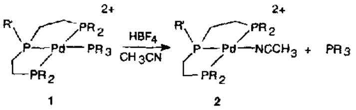
A large number of metal electrodes have been evaluated for their ability to catalyze the electrochemical reduction of $CO_2$.[21] One of the most interesting metals is copper. Under the appropriate conditions, these electrodes catalyze the reduction of $CO_2$ to methane with a current efficiency of approximately 65%.[22–25] Although the high overpotential of nearly 1 V results in a low energy efficiency, this is an important result because it demonstrates the feasibility of carrying out an eight-electron reduction in a single process with relatively high selectivity.

# DEVELOPMENT OF MONOMETALLIC PALLADIUM TRIPHOSPHINE CATALYSTS

## Design of the Catalyst Screening Process

Research in our laboratory has focused on the development of transition metal phosphine complexes as catalysts for the electrochemical reduction of $CO_2$. Our initial efforts involved a systematic study of Fe, Co, and Ni complexes containing polyphosphine ligands and weakly coordinated acetonitrile ligands.[26] Our objective was to use the polyphosphine ligands to systematically control several features of these complexes. By varying the number of phosphorus atoms in the polyphosphine ligand, the number of sites occupied by weakly coordinating solvents such as acetonitrile could be controlled. We viewed these weakly bound acetonitrile ligands as potential binding sites for $CO_2$ and hydride ligands. For example, $[Fe(PP_3)(CH_3CN)_2](BF_4)_2$, (where $PP_3$ is tris(2-diphenylphosphinoethyl) phosphine) has two acetonitrile ligands or substrate binding sites, $[Fe(CP_3)(CH_3CN)_3](BF_4)_2$, (where $CP_3$ is 1,1,1-tris(diphenylphosphinomethyl)ethane) has three, and $[Ni(etp)(CH_3CN)](BF_4)_2$ (where etp is bis(2-diphenylphosphinoethyl)phosphine) has one. In addition, it is possible to control the stereochemical relationship of these binding sites. For $[Fe(PP_3)(CH_3CN)_2](BF_4)_2$, the two acetonitrile ligands are cis and for $[Fe(dppe)_2(CH_3CN)_2](BF_4)_2$ (where dppe is bis(diphenylphosphino) ethane) they are trans. Fe, Co, and Ni were selected as the initial metals for study because they are not highly oxyphilic metals in their normal oxidation states, and it was anticipated that M–O bond cleavage could be an important step in a catalytic cycle. As a result of our studies of these complexes, it was found that some of the Fe complexes could catalyze $CO_2$ reduction, but with low rates and at very negative potentials. The Ni complexes, although not catalytic, exhibited more interesting electrochemical properties, because there were two closely spaced, one-electron reductions that occurred at potentials of interest for possible $CO_2$ reduction catalysts. This lead to the evaluation of palladium complexes as well.

As a result of screening several palladium complexes it was found that $[Pd(triphosphine)(PR_3)](BF_4)_2$ complexes, **1**, would catalyze the reduction of $CO_2$ to CO in acidic acetonitrile solutions.[13a] Further studies indicated that the monodentate phosphine dissociates during the catalytic cycle, and that the active form of the catalyst was $[Pd(triphosphine)(solvent)](BF_4)_2$, **2**.[14]

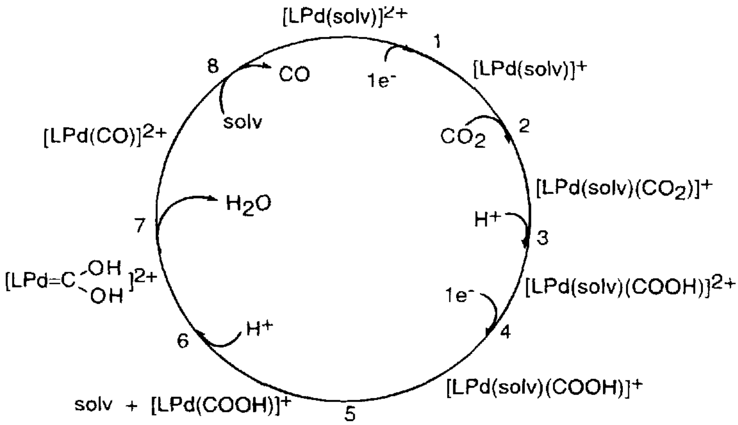


(1)

$^{31}P$ NMR studies clearly indicated that, in acidic acetonitrile, reaction 1 lies well to the right, while in dimethylformamide and other less-coordinating solvents the equilibrium lies to the left. In these noncoordinating solvents, complexes **1** are not catalysts for $CO_2$ reduction, but the solvated species that form on dissolving the acetonitrile complexes **2** in dimethylformamide are good catalysts. For example, $CO_2$ is reduced to CO with current efficiencies in excess of 95% in acidic DMF solutions using $[Pd(etpC)(CH_3CN)](BF_4)_2$ as the catalyst (where etpC is bis(2-dicyclohexylphosphinoethyl)phenylphosphine). It is also worth noting that $[Pd(diphosphine)_2](BF_4)_2$ complexes, for which the dissociation of a phosphine ligand is not facile, are not catalysts for $CO_2$ reduction. All of these results support complex **2** as the active form of the catalyst.

## Mechanistic Studies

Electrochemical studies of $[Pd(etpC)(CH_3CN)](BF_4)_2$ under various conditions in dimethylformamide led to Scheme 1 as the proposed mechanism by which these catalysts operate.[14] In step 1, $[LPd(solv)]^{2+}$ (where L is a triphosphine ligand and solv is a coordinated solvent molecule) is reduced by one electron to produce a Pd(I) intermediate. A one-electron rather than a two-electron reduction is proposed because under noncatalytic conditions (i.e., for nonacidic solutions), the current observed by both cyclic voltammetry and chronoamperometry for the first reduction wave of the catalyst in the presence of $CO_2$ is consistent with a one-electron reduction. Since our original studies, others have found that palladium complexes containing triarsine ligands have two closely spaced one-electron reductions, and that electron transfer for the Pd(I/O) couple is significantly slower than for the Pd(II/I) couple.[27] The second step in the catalytic cycle is the reaction of the Pd(I) intermediate with $CO_2$. If this reaction is fast compared to the second electron transfer, then a one-electron reduction of the catalyst in the presence of $CO_2$ would be expected.



SCHEME 1

The reaction of the Pd(I) species with $CO_2$ can be studied under noncatalytic conditions by monitoring the shift in the peak potential of the first reduction wave as a function of the concentration of $CO_2$. These studies indicated that the reaction is first order in catalyst and first order in $CO_2$. The catalytic rate, which is determined by measuring the peak current, also has a first-order dependence on the concentrations of $CO_2$ and catalyst at high acid concentrations. This indicates that, *at high acid concentrations, the rate-determining step is the reaction of a Pd(I) intermediate with* $CO_2$. Within experimental error, the rates of reaction of the Pd(I) intermediate with $CO_2$ measured under catalytic and noncatalytic conditions are the same.

The next two steps in the catalytic mechanism, protonation (3) and a second electron transfer (4), were inferred from experiments in which catalyst solutions saturated with $CO_2$ were titrated with acid. Loss of the solvent ligand, step 5, also occurs during the catalytic cycle. This is indicated by the inhibition produced by monodentate phosphines (discussed above) and by strongly coordinating solvents such as dimethylsulfoxide.[14]

A biphasic dependence of the catalytic current on acid concentration is observed for these catalysts as shown in Fig. 1 for [Pd(IPNetpE)($CH_3CN$)]$(BF_4)_2$ (where IPNetpE is bis (2-diethylphosphinoethyl)(diisopropylamino)phosphine).[17] At low acid concentrations, the current exhibits a first-order dependence on the acid concentration, but no acid dependence is seen at high acid concentrations. The dependence of the catalytic current on acid concentrations is consistent with two protons

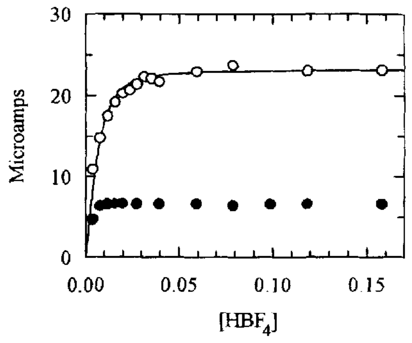


FIGURE 1 Graph showing the dependence of the catalytic current on the concentration of $HBF_4$ for a $2.2 \times 10^{-3}$ M solution of $[Pd(IPNetpE)(CH_3CN)](BF_4)_2$ in dimethylformamide purged with $N_2$ (solid circles) and with $CO_2$ (open circles). The solid line is the best fit curve assuming steps 2 and 7 of Scheme 1 are rate-determining (see Ref. 18 for further details).

being involved in the transition state (steps 3 and 6 of Scheme 1). Although the second protonation step could be rate-determining, we have interpreted this result to imply that, *at low acid concentrations, the rate-determining step is the cleavage of the C–O bond to form coordinated CO and water as shown in step 7 of Scheme 1.* This bond cleavage reaction is sensitive to the nature of the triphosphine ligand structure, as will be discussed in more detail below. To complete the catalytic cycle, CO is lost rapidly from the Pd(II) species and solvent is coordinated (step 8).

## Structure–Activity Relationships

In subsequent studies, we have investigated the effects of different structural features of the triphosphine ligand on the catalytic rate, the mechanism, and the catalyst decomposition products. By varying the substituents on the triphosphine ligand, it was observed that a linear free-energy relationship exists between the redox potential of the catalyst and the log of the rate constant for the reaction of the catalyst with $CO_2$, Fig. 2.[15] This is reasonable if this reaction is viewed as a nucleophilic attack of the metal on $CO_2$ with a transfer of charge from the metal to $CO_2$ with a transfer of charge from the metal to $CO_2$. A second observation was that bulky substituents on the central phosphorus atom retarded the catalytic rates by approximately a factor of 2 (solid circles), whereas bulky substituents on the terminal phosphorus atoms had little effect.[15]

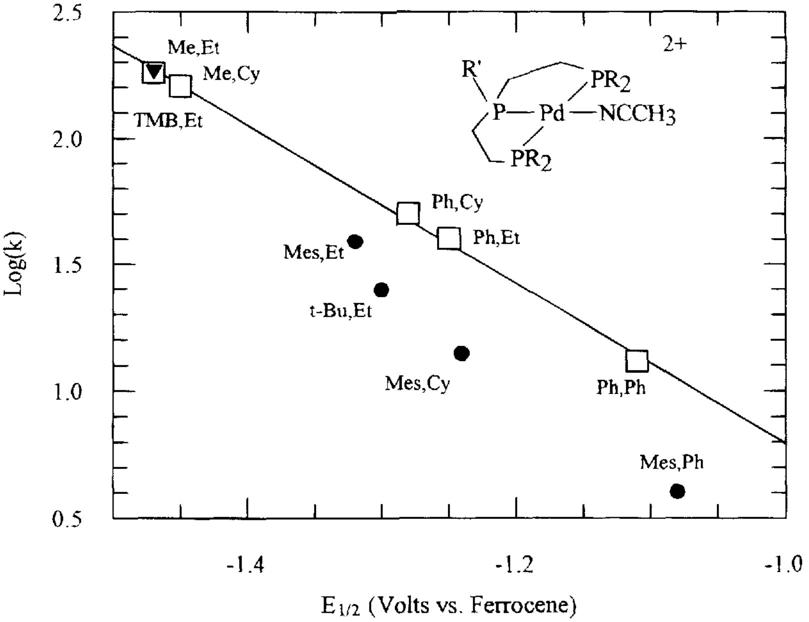


FIGURE 2 Plot of the log of the second-order rate constants measured for $[R'P(CH_2CH_2PR_2)_2Pd(CH_3CN)](BF_4)_2$ complexes versus the half-wave potentials of the catalysts. Open boxes are for complexes with phenyl or methyl substituents on the central phosphorus atom. Solid circles are for complexes with *tert*-butyl or mesityl substituents on the central phosphorus atom. The solid triangle is for a complex with a trimethoxybenzene substituent on the central phosphorus atom.

This result can be understood from the structure of [Pd (MesetpE) $(CH_3CN)]^{2+}$ cation (where MesetpE is bis (2-diethylphosphinoethyl) mesitylphosphine) shown in Fig. 3. In this structure, a methyl group of the mesityl substituent on the central phosphorus atom effectively blocks one face of the catalyst. Consequently, only one side of the catalyst is available for $CO_2$ binding, and the rate decreases by a factor of 2. The presence of the methyl group above the palladium atom also suggests that six-coordinate intermediates can be excluded, because such complexes are not sterically feasible. This result is significant, because coordination of a sixth ligand has been suggested to play an important role in $CO_2$ binding for some Ni(I) catalysts containing macrocylic amine ligands.[6f,g,o] This result illustrates the use of a polydentate ligand to probe mechanistic questions that would be difficult if monodentate ligands were used.

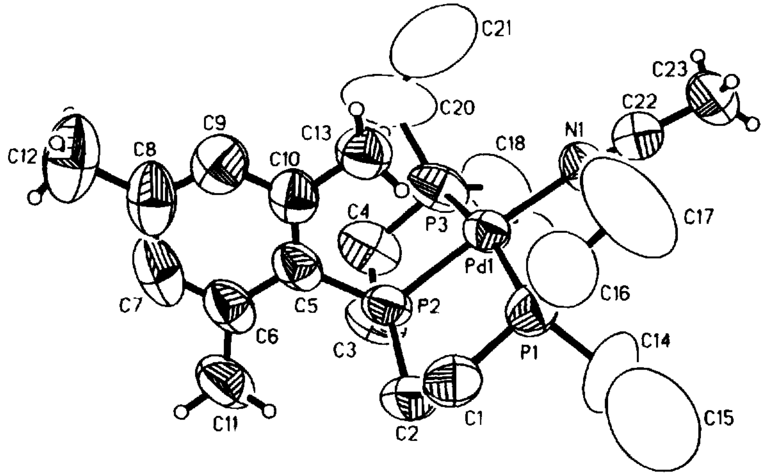
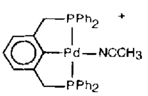
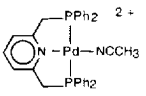


FIGURE 3 Drawing of the [Pd (MesetpE)($CH_3CN$)]$^{2+}$ cation showing the atom-numbering scheme.

Variation of the donor set of the tridentate ligand was also studied as shown by structures **3–6**, which contain C, N, S or As atoms as the central donor atom of the tridentate ligand.[17] It was found that triphosphine ligands give the best catalysts, but insight into the pathway for hydrogen production, a side reaction that decreases the current efficiency, was obtained from a study of [Pd(PCP)($CH_3CN$)]($BF^{4+}$), **3**. Electrochemical reduction of **3** in the presence of $CO_2$ and acid produces only hydrogen. However, the catalytic current at high acid concentrations is consistent with a first order reaction of a Pd(I) species with $CO_2$ and is independent of acid concentrations similar to the [Pd(triphosphine)(solvent)]($BF_4$)$_2$ complexes discussed above. For complex **3**, $CO_2$ acts as a cofactor for hydrogen production, but $CO_2$ is not reduced. This indicates that the hydrogen that forms during $CO_2$ reduction by the [Pd(triphosphine)(solvent)]($BF_4$)$_2$ catalysts involves the same $CO_2$ intermediate that produces CO. The branching that leads to the different pathways resulting in hydrogen or CO production occurs after formation of the $CO_2$ complex. The preference for forming hydrogen or CO appears to depend on the basicity or redox potential of the complexes. A more negative redox potential favors protonation at Pd to form a hydride with subsequent $H_2$ production, whereas less negative redox potentials or a less basic Pd atom favor protonation at oxygen atom of coordinated $CO_2$, which results in CO formation.[17]



3



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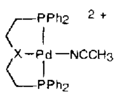
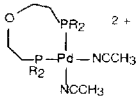


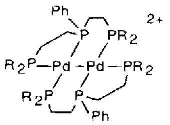
X

**5a** NH
**5b** S
**5c** AsPh

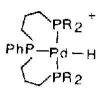


6

The size of the chelate bite of the triphosphine ligand has significant effects on the catalyst decomposition products and on the catalytic mechanism. The main decomposition pathway for complexes with two ethylene bridges between the central and terminal phosphorus atoms of the tridentate ligand is the formation of Pd(I) dimers with a bridging triphosphine ligand, e.g., **7**. Two of these dimers have been characterized by x-ray diffraction studies.[14] When the triphosphine ligand contains two trimethylene linkages, the catalysts decompose by forming [Pd(triphosphine)H]($BF_4$) complexes, **8**.[20] One of the hydride complexes has been characterized by an X-ray diffraction study as well. Complexes **7** and **8** are also formed when the reductions of the corresponding Pd(II) complexes are carried out under $CO_2$ in the absence of acid. The formation of both **7** and **8** is faster in the presence of $CO_2$ than under nitrogen atmospheres. This result suggests that the Pd(I)$CO_2$ intermediates discussed above play an important role in both catalytic reactions and in catalyst decomposition. At first sight, it would appear that hydride **8** should not produce catalyst deactivation, because this complex could protonate to form a dihydride or dihydrogen complex, eliminate hydrogen, and regenerate the catalyst. However, hydride **8** is relatively stable to acid while its two-carbon chain analog is not. The greater stability observed for **8** is attributed to the much lower hydridic character for the hydride ligand in **8**, which results from the larger chelate bite. Qualitative molecular orbital calculations suggest that the correlation of decreasing hydride character with increasing chelate bite size should be true for hydrides in general.[20]



7



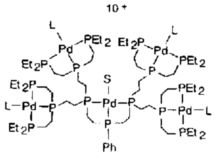
8

There is also a subtle difference in the reaction mechanism for $CO_2$ reduction depending on the chelate bite size.[20] For complexes with a two-carbon linkage between phosphorus atoms, the rate-determining reaction at low acid concentrations has a second-order dependence on acid concentration, which is consistent with the loss of water from the activated complex as discussed above. For complexes with a three-carbon linkage in the triphosphine ligand, a first-order dependence on acid is observed. This is consistent with the loss of hydroxide from the activated complex, and suggests that the C–O bond is more easily cleaved than it is in the two-carbon chain analog. A structural study of $[Pd(ttpE)(CH_3CN)](BF_4)_2$ (where ttpE is bis (3-diethylphosphino-propyl)phenylphosphine) shows a significant steric interaction exists between two of the terminal ethyl groups of the tridentate ligand and the acetonitrile ligand. It is this steric interaction which promotes the cleavage of the C–O bond in the catalytic cycle of $[Pd(ttpE)(CH_3CN)] (BF_4)_2$.

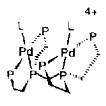
As a result of these studies, a good understanding has been obtained for the relationship between various structural features of these complexes and catalytic rates, mechanisms, selectivities, and decomposition products. These complexes can exhibit rate constants as high as 300 $M^{-1}s^{-1}$ for the reaction of $CO_2$ with Pd(I) intermediates. Current efficiencies for CO production as high as 99% have been observed, and some of the catalysts operate at relatively low overpotentials (estimated to be less than 200 mV). However, the turnover numbers for these catalysts are relatively low, typically between 10 and 100. Improving the turnover numbers of these catalysts is an important area for future work.

## DEVELOPMENT OF CATALYSTS EXHIBITING COOPERATIVE EFFECTS

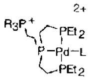
There is considerable evidence in the literature that $CO_2$ binding can be stabilized by interaction with two metals.[3a,j,28] In such complexes, one metal binds to a carbon atom while a second metal binds to oxygen. However, there has been no unambiguous evidence that such cooperative effects are operative during catalytic cycles. Such cooperative interactions could accelerate reaction rates and/or decrease overpotentials. In an effort to explore this possibility, we synthesized complexes **9–11**. In the first complex, a dendritic structure, a single central Pd complex is surrounded by four Pd complexes linked to the terminal phosphorus atom via an ethylene linkage.[16] Alternatively, complex **9** can be viewed as four Pd complexes with a metal complex attached of the central phosphorus atoms. Although complex **9** and closely related complexes were the first examples of catalytically active dendrimers, no evidence was found for beneficial cooperative effects. When **9** was compared to its monomeric analogs, the rate of $CO_2$ binding to the catalyst was decreased, and its selectivity for CO production was also decreased.



**9**



**10**



**11**

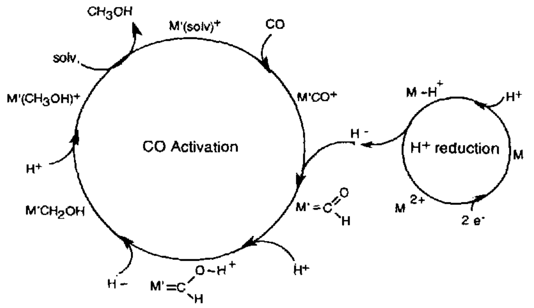
L = $CH_3CN$

Complex **10** consists of two of the monomeric [Pd(triphosphine)(solvent)]$^{2+}$ units discussed above linked to each other via a methylene bridge.[18] The hexadentate ligand used to prepare **10** was first reported by Stanley and co-workers.[29] Kinetic studies of **10** are consistent with a cooperative interaction between the two Pd sites. The rate-determining reaction at high acid concentration is first order in catalyst and first order in $CO_2$. This indicates that there are two Pd atoms per $CO_2$ molecule. The rate-determining reaction at low acid concentration is first order in acid. This contrasts with analogous monomeric complexes for which a second-order dependence is observed. This change in reaction order can be easily accounted for by the binding of the second Pd atom to an oxygen of coordinated $CO_2$, thereby replacing one of the protons normally required in the transition state. Finally, the second-order rate constant for the reaction of $CO_2$ with reduced **10** has been bracketed as greater than $10^4$. This represents a more than $10^3$ increase in the rate constant compared to its monomeric analog. All of these results support a beneficial cooperative binding of $CO_2$ by a reduced form of **10** during the catalytic cycle. Unfortunately, the decomposition rate of **10** is also extremely high, because of rapid Pd–Pd bond formation, and low turnover numbers (~10) were obtained for this complex.

Catalyst **11** contains a pendant phosphonium group attached to the central phosphorus atom of the triphosphine ligand.[30] One reason this complex was prepared was to determine if a simple coulombic interaction between the positively charged phosphonium ion and the negatively charged oxygen atom of the coordinated $CO_2$ could stabilize the transition state and enhance the rate of $CO_2$ reduction. The structure of **11** has been determined for R equals butyl, and kinetic studies have been carried out for this complex.[30] These data indicate that the rate of $CO_2$ binding to **11** is approximately twice as large as expected for a monomeric complex with the same redox potential. Similar results were obtained for the methylphosphonium analog. Apparently the phosphonium groups have little effect on the catalytic rate, and the catalytic mechanism is the same as that shown in Scheme 1. Future studies of these complexes will examine the ability of these phosphonium substituted complexes to stabilize catalysts bound to electrode surfaces modified with cationic exchange membranes. However, from the perspective of significant rate enhancements, bimetallic catalysts such as **10** appear to be superior. We plan to continue the development of bimetallic catalysts which cooperatively bind $CO_2$, while attempting to improve their turnover numbers.

## STOICHIOMETRIC REDUCTION OF CO BY ELECTROCHEMICALLY GENERATED HYDRIDES

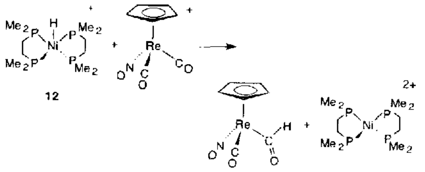
The catalysts described above reduce $CO_2$ to CO. In order to develop catalysts that will reduce CO to methanol or methane, we have begun a study of the reduction of coordinated CO by electrochemically generated hydrides. One possible catalytic cycle is shown in Scheme 2. In this scheme there are two cycles. One cycle is for the electrochemical generation of a metal hydride, and the second cycle is for the activation of CO. These two cycles intersect during the transfer of a hydride ligand from the electrochemically generated hydride to coordinated CO to form a formyl complex and regenerate the hydride precursor.



SCHEME 2

A general route to metal formyl complexes is the intermolecular transfer of a hydride ligand from a borohydride or closely related reducing agent to coordinated carbon monoxide.[31] Transition metal hydrides have also been used to generate formyl complexes,[32] which suggested the feasibility of using electrochemically generated hydrides to reduce coordinated CO. We have shown that five-coordinate metal hydrides of Ni and Pt of general formula [M(disphosphine)$_2$H](PF$_6$) can be generated by the electrochemical reduction of [M(disphosphine)$_2$](PF$_6$)$_2$ in protic environments. [33] For example, controlled-potential electrolysis of [Ni(dmpe)$_2$](BF$_4$)$_2$ (where dmpe is bis(dimethylphosphino)ethane) in acetonitrile in the presence of excess NH$_4$PF$_6$ results in the passage of 2.0 Faradays per mole of complex and the clean formation of [Ni(dmpe)$_2$H](BF$_4$), **12**. Similarly, the reduction of [Pt(depe)$_2$](BF$_4$)$_2$ in methanol or wet acetonitrile leads to the formation of [Pt(depe)$_2$H](BF$_4$), which has been structurally characterized.

These electrochemically generated hydrides can reduce a number of metal carbonyl complexes to produce formyl complexes while regenerating the original [M(diphosphine)$_2$](PF$_6$)$_2$ complexes.[33] For example, both of the hydrides discussed in the preceding paragraph react with [CpRe(CO)$_2$(NO)]$^+$ to form the well-characterized formyl complex [CpRe(CO)(NO)(CHO)] as shown in reaction 2 for [Ni(dmpe)$_2$H](BF$_4$).



(2)

Reaction 2 appears to be fairly general as other carbonyl complexes that are known to form stable formyl complexes when reduced with borohydride reagents are also reduced by [Ni(dmpe)$_2$H](BF$_4$) and [Pt(depe)$_2$H] (BF$_4$). It is felt that an important aspect of reaction 2 is the formation of stable square-planar Ni$^{2+}$ and Pt$^{2+}$ complexes as products. Other metal hydrides, such as octahedral hydrides that are probably more hydridic than these two hydrides, may not be able to transfer the hydride because less-stable products are formed. Other factors which may be important in this reaction are the strength of the metal-hydrogen bond and the redox potentials of both metal complexes. Further studies are needed to determine the mechanism of the reaction and the structural factors which promote this type of reaction.

In one case, the reaction of [Pt(depe)$_2$H](PF$_6$) with [Cp*Re(CO)$_2$NO]$^+$ in wet acetonitrile, the formation of the known hydroxymethyl complex, [Cp*Re(CO)($CH_2OH$)NO], is also observed.[34] These results suggest that a cycle such as that shown in Scheme 2 is possible, but the hydride and carbonyl reagents need to be further optimized before such a cycle can become truly catalytic. Future research will pursue the development of a complete catalytic cycle.

## SUMMARY

A series of transition metal complexes containing polyphosphine ligands and weakly coordinated acetonitrile molecules were synthesized and screened for their ability to catalyze the electrochemical reduction of $CO_2$. The objective was to systematically vary the metal as well as the number of available coordination sites and their relative disposition. As a result of this screening process, it was found that [Pd(triphosphine) ($CH_3CN$)]($BF_4$)$_2$ complexes catalyze the electrochemical reduction of $CO_2$ to CO. Electrochemical studies were carried out to determine the mechanism of this reaction. It was found that there were two rate-determining steps depending on the acid concentration. At high acid concentrations, the rate-limiting step is the reaction of a Pd(I) intermediate with $CO_2$. At low acid concentrations, the rate-determining reaction is the cleavage of a C–O bond to form CO.

Variation of the ligand produced further insight into relationships between the catalyst structure and the catalytic rate, mechanism, and the catalyst decomposition products. A linear free-energy relationship exists between the potential of the Pd(II/I) couple and the log of the rate constant for the reaction of the Pd(I) intermediate with $CO_2$. This reaction involves a five-coordinate intermediate formed by the addition of $CO_2$ to the Pd(I) complex generated by the reduction of [Pd(triphosphine) ($CH_3CN$)]($BF_4$)$_2$ at the electrode surface. In the presence of acid, this intermediate enters into a reaction channel that will lead to either the production of CO or hydrogen. If no acid is present, the Pd(I)$CO_2$ complex decomposes to form either a Pd(I) dimer such as **7** or a palladium hydride such as **8**. Which product is formed is determined by the bite size of the tridentate ligand. For catalysts with two ethylene bridges between the three phosphorus atoms, dimers are formed. For catalysts with two trimethylene bridges, hydrides are formed. In the presence of acid, the Pd(I)$CO_2$ complex is protonated and undergoes a second reduction. Again, the pathway taken depends on the bite size of the triphosphine ligand. For a triphos-

phine with trimethylene bridges, cleavage of the C–O bond occurs to produce CO and hydroxide. In this case, CO loss is assisted by an unfavorable steric interaction between the triphosphine ligand and the coordinated hydroxycarbonyl. For a triphosphine with ethylene linkages, a second protonation occurs at an oxygen atom of the hydroxycarbonyl ligand to produce an activated complex that undergoes a C–O bond cleavage reaction to produce CO and water. If the Pd(II/I) reduction potential is sufficiently negative, the second protonation reaction can occur at the metal to form a metal hydride which leads to hydrogen production.

Studies to determine if cooperative effects can be used to enhance catalytic rates have been successful in one case, that of the bimetallic complex **10**. In this case, a rate enhancement of greater than $10^3$ has been observed. Because the polymetallic dendritic complex **9** is less active, it appears that conformations and the precise relationship between different metal sites is important. An approach based on a purely electrostatic interaction between bound $CO_2$ and a phosphonium substituent did not produce a significant rate enhancement. Further research on bimetallic catalysts is needed before meaningful structure–activity relationships can be developed.

Initial studies on the reduction of coordinated CO using electrochemically generated hydrides indicate that a number of hydrides and carbonyl complexes can react to form formyl complexes. In one case, further reduction to a hydroxymethyl complex has been observed. These preliminary results suggest that the electrochemical reduction of CO via this pathway should be feasible. Again, sufficient research has not been carried out to develop meaningful structure–activity relationships.

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