Development of Molecular Electrocatalysts for CO$_2$ Reduction and H$_2$ Production/Oxidation

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RECEIVED ON APRIL 3, 2009

CONSPECTUS

The conversion of solar energy to fuels in both natural and artificial photosynthesis requires components for both light-harvesting and catalysis. The light-harvesting component generates the electrochemical potentials required to drive fuel-generating reactions that would otherwise be thermodynamically uphill. This Account focuses on work from our laboratories on developing molecular electrocatalysts for CO$_2$ reduction and for hydrogen production.

A true analog of natural photosynthesis will require the ability to capture CO$_2$ from the atmosphere and reduce it to a useful fuel. Work in our laboratories has focused on both aspects of this problem. Organic compounds such as quinones and inorganic metal complexes can serve as redox-active CO$_2$ carriers for concentrating CO$_2$. We have developed catalysts for CO$_2$ reduction to form CO based on a [Pd(triphosphine)(solvent)]$^{2+}$ platform. Catalytic activity requires the

presence of a weakly coordinating solvent molecule that can dissociate during the catalytic cycle and provide a vacant coordination site for binding water and assisting C−O bond cleavage. Structures of [NiFe] CO dehydrogenase enzymes and the results of studies on complexes containing two [Pd(triphosphine)(solvent)]$^{2+}$ units suggest that participation of a second metal in CO$_2$ binding may also be required for achieving very active catalysts.

We also describe molecular electrocatalysts for H$_2$ production and oxidation based on [Ni(diphosphine)$_2$]$^{2+}$ complexes. Similar to palladium CO$_2$ reduction catalysts, these species require the optimization of both first and second coordination spheres. In this case, we use structural features of the first coordination sphere to optimize the hydride acceptor ability of nickel needed to achieve heterolytic cleavage of H$_2$. We use the second coordination sphere to incorporate pendant bases that assist in a number of important functions including H$_2$ binding, H$_2$ cleavage, and the transfer of protons between nickel and solution. These pendant bases, or proton relays, are likely to be important in the design of catalysts for a wide range of fuel production and fuel utilization reactions involving multiple electron and proton transfer steps.

The generation of fuels from abundant substrates such as CO$_2$ and water remains a daunting research challenge, requiring significant advances in new inexpensive materials for light harvesting and the development of fast, stable, and efficient electrocatalysts. Although we describe progress in the development of redox-active carriers capable of concentrating CO$_2$ and molecular electrocatalysts for CO$_2$ reduction, hydrogen production, and hydrogen oxidation, much more remains to be done.
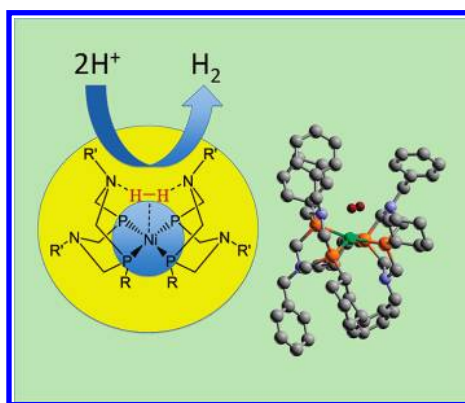
## Introduction

In photosynthesis, the energy of a photon is converted into an electrochemical potential that is used to drive the reduction of CO$_2$ to a variety of higher energy products. This reaction is useful because it allows intermittent solar energy to be stored in the form of chemical energy (sugars, etc.), which can be released in the process of respiration to do useful work as required by the organism. In addition, photosynthesis allows living organisms to produce the materials that they require for life in a broad range of environments. In a similar manner, humans would like to be able

SCHEME 1
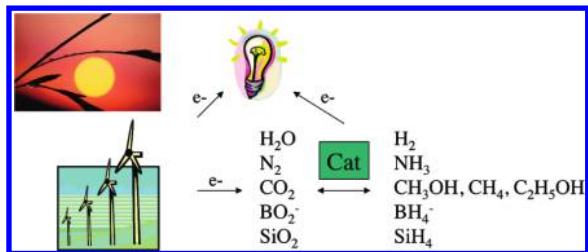
SCHEME 2. Reaction Scheme for Electrochemical CO_2 Pumping with Quinones
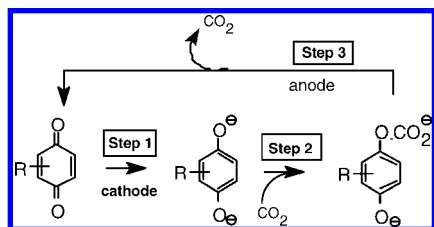
to harvest and store solar energy for future use and to use solar energy to produce many of the basic materials we need for our survival and prosperity.

A number of potentially important reactions that could be driven by solar energy to produce fuels and chemicals are shown in Scheme 1. These reactions involve multiple electron and proton transfer steps, and they will require electrocatalysts for efficient energy conversion. The two reactions considered most often in the context of artificial photosynthesis are CO_2 reduction and water splitting. This Account focuses on the efforts of our laboratories to develop molecular electrocatalysts for CO_2 reduction and the production of H_2.

Electrochemical CO_2 Concentration

Artificial photosynthesis using CO_2 from the atmosphere will require both CO_2 recovery and CO_2 reduction. Biological systems remove CO_2 directly from the atmosphere during photosynthesis. In this process, potential energy gradients are used to concentrate CO_2 from atmospheric levels up to 1000-fold in the presence of Rubisco, the enzyme responsible for CO_2 fixation.[1] These biological systems provide inspiration for using electrochemical gradients for CO_2 concentration or pumping.

The concept of electrochemical CO_2 pumping using redox-active carrier molecules is illustrated in Scheme 2. In step 1, the carrier molecule (a quinone in this example) is reduced to its anionic form (a dianion). In step 2, the anionic carrier selectively binds CO_2 to form a "carbonate-like" adduct. In step 3, the carrier−CO_2 complex is oxidized to liberate pure CO_2 at high pressure. Because redox potentials reflect the electron density on carrier molecules, systematic variations in redox

potentials can be used to control CO_2 binding constants. With 2,6-di-*tert*-butylbenzoquinone as a redox active carrier, CO_2 was concentrated from 0.5% in the feed stream to nearly 100% at 1 atm in the exit stream, and this carrier is capable of binding CO_2 at even lower pressures.[2]

Although quinone carriers are capable of pumping CO_2 over significant pressure ranges, the reduced CO_2-binding forms react with oxygen in the air decreasing the pumping efficiency or degrading the carrier. In addition, they require organic solvents. To overcome these problems, we designed new air-stable, water-soluble carriers based on dinuclear copper complexes with pyridyl and amine donors that bind CO_2 in the form of carbonate as shown in the dication, structure **1**.[3] Although these complexes are stable to oxygen in their CO_2 binding form, their binding constants were too low to recover atmospheric CO_2. Pumping experiments demonstrated CO_2 concentration changes from 10% to 75% in aqueous solutions upon cycling the copper carrier between oxidized (Cu^{II}) and reduced (Cu^{I}) forms.

1
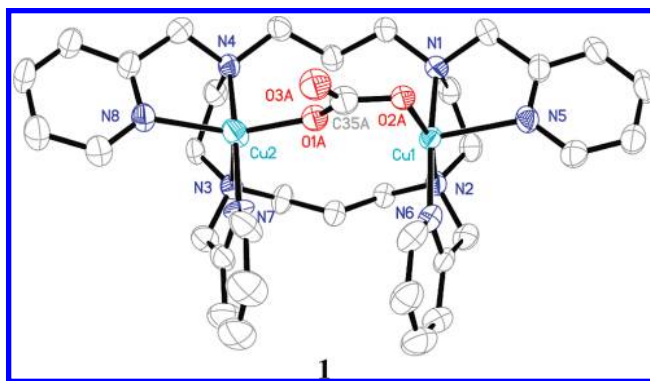
The experiments using 2,6-di-*tert*-butylbenzoquinone and other quinone carriers demonstrated the feasibility of pumping CO_2 over large ranges of concentrations and pressure, and the bimetallic copper complexes demonstrated the feasibility of using air-stable and water-soluble carriers for CO_2 pumping. However, combining all of the desirable features into a single carrier molecule has not been achieved and must await further advances in carrier design.

Development of Molecular Electrocatalysts for CO_2 Reduction

Following CO_2 recovery, the next step in artificial photosynthesis is CO_2 reduction, and reviews of this area are available.[4,5] Our initial efforts to develop catalysts for CO_2 reduction focused on iron, cobalt, and nickel complexes containing polyphosphine ligands and weakly coordinating solvent molecules, for example, $[M(P)_n(CH_3CN)_x]^{2+}$.[6] Late transition metal complexes should not form undesirably strong M−O

SCHEME 3. Catalytic Cycle for CO_2 Reduction to CO[a]
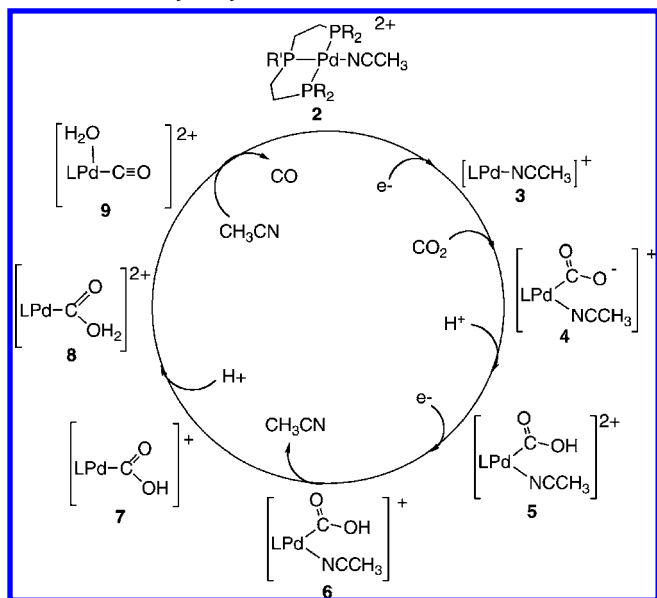
[a] L = triphosphine ligand.

bonds upon reduction that are common for early transition metals, and polyphosphine ligands can control the number and orientation of weakly bound solvent molecules. We hypothesized that weakly bound solvent molecules would be important for catalysis. For many catalytic processes, vacant coordination sites are required. In particular, two adjacent sites, one for coordination of a hydride ligand and the second for coordination of CO_2, could facilitate C−H bond formation as shown in reaction 1 for formate production.
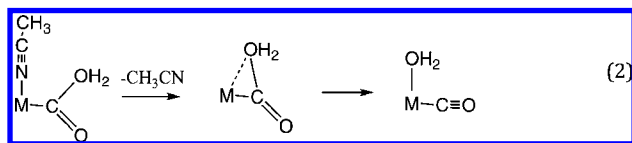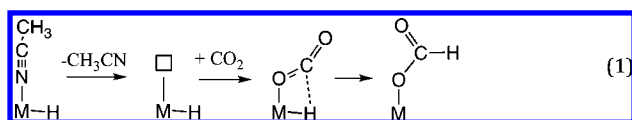
Alternatively, the production of CO from CO_2 requires the cleavage of a C−O bond, and this should be favored by the presence of a vacant coordination site to form a M−O bond as the migrating water molecule or hydroxide ion cleaves the C−O bond, as shown in reaction 2.

Evaluation of $[M(P)_n(CH_3CN)_x]^{m+}$ complexes for M = Fe, Co, Ni, and Pd led to the discovery that [Pd(triphosphine)-$(CH_3CN)]^{2+}$ complexes having structure **2** (see Scheme 3) are active catalysts for the electrochemical reduction of CO_2 to CO. Kinetic studies of this class of catalysts using cyclic voltammetry revealed the following general features. At low acid concentrations, the catalytic rates are first-order in catalyst, first-

order in CO_2, and second-order in acid. At higher acid concentrations, the catalytic rates become independent of the acid concentration, but remain first-order in catalyst and CO_2.[7−9] In addition, it was found that monodentate phosphine ligands strongly inhibited the catalytic reaction, as did strongly coordinating solvents such as dimethylsulfoxide. The latter results supported our initial hypothesis on the requirement for dissociation of a weakly coordinating solvent molecule, acetonitrile in structure **2**, during the catalytic cycle. Finally, electron-donating substituents on the triphosphine ligand resulted in increased catalytic rates. The more active catalysts of this class exhibited second-order rate constants between 5 and 300 $M^{-1} s^{-1}$.

Based on these results, we proposed the catalytic mechanism shown in Scheme 3.[6] The rate-determining reaction at high acid concentrations is the binding of CO_2 to a Pd^I intermediate, **3**, to form **4**. It is this step that determines the selectivity of these catalysts. Because H_2 production is thermodynamically favored over CO_2 reduction, it is important that the Pd^I intermediate preferentially reacts with CO_2 rather than protons. In fact selectivities for CO production as high as 97% can be observed for some catalysts even with very strong acids, such as HBF_4.[9] The rate-determining step at low acid concentrations is the cleavage of the C−O bond in which species **8** is converted to **9**. If the solvent molecule (acetonitrile in Scheme 3) is not lost, cleavage of the C−O bond requires much more reducing potentials. The incipient vacant coordination site in complexes with structure **6** leads to solvent loss to form **7** and facile C−O bond cleavage in which **8** is converted to **9**. This results in high catalytic rates and relatively low overpotentials. It is this C−O bond cleavage reaction that is rate-determining or that requires large overpotentials for most other classes of catalysts for CO_2 reduction to CO.[4]

Catalysts such as **2** typically degrade to form bimetallic palladium complexes having structure **10**.[7] As expected, the incorporation of sterically bulky substituents on the terminal phosphorus atoms of the triphosphine ligands results in increased turnover numbers for these catalysts. For example, $[Pd(etpE)(CH_3CN)]^{2+}$, (where etpE is $PhP(CH_2CH_2PEt_2)_2$) has a turnover number of 10, $[Pd(etpC)(CH_3CN)]^{2+}$ (where etpC is $PhP(CH_2CH_2PCy_2)_2$) has a turnover number of 130,[7] and complex **11** has a turnover number greater than 200 with less than 20% degradation and a rate constant of $\sim$50 $M^{-1} s^{-1}$ under normal operating conditions.[10]

The most active catalysts for CO_2 reduction to CO are carbon monoxide dehydrogenase enzymes. The [NiFe] CO dehydrogenase enzymes catalyze the rapid reduction of CO_2 to CO

10   **11**
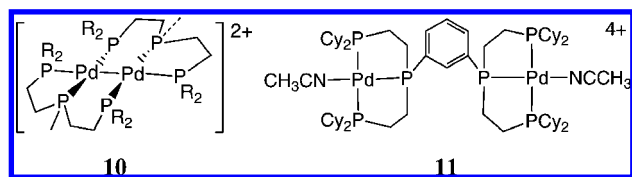
with turnover rates of 31 000 s^{-1}, and they use inexpensive metals.[11] Structural studies provide important insights into those features of the active site that contribute to high catalytic activity. The active site of *Carboxydothermus hydrogenoformans* in the reduced form is depicted in structure **12**, and the reduced form plus CO_2 is shown by structure **13**. In both structures, three sulfur atoms surround a Ni atom. Water or a bridging hydroxide occupies a fourth coordination site in **12**. In structure **13**, CO_2 is bound to Ni through the carbon atom and to iron via an oxygen ligand. There are also additional hydrogen-bonding interactions between the oxygen atoms in structures **12** and **13** and nitrogen-containing histidine and lysine residues (not shown). The presence of the Fe−O bond suggests that a vacant coordination site on Fe assists both the binding of CO_2 and the cleavage of a C−O bond. This Fe atom is positioned so that it forms a seven-membered ring upon binding CO_2. The positioning of the Ni and Fe atoms is achieved by a S−Fe−S linkage.
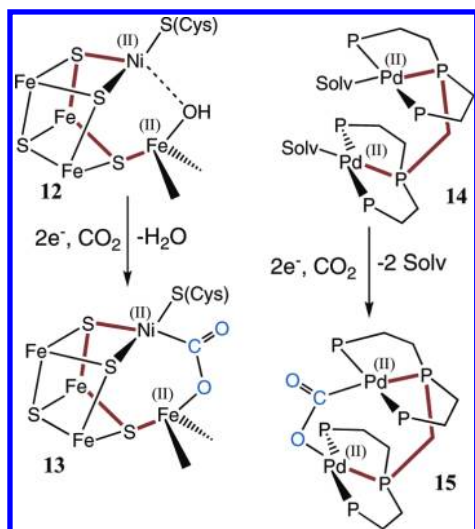

In studies that preceded the structural studies of the [NiFe] CO dehydrogenase enzymes, we observed very high catalytic rates ($k > 10^4$ M^{-1} s^{-1}) for CO_2 reduction using the bimetallic palladium complex **14** in which two triphosphine units were bridged by a methylene group.[12] Although this catalyst was prepared and studied before the structure of the CO dehydrogenase active site was known, it shares some interesting structural features with the enzyme. Complex **14** was designed to interact with CO_2 in much the same way as the enzyme, as shown in structure **15**. In particular, it has a binding site for the

carbon atom of CO_2 on one Pd, and the other Pd atom is thought to bind an oxygen atom of the substrate. In addition, both the enzyme and the bimetallic palladium complex form seven-membered rings upon binding CO_2. It is these structural features that are thought to contribute to the remarkably high activity observed for **14** for electrocatalytic reduction of CO_2 to CO. On the negative side, the turnover number for **14** is low, approximately 10. The structure of the CO dehydrogenase active site suggests that a more rigid ring system for separating the two metals may be important in preventing Ni−Fe bond formation, and complex **11** was an attempt to design a complex in which catalyst-inhibiting Pd−Pd bond formation was suppressed by the intervening arene ring.[10] However, complex **11** appears to function as two independent catalytic sites with no evidence for cooperative interactions between the two metal centers, and the rates are typical of mononuclear [Pd(triphosphine)(CH$_3$CN)]$^{2+}$ catalysts. A second approach to preventing M−M bond formation that is suggested by structures **12** and **13** of the enzyme active site is the use of two different metals with significantly different redox potentials. This would prevent the generation of two metal radicals in close proximity at the same potential.

Toward Molecular Electrocatalysts for CO Reduction

Although the development of electrocatalysts for the reduction of CO_2 to CO is an important first step, further reduction of CO to methanol or methane is desirable, because it would produce fuels with higher energy densities. In a series of studies by the groups of Casey,[13] Gladysz,[14] and Graham,[15] it was demonstrated that CO ligands bound to cationic rhenium complexes could be reduced to formyl, hydroxymethyl, and methyl ligands. These reactions were intriguing and led us to study the reactions of a number of [HM(diphosphine)$_2$]$^+$ complexes (where M = Ni or Pt) with [CpRe(NO)(CO)(PR$_3$)]$^+$ and other cationic carbonyl complexes (e.g., reaction 3).[16] It was found that a number of these complexes could indeed transfer a hydride ion to the coordinated CO ligand to form formyl complexes as desired. We were particularly interested in [HM(diphosphine)$_2$]$^+$ complexes, because they can be generated in an electrochemical cycle by reduction to M^0-(diphosphine)$_2$ complexes (at approximately −1.1 ± 0.2 V vs the ferrocenium/ferrocene couple) followed by protonation. As a result, one could envision electrocatalytic cycles in which such hydrides were generated at an electrode followed by hydride transfer to CO coordinated to rhenium. Whether this hydride transfer will occur depends on the correct matching of
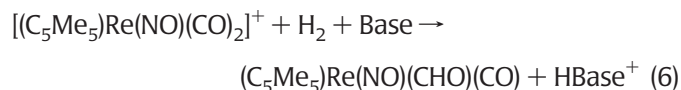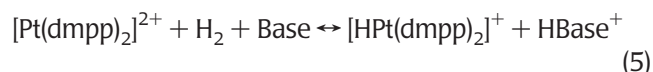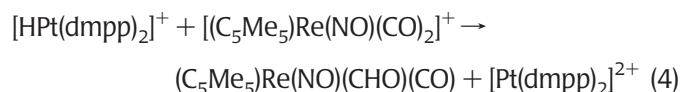
the hydride donor ability of the metal hydride and the hydride acceptor ability of the metal–carbonyl complex.
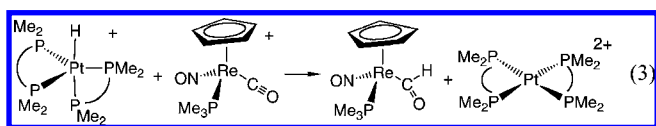
This line of inquiry led us to study those factors controlling the hydride donor abilities of [HM(diphosphine)$_2$]$^+$ complexes[17] and the hydride acceptor abilities of [CpRe(NO)(CO)(PR$_3$)]$^+$ complexes.[18] The hydride donor abilities of [HM(diphosphine)$_2$]$^+$ complexes were shown to depend on three factors: the substituents on the diphosphine ligands,[19] the natural bite angles of the diphosphine ligands,[20] and the nature of the metal.[21] Increasing the electron donor abilities of the substituents on the diphosphine ligands correlated with better hydride donor abilities, as expected. For example, $\Delta G^\circ_{H^-}$ for [HNi(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$]$^+$ is 51 kcal/mol, while that of [HNi(Ph$_2$PCH=CHPPh$_2$)$_2$]$^+$ is 66 kcal/mol. $\Delta G^\circ_{H^-}$ corresponds to the free energy for the cleavage of a MH bond to form M$^+$ and H$^-$ in acetonitrile solution. A more positive value of $\Delta G^\circ_{H^-}$ indicates a poorer hydride donor.[19] A somewhat unanticipated discovery was that the hydride donor ability correlated strongly with the natural bite angle (NBA) of the diphosphine ligand (defined as the P–M–P bond angle preferred by the backbone of the diphosphine ligand). Small NBAs corresponded with increased hydride donor abilities and large NBAs correlated with poor hydride donor abilities. For example, in a series of [HPd(diphosphine)$_2$]$^+$ complexes, the hydride donor ability increases by 20 kcal/mol as the NBA decreases from 111° to 78°.[20] Also surprising is the fact that the pK_a values and homolytic solution bond dissociation free energies are unaffected by the NBA. This means that the NBA provides a "knob" for tuning the hydride donor ability of [HM(diphosphine)$_2$]$^+$ complexes without changing their pK_a values or homolytic bond dissociation free energies. Regarding the influence of the metal, for the same diphosphine ligand, palladium hydrides are equal or slightly better hydride donors than platinum, and both are much better hydride donors than nickel complexes. For example, for the series of [HM(PNP)$_2$]$^+$ complexes (where PNP is Et$_2$PCH$_2$NMeCH$_2$PEt$_2$), $\Delta G^\circ_{H^-}$ is 66 kcal/mol for Ni, 55 kcal/mol for Pt, and 51 kcal/mol for Pd.[21]

Once the hydride donor abilities of [HM(diphosphine)$_2$]$^+$ complexes had been determined, it was possible to use hydride transfer reactions to establish the relative hydride donor abilities of a series of rhenium formyl complexes.[18] For example, the equilibrium constant for the reaction of [HPt(dmpe)$_2$]$^+$ ($\Delta G^\circ_{H^-}$ = 42.5 kcal/mol) with [CpRe(NO)(PMe$_3$)(CO)]$^+$ to form CpRe(NO)(CHO)(PMe$_3$) and [Pt(dmpe)$_2$]$^{2+}$

was used to determine a hydride donor ability of 44 kcal/mol for CpRe(NO)(CHO)(PMe$_3$) (reaction 3). Using these hydride donor abilities, one could predict that [HPt(dmpp)$_2$]$^+$ ($\Delta G^\circ_{H^-}$ = 51 kcal/mol) should transfer a hydride ligand to [CpRe(NO)(CO)$_2$]$^+$ to form CpRe(NO)(CHO)(CO) ($\Delta G^\circ_{H^-}$ = 53 kcal/mol) as shown in reaction 4. In addition, the hydride donor ability of [HPt(dmpp)$_2$]$^+$ determines the pK_a value of the protonated base (18.2 or greater) required for reaction 5 to occur.[22] Proton sponge, 1,8-bis(dimethylamino)naphthalene, has a pK_a of 18.2, and the equilibrium shown in reaction 5 is observed. The sum of reactions 4 and 5 is reaction 6, which is a simple and *predictable* example of heterolytic activation of H$_2$ to form a formyl complex at room temperature and 1.0 atm of H$_2$. Although the overall yield is low (10–20%) due to the instability of the product formyl complex and the time required for both reactions, these results clearly demonstrate the utility of hydride donor abilities in developing new strategies for achieving CO reduction under mild conditions. As discussed in the next section, knowledge of hydride donor abilities is also useful in the development of catalysts for H$_2$ oxidation and production.

$$[HPt(dmpp)_2]^+ + [(C_5Me_5)Re(NO)(CO)_2]^+ \rightarrow$$
$$(C_5Me_5)Re(NO)(CHO)(CO) + [Pt(dmpp)_2]^{2+} \quad (4)$$

$$[Pt(dmpp)_2]^{2+} + H_2 + Base \leftrightarrow [HPt(dmpp)_2]^+ + HBase^+$$
$$(5)$$

$$[(C_5Me_5)Re(NO)(CO)_2]^+ + H_2 + Base \rightarrow$$
$$(C_5Me_5)Re(NO)(CHO)(CO) + HBase^+ \quad (6)$$

Development of Catalysts for Hydrogen Oxidation and Production

Another important energy storage reaction is the reduction of protons to form H$_2$. Platinum metal is an excellent catalyst for this reaction and its reverse, and this is the reason for its long use in hydrogen fuel cells. However, the hydrogenase enzymes use cheaper and more abundant metals to catalyze these reactions at very high rates. Structural studies have revealed dinuclear iron or nickel–iron complexes at the active sites of the enzymes.[23] A proposed structure of the active site of the [FeFe] hydrogenase enzyme is shown by structure **16**. The ligand set of the dinuclear iron unit contains unusual CO and CN$^-$ ligands as well as a dithiolate ligand in which the two sulfur atoms are connected by three light atoms. It has been proposed that the central atom is nitrogen, and this would provide a natural pathway for achieving the known heterolytic cleavage of H$_2$ and the transfer of the resulting proton to a proton conduction channel of the enzyme.[23]

16
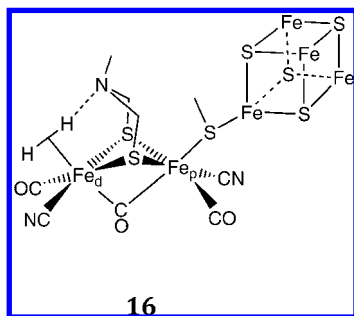
For the [FeFe] hydrogenase enzymes, the overall catalytic process is rapid and reversible. As a result, the hydride acceptor ability of the iron atom and the proton acceptor ability of the nitrogen atom in structure **16** must be matched so that the free energy associated with the heterolytic cleavage of H_2 is near 0 kcal/mol in order to avoid a high energy barrier in either direction. This energy matching can be achieved in synthetic catalysts if the hydride acceptor abilities of metal complexes are known. Based on the studies of the hydride donor abilities of [HM(diphosphine)$_2$]$^{2+}$ complexes, we realized that the hydride acceptor abilities of the corresponding [Ni(diphosphine)$_2$]$^{2+}$ complexes could be matched to the proton acceptor ability of appropriate nitrogen bases. For example, the complex [Ni(depp)$_2$]$^{2+}$, **17**, reversibly cleaves H_2 in the presence of 2,4-dichloroaniline (pK_a = 8.0 for 2,4-dichloroanilinium in acetonitrile) to form **18** and the protonated base, as shown in reaction 7.[22]

17   **18**
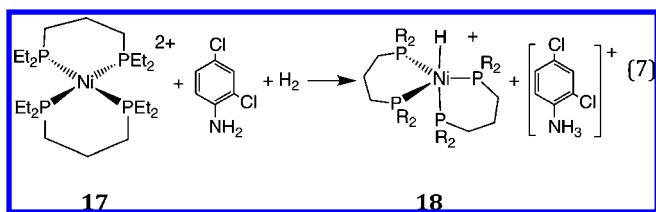
These thermodynamic studies and the proposed structure of the [FeFe] hydrogenase active site led us to incorporate a nitrogen atom in the backbone of the depp ligand to form [Ni(PNP)$_2$]$^{2+}$, **19**, where PNP is Et$_2$PCH$_2$NMeCH$_2$PEt$_2$.[24] Reaction of H_2 with [Ni(PNP)$_2$]$^{2+}$ resulted in a very rapid bleaching of the solution and the formation of the corresponding heterolytic cleavage product [HNi(PNHP)(PNP)]$^{2+}$, **20**, in which a hydride ligand was bound to nickel and a proton was bound to a nitrogen atom of one PNP ligand (reaction 8). The role of the pendant base in this heterolytic cleavage reaction is of course the same as that proposed for the pendant amine of the azadithiolate ligand of the [FeFe] hydrogenase active site.[23] Further studies of [HNi(PNHP)(PNP)]$^{2+}$ revealed that the nickel hydride and the proton attached to the pendant nitrogen base were exchanging with each other at rates of at least 10^4 s^{-1} at room temperature. This *intramolecular* exchange

process likely involves either a nickel dihydrogen or dihydride complex as an intermediate that results from proton transfer from the amine to Ni. *Intermolecular* exchange rates for the hydride ligand with protons of water added to acetonitrile solutions of [HNi(PNHP)(PNP)]$^{2+}$ and [HNi(PNP)$_2$]$^+$ are greater than 10^6 times faster than that observed for [HNi(depp)$_2$]$^+$. These results demonstrate that the pendant bases of [Ni(PNP)$_2$]$^{2+}$ play an important role in the heterolytic activation of H_2 and in the inter- and intramolecular exchange processes of the hydride ligand of the product, **20**.

19   **20**
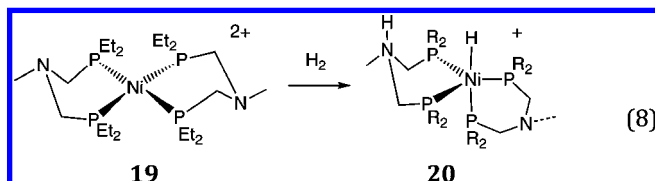
In addition to rapid intra- and intermolecular proton transfer, the pendant base also facilitates the coupling of proton and electron transfer processes for [HNi(PNP)$_2$]$^+$.[24] The oxidation of [HNi(depp)$_2$]$^+$ in the presence of an exogenous base, such as NEt$_3$, occurs at 0.0 V versus the ferrocenium/ferrocene couple, while that of [HNi(PNP)$_2$]$^+$ is observed at -0.65 V. This very large shift in potential (-0.65 V) is attributed to the presence of the pendant amine. The base provides a physical pathway for coupling of the electron and proton transfer events. This may occur by one of three conceptually distinct sequences: proton transfer followed by electron transfer, electron transfer followed by proton transfer, or a concerted process in which both proton and electron transfer simultaneously.

Although the incorporation of an amine in the backbone of the depp ligand resulted in dramatic improvements in the overpotential for hydrogen oxidation for the resulting [Ni(PNP)$_2$]$^{2+}$ complex, the rate of H_2 oxidation remained low, less than 0.2 s^{-1}. The structure of the active site of the [FeFe] hydrogenase enzyme suggested a plausible way to improve the catalytic rate of these synthetic complexes. In structure **16**, the six-membered ring formed by the azadithiolate ligand adopts a boat conformation, which positions the pendant amine nitrogen so that it can easily interact with a coordinated H_2 ligand. This interaction should stabilize the H_2 adduct, and lead to more efficient catalysis. To test this hypothesis, we prepared a series of three nickel complexes containing cyclic diphosphine ligands as shown in structure **21**.[25] The presence of a second chelate ring system results in a boat conformation for at least one ring in each diphosphine ligand. In addition to achieving the positioning of a pendant amine, we wanted to vary its basicity so that the reaction could be biased

toward either H$_2$ production or oxidation. Similarly, phenyl and cyclohexyl groups on phosphorus would allow us to probe the influence of electronic and steric properties at this position.

21a R = Ph R' = Ph   **22**   **23**

21b R = Ph R' = Bz (benzyl)

21c R = Cy R' = Bz
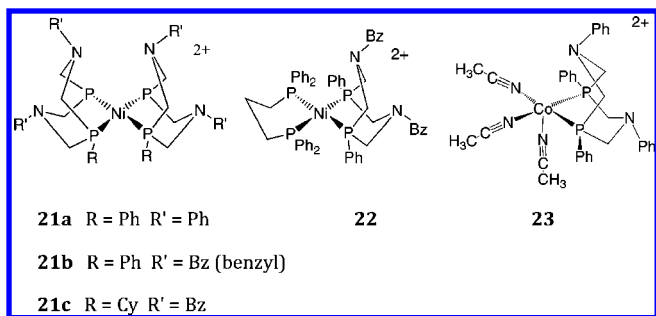
Catalytic studies of complexes **21a**−**21c** showed that complexes **21a** and **21b** are catalysts for H$_2$ production with turnover rates of 350 s^{-1} (overpotential $\approx$ 300 mV using protonated dimethylformamide as the acid) and 5 s^{-1} (overpotential $\approx$ 200 mV using bromoanilinium as the acid), respectively, in acetonitrile at 22 °C.[25,26] In contrast to **21a** and **21b**, **21c** is a catalyst for H$_2$ oxidation with a turnover frequency of 10 s^{-1} under 1.0 atm of H$_2$. These experiments clearly demonstrate that two positioned pendant bases are superior to complexes having two bases that are not positioned near the metal center. Computational studies also supported the importance of two positioned bases for the nickel complexes.[26] However, in concurrent studies of related cobalt complexes, we discovered that [Co(P$^{Ph}_2$N$^{Ph}_2$)(CH$_3$CN)$_3$]$^{2+}$ (**23**) is also an efficient catalyst for H$_2$ production with a turnover frequency of 90 s^{-1} and an overpotential of 285 mV using bromoanilinium as the acid.[27] Because this cobalt complex contains a single positioned pendant base, this raised the question, "For nickel complexes, are two positioned bases required for high catalytic activity, or is one positioned base sufficient?"

To address this question, we synthesized the mixed ligand complex [Ni(P$^{Ph}_2$N$^{Bz}_2$)(dppp)]$^{2+}$ (**22**, where dppp = bis(diphenylphosphino)propane), which contains only one amine positioned near the nickel center.[28] Complex **22** has a turnover frequency for H$_2$ oxidation in the presence of 1.0 atm of H$_2$ and excess base of 0.4 s^{-1}. This value is greater than that of **19** but less than that of **21c**. Table 1 lists both the experimentally determined free energy for H$_2$ addition to catalysts **19**,[24] **21c**,[25] and **22**[28] to form the corresponding heterolytic cleavage products and their catalytic rates for H$_2$ oxidation. It is clear from these data that the thermodynamic driving force for H$_2$ addition for these complexes does not correlate with the observed catalytic rates. Instead, for these nickel complexes, the catalytic rates correlate with the number of positioned pen-

**TABLE 1.** Free Energy of H$_2$ Addition and Turnover Frequencies of [Ni(diphosphine)$_2$](BF$_4$)$_2$ Complexes with Pendant Amines

complex	$\Delta G^{\circ}_{(H_2)}$ (kcal/mol)	turnover frequency (s^{-1})[a]
21c	−3.1	10
22	−4.0	0.4
19	−6.0	<0.2

[a] Turnover frequency for oxidation of H$_2$ under 1.0 atm H$_2$ at 22 °C.

dant bases present in these catalysts, with the complex containing two positioned amines exhibiting the highest catalytic activity. For nickel, two positioned bases appear to be optimal, while for cobalt only one positioned base results in a very active catalyst.

Mechanistic Studies

The high activity exhibited by the nickel catalysts containing the cyclic P$^R_2$N$^{R'}_2$ ligands led us to investigate the mechanism of H$_2$ oxidation and production in more detail.[25,26,28] The H$_2$ oxidation catalysts were particularly enlightening, because several of the products of H$_2$ addition and sequential deprotonation could be observed by NMR spectroscopy. Perhaps the most revealing of these studies were those for the H$_2$ oxidation catalyst [Ni(P$^{Ph}_2$N$^{Bz}_2$)(dppp)]$^{2+}$, **22**.[28] Addition of H$_2$ to **22** is thought to involve the experimentally undetected dihydrogen intermediate [(H$_2$)Ni(P$^{Ph}_2$N$^{Bz}_2$)(dppp)]$^{2+}$ (**24**), based on theoretical calculations of similar complexes.[25,26] This undetected intermediate evolves to form the unusual Ni^{IV} dihydride complex [H$_2$Ni(P$^{Ph}_2$N$^{Bz}_2$)(dppp)]$^{2+}$ (**25**) identified by NMR at low

24   **25**   **26**
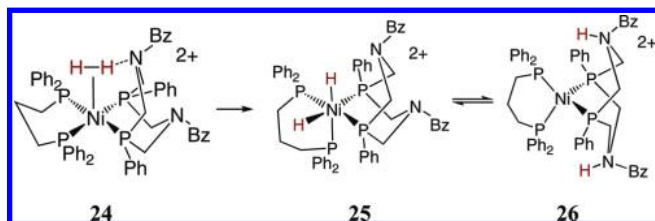
temperature. The oxidative addition of the coordinated H$_2$ molecule appears to be the rate-determining step in the overall catalytic cycle for the oxidation of H$_2$.[28] Spectroscopic studies indicate that the resulting Ni^{IV} dihydride is in rapid equilibrium with a Ni^0 complex (**26**), in which both of the N atoms of the pendant amines are protonated. This remarkable transformation, which involves a change in the formal oxidation state by four and the transfer of two protons, occurs at a rate of 10−100 s^{-1} at −20 °C. These studies have led us to propose the catalytic mechanism shown in Scheme 4 for the more active catalysts, **21a**−**c**. The cleavage of H$_2$ by these more symmetric complexes with two cyclic P$^R_2$N$^{R'}_2$ ligands (steps 1−3) is thought to occur in a manner strictly analogous to that observed for [Ni(P$^{Ph}_2$N$^{Bz}_2$)(dppp)]$^{2+}$, **22**.

SCHEME 4. Proposed Mechanism for H$_2$ Oxidation and Production by **21a**−**c**
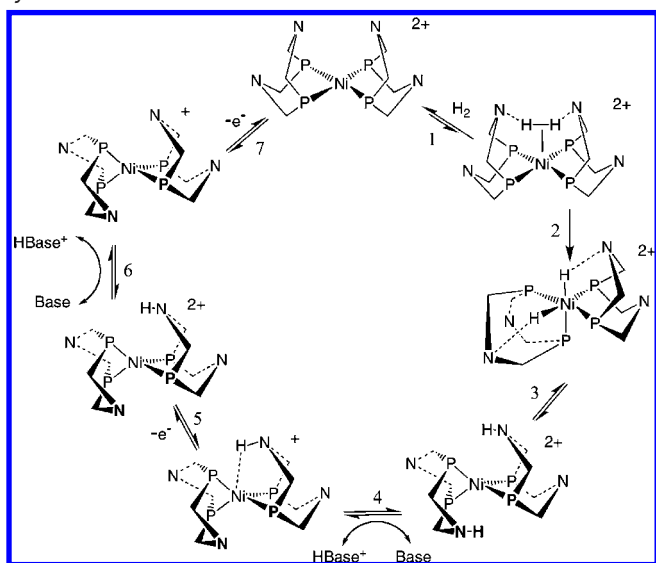
Because the pendant nitrogen atoms can shuttle the protons from the Ni center to the exterior of the catalytic molecule, access of exogenous bases to the protons bound to these nitrogen relays result in kinetically facile deprotonation as shown in step 4. As a result of this deprotonation, the oxidation shown in step 5 becomes much easier. It can be estimated that the oxidation potential associated with step 5 is 0.8 V more negative than would be observed for the corresponding hydride complex in which the nitrogen atoms of the pendant bases are replaced with methylene (CH$_2$) groups.[28] This is comparable to the difference in oxidation potentials observed for [HNi(depp)$_2$]$^+$ and [HNi(PNP)$_2$]$^+$ discussed above. The oxidation in step 5 results in an increase in acidity of the protonated pendant base, which reacts with base in solution to form the Ni^I species, step 6. A final oxidation step, 7, completes the catalytic cycle. In Scheme 4, the pendant bases play multiple roles. They assist in the binding of H$_2$ (step 1), the cleavage of H$_2$ (step 2), and the transfer of protons between the metal center and solution (steps 3, 4, and 6).

Summary and Prospects

The generation of fuels from abundant substrates such as CO$_2$ and water remain daunting challenges for future research. It will require significant advances in new inexpensive materials for light harvesting and the development of fast, stable, and efficient electrocatalysts. In this Account, we have described efforts by our research groups to develop redox-active carriers capable of concentrating CO$_2$ and molecular electrocatalysts for CO$_2$ reduction, hydrogen production, and

hydrogen oxidation. Progress has been made in each of these areas, but much more remains to be done.

Studies of quinones as redox-active CO$_2$ carriers have demonstrated the feasibility of selectively pumping CO$_2$ over significant concentration ranges. This offers promise for the ultimate development of redox-active CO$_2$ carriers for recovering CO$_2$ directly from the atmosphere as is done in natural photosynthesis. However, the sensitivity of the quinone carriers to oxygen in the CO$_2$ binding form is problematic for CO$_2$ recovery from the atmosphere. Copper-based carriers for electrochemical CO$_2$ pumping can overcome the problems of oxygen sensitivity in the CO$_2$ binding form (in this case CO$_2$ is bound as carbonate) and are water-soluble. However, this first generation of metal complexes is only capable of pumping over a very limited pressure range and cannot bind CO$_2$ at atmospheric concentrations. Future studies need to develop carriers that have the best features of both of the previously studied systems. This represents an interesting and scientifically challenging goal.

Electrocatalysts of the general formula [Pd(triphosphine)-(solvent)]$^{2+}$ have been developed for the reduction of CO$_2$ to CO. A key structural feature of these catalysts is the weakly bound solvent molecule, which provides an incipient vacant coordination site for the water molecule formed during C−O bond cleavage. Under sufficiently acidic conditions, the catalytic rates are first order in catalyst and CO$_2$ with second-order rate constants of 5 to 200 M^{-1} s^{-1}. An even more active catalyst is observed if a second metal is introduced into the second coordination sphere as shown in structure **15** and as observed in the structure of the [NiFe] CO dehydrogenase enzyme, **13**. These results suggest the inclusion of vacant coordination sites (to assist C−O bond cleavage) and a metal in the second coordination sphere to assist CO$_2$ binding (one metal through C and the other through O) are important considerations for the design of future CO$_2$ reduction catalysts.

The development of new nickel-based catalysts for H$_2$ production and oxidation has built on fundamental thermodynamic studies of the hydride donor/acceptor ability of metal complexes. By combining structural features of the first coordination sphere suggested by these thermodynamic studies with appropriately matched pendant bases in the second coordination sphere, nickel-based catalysts have been developed with catalytic rates for H$_2$ production approaching those of [NiFe] hydrogenase enzymes and that are not inhibited by CO. These studies have demonstrated the important roles of the pendant bases in these molecules: stabilizing H$_2$ binding, promoting H$_2$ cleavage, and providing a low-energy pathway for the transfer of protons from the metal center to solution. Struc-

tural and mechanistic studies have demonstrated that the number and positioning of relays present in these catalysts are critical factors in the catalytic activity. These studies suggest that understanding M–H bond energetics and the function of pendant bases in the second coordination sphere will play an important role in the rational development of electrocatalysts for a number of multiproton/multielecton reactions of importance to the generation of solar fuels.

BIOGRAPHICAL INFORMATION

Daniel L. DuBois is a Senior Scientist at Pacific Northwest National Laboratory. He received his Ph.D. from The Ohio State University and did postdoctoral work at Cornell University. His research interests include the catalytic interconversion of fuels and electricity, synthetic organometallic and inorganic chemistry, and thermodynamic studies relevant to catalysis.

Mary Rakowski DuBois joined the faculty of the University of Colorado in 1976, after completion of her Ph.D. at The Ohio State University and postdoctoral work at Cornell University. In 2007, she moved to the Pacific Northwest National Laboratory at Richland, Washington. Her research interests have included the syntheses and studies of organometallic and metallosulfur complexes that function as catalysts or models for heterogeneous catalysts.

FOOTNOTES

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