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Molecular Electrocatalysts for the Oxidation of Hydrogen and the Production of Hydrogen – The Role of Pendant Amines as Proton Relays

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Electrocatalysts for efficient conversion between electricity and chemical bonds will play a vital role in future systems for storage and delivery of energy. Our research on functional models of hydrogenase enzymes uses nickel and cobalt, abundant and inexpensive metals, in contrast to platinum, a precious metal used in fuel cells. A key feature of our research is a focus on the use of pendant amines incorporated into diphosphane ligands. These pendant amines function as proton relays, lowering the barrier to proton transfers to and from the catalytically active metal site. The hydride acceptor ability of metal cations, along with the basicity of pendant amines, are key thermochemical values that determine the thermodynamics of addition of H_2 to a metal complex with a pendant amine incorporated into its ligand. Nickel catalysts for oxidation of H_2 have turnover frequencies up to 50 s^{-1} (at 1 atm H_2 and room temperature). Nickel and cobalt catalysts for production of H_2 by reduction of protons were studied; one of them has a turnover frequency over 1000 s^{-1}.

Introduction

Production of H_2 by reduction of protons, as well as the oxidation of H_2, is carried out in nature by microbial organisms. Structural studies revealed that hydrogenase enzymes[1] exist in several forms; they have first-row metals Fe and Ni in their active site, bound to ligands that include CO and CN.[2] The remarkable discovery that natural enzymes included organometallic complexes as a key component led to intense interest from organometallic/inorganic chemists along with scientists focused on biological and structural aspects of hydrogenase enzymes.

Two of the most well-studied hydrogenase enzymes are [FeFe] hydrogenase and [NiFe] hydrogenase. Equation (1) shows a simplified drawing of the active site of the [FeFe] hydrogenase and its reaction with H_2. This drawing focuses only on the active metal site and does not show the complexity of the protein surrounding the active site. Delivery of electrons occurs through an Fe_4S_4 cluster; protons and H_2 are delivered to and from the active site by channels [not shown in Equation (1)], so that the precise delivery of reactants and removal of the products from the catalytically active metal site is accomplished in the enzymes. The proposed mechanism shown in Equation (1) involves the binding of H_2 to an iron atom, followed by heterolytic cleavage of H_2, such that an iron hydride forms, the proton being transferred to the nitrogen atom.

Several groups have successfully prepared and characterized *structural* models of [FeFe] hydrogenases that perform some of the same reactions as the hydrogenase enzymes.[3,4] Pickett and co-workers synthesized an $Fe_2(CO)_5$ complex with two sulfur bridges, bound through another

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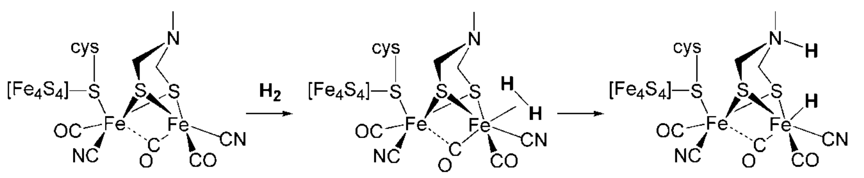

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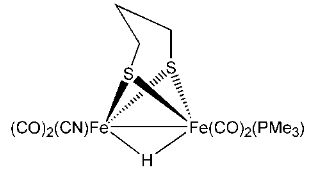

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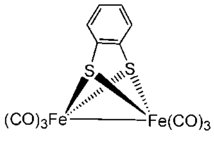

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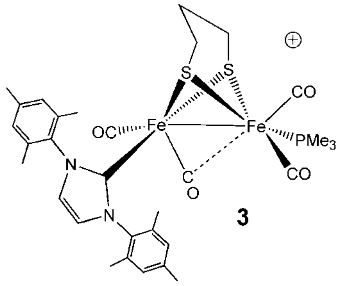

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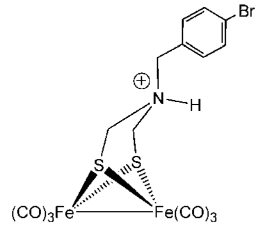

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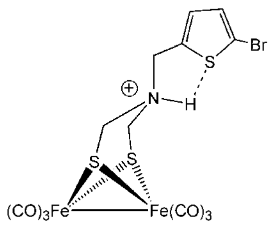

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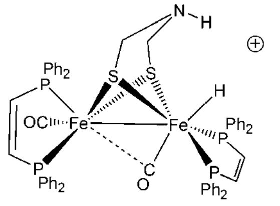

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sulfur atom to a cubane Fe_4S_4 cluster, which models many of the structural features shown in Equation (1), and their complex was shown to be an electrocatalyst for proton reduction to produce H_2.[5]

Rauchfuss and co-workers found that a Fe_2 complex with a bridging hydride, **1**, catalyzes the production of H_2 by using toluenesulfonic acid (HOTs).[4,6] The catalytic reduction occurs at a potential of about –1.43 V, corresponding to an overpotential of about 780 mV. This potential, and all others discussed in this Microreview, are referenced to Cp_2Fe^+/Cp_2Fe. Darensbourg and co-workers found that $[Fe_2(CO)_5(PTA)\{\mu\text{-}S(CH_2)_3S\}]$ (PTA = 1,3,5-triaza-7-phosphaadamantane) catalyzes the reduction of HOAc in mixed CH_3CN/H_2O solvent at –1.4 V.[7] Gloaguen and co-workers reported electrocatalytic reduction of HOTs by using Fe_2S_2 complex **2**; electrochemical simulations suggested that the neutral iron complex was reduced to the dianion, followed by protonation.[8] Lichtenberger and co-workers reported electrocatalytic reduction of HOAc at –2.1 V with **2**.[9]

Liu and Darensbourg synthesized cationic complex **3**, with an N-heterocyclic carbene ligand on one Fe.[10] This paramagnetic Fe^IFe^{II} complex has a semibridging CO and an open coordination site that mimics the salient structural features of the unprecedented Fe_2 unit in the [FeFe] hydrogenase. This active site is in an "entatic," or rotated, state in the Fe^IFe^{II} form of the enzyme. Such rotated or inverted square pyramids are unknown for the many derivatives of $(\mu\text{-SRS})[Fe^I(CO)_3]_2$. Oxidation of the Fe^IFe^I form to give the Fe^IFe^{II} form (complex **3**) is reversible and can be carried out chemically or electrochemically. The crystal structure of **3** was reported, as well as IR and EPR spectra.

Several groups have studied Fe_2 complexes containing azadithiolate ligands similar to that in Equation (1).[11–14] Ott and co-workers reported an Fe_2S_2 complex with an azadithiolate ligand, which is protonated at the nitrogen atom by $HClO_4$ to give **4**. Reduction of this protonated complex occurs at a potential that is about 400 mV more positive than that of the neutral complex. When excess $HClO_4$ is added, catalytic production of H_2 is observed at –1.48 V. Sun and co-workers prepared Fe_2S_2 complex **5**, which has a thiophene appended near the azadithiolate ligand, shown in its protonated form.[12] This complex catalyzes the reduction of $HClO_4$ at –1.09 V, a potential more positive than those found for other $Fe_2(CO)_6$ complexes. Terminal Fe–H hydrides can be formed at low temperatures, but they isomerize to bridging hydrides at higher temperatures.[13] Rauchfuss and co-workers found that **6** catalyzes the reduction of strong acids at –20 °C to produce H_2 at about –1.5 V;[14] the low temperature was used to minimize isomerization of the terminal hydride to the bridging form.

In contrast to these extensive studies on *structural* models of [FeFe] hydrogenase, our approach[15,16] has been to design, prepare, and characterize biologically inspired *functional* models of hydrogenases. Our approach retains two of the critical features of enzymes: the use of abundant, inexpensive metals, and the incorporation of a pendant amine as a proton relay, but we do not attempt to emulate the precise structural features exhibited by the [FeFe] enzymes. A particularly salient feature of the structure shown in Equation (1) is the presence of an amine functionality in the structure of the ligand, such that the amine is properly positioned to facilitate the heterolytic cleavage of H_2. Much of the focus of our work has been on an examination of the many roles that pendant amines have, and the profound changes in reactivity resulting from the incorporation of these amines in the ligand structure.

Our interest in developing new catalysts that exhibit reactivity akin to that of hydrogenase enzymes is because of the need to find new sustainable catalysts for conversion between different forms of energy. A dramatic increase in the use of nonfossil energy sources is needed to address the problems of increasing worldwide demand for energy and higher emissions of CO_2 to the atmosphere.[17] Solar and wind sources of energy are sustainable, but an increased reliance on these sources of energy will require methods to store the energy for times when the sun is not shining or the wind is not blowing. Nuclear and geothermal sources of energy can be generated essentially continuously, but energy storage is still needed due to the temporal mismatch of supply and demand for electrical energy.

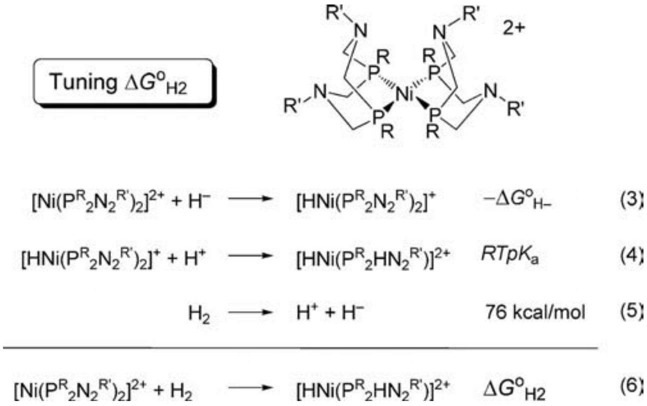
Electrocatalysts for efficient conversion between electricity and chemical energy will play a vital role in future systems for storage and delivery of energy. An immense scale of energy storage is needed, and storing energy in chemical bonds is attractive since fuels have a much higher energy density than other forms of energy storage, such as batteries. Equally important are reactions that operate in the reverse direction, efficiently converting the energy stored in a chemical bond into electricity. In this Microreview, we discuss our research on electrocatalysts for oxidation of H_2 and for production of H_2 by reduction of protons [Equation (2)], and the role that proton relays have in facilitating these reactions. While the long-term intent is to produce H_2 from water, our experiments generally use organic acids as the source of protons for the production of H_2. The oxidation of H_2 can be carried out in fuel cells, but low-temperature fuel cells use Pt as the catalyst for both the oxidation of H_2 as well as the companion half-reaction, the reduction of oxygen to give water. Considering the large scale needed, the use of Pt catalysts would be prohibitively expensive, so our efforts focus instead on catalysts based on abundant, inexpensive metals like Ni and Co. In addition to the high cost, an additional issue of concern in terms of sustainability is the low availability of precious metals like Pt.[18] All of these considerations have led to the search for alternatives to precious metals in many types of catalytic reactions,[19] in addition to those discussed here that focus on energy-related reactions.

$$\xrightarrow{\text{Hydrogen Oxidation}}$$
$$H_2 \rightleftharpoons 2\,e^- + 2\,H^+ \qquad (2)$$
$$\xleftarrow[\text{Hydrogen Production}]{}$$

The oxidation and production of H_2 [Equation (2)] appear to be simple reactions, involving only two protons and two electrons. But one-electron oxidation of H_2 is highly endergonic, and H_2 is very weakly acidic, so removal of either an electron or a proton is very difficult in the absence of a catalyst. In addition to oxidation/production of H_2, other reactions could provide excellent methods for energy storage, such as reduction of CO_2 to produce methanol as a fuel. Conversion of CO_2 to methanol is more complicated than the reactions of H_2 shown in Equation (2), as more electrons and protons are involved, as well as the need to break the bond between carbon and oxygen. We are pursuing catalysts for reduction of CO_2[15] along with the work described here that focuses on oxidation and production of H_2. We hope that the information gained in development of molecular electrocatalysts for reactions of H_2 will provide guidance that is useful in the development of other types of catalysts. Reactions that involve movement of multiple electrons and protons are pervasive in the chemistry of energy storage and utilization. Our focus is on minimizing the barriers for movement of protons through the use of pendant amines functioning as proton relays. Electrons can tunnel over several Angstroms, but protons often need to be "pushed" by providing an appropriate mechanism to facilitate their transfer from one site to another. The need to accelerate proton transfer may seem surprising, since commonly encountered proton transfers to organic compounds, such as amines, are often fast. Large steric effects can impede the rate of proton transfer, and proton transfer to and from metals can be slow in metal hydride chemistry[20] and in some bioinorganic reactions.[21]

Thermodynamics of H_2 Addition to $[Ni(P^R{}_2N^{R'}{}_2)_2]^{2+}$ Complexes – Roles of Hydricity of the Metal Hydride and Acidity of N–H Bonds

Thermochemical measurements are exceedingly valuable in the study of catalysis, even if the necessary data are sometimes tedious to determine experimentally with good accuracy. An ideal catalytic cycle will not only avoid large barriers for all elementary reactions, but will also have no highly exothermic reactions, since the resultant low-energy intermediate would face a high barrier for a subsequent step. Scheme 1 shows the free energy for addition of H_2 to $[Ni(P^R{}_2N^{R'}{}_2)_2]^{2+}$, a class of Ni complexes to be discussed in this Microreview. Equation (3) shows the hydride acceptor ability of the metal complex; $-\Delta G^\circ_{H-}$ is the free energy associated with this reaction. The energy of protonation of a pendant amine on the ligand [Equation (4)] can be altered by changing to more electron-donating alkyl groups to give more basic amines, compared to aryl substituents that make the amine less basic (methyl > benzyl > phenyl as electron-donating substituents). Identifying and understanding the factors that control hydricity and acidity has enabled the successful rational design of improved catalysts.



$$[Ni(P^{R}_{2}N_{2}^{R'})_{2}]^{2+} + H^{-} \longrightarrow [HNi(P^{R}_{2}N_{2}^{R'})_{2}]^{+} \quad -\Delta G^{o}_{H-} \quad (3)$$

$$[HNi(P^{R}_{2}N_{2}^{R'})_{2}]^{+} + H^{+} \longrightarrow [HNi(P^{R}_{2}HN_{2}^{R'})]^{2+} \quad RTpK_{a} \quad (4)$$

$$H_{2} \longrightarrow H^{+} + H^{-} \quad 76\ \text{kcal/mol} \quad (5)$$

$$[Ni(P^{R}_{2}N_{2}^{R'})_{2}]^{2+} + H_{2} \longrightarrow [HNi(P^{R}_{2}HN_{2}^{R'})]^{2+} \quad \Delta G^{o}_{H2} \quad (6)$$

Scheme 1.

The origin of the value of 76 kcal/mol for the heterolytic cleavage of H_2 [Equation (5)] is shown by the thermochemical cycle in Scheme 2.[22,23] The free energy values shown are those in acetonitrile and will vary in different solvents, as explained in detail by Wayner and Parker.[23] The free energy of 76 kcal/mol for heterolytic cleavage of H_2 is significantly *less* than the free energy of homolytic cleavage of H_2 in acetonitrile, because of solvation of the proton and hydride by the solvent.

$$\begin{array}{lll} & & \Delta G^{0}\ [\text{kcal/mol}]\ (\text{MeCN}) \\ H_2\ (\text{gas}) \longrightarrow & 2\ H\bullet\ (\text{solv}) & 103.6 \\ H\bullet\ (\text{solv}) \longrightarrow & H^{+}\ (\text{solv}) + e^{-} & -53.6 \\ H\bullet\ (\text{solv}) + e^{-} \longrightarrow & H^{-}\ (\text{solv}) & 26.0 \\ \hline H_2\ (\text{gas}) \longrightarrow & H^{+}\ (\text{solv}) + H^{-}\ (\text{solv}) & 76.0 \end{array}$$

Scheme 2. Thermochemical cycle for heterolytic cleavage of H_2 in MeCN.

Extensive studies of the transfer of hydride [Equation (7)] from a series of metal hydrides have revealed the factors controlling hydricity.[22,24–28] Hydricity is the ability of a transition metal hydride to donate a hydride (H^-). As for acidity of metal hydrides, where a proton is transferred from a metal hydride complex, kinetics and thermodynamics of hydricity can be measured separately. Hydride transfer from a cationic metal hydride is shown in Equation (7); this reaction is the reverse of the hydride acceptor reaction shown in Equation (3). These measurements are generally carried out in acetonitrile, the same solvent typically used in our electrochemical studies and catalytic studies.

$$[(\text{diphosphane})_2M\text{–}H]^{+} \xrightarrow{\Delta G^{0}_{H-}} [(\text{diphosphane})_2M]^{2+} + H^{-} \quad (7)$$

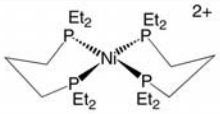
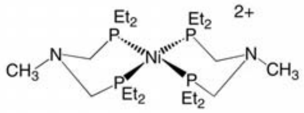
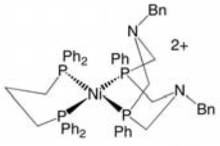
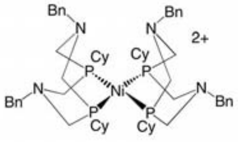
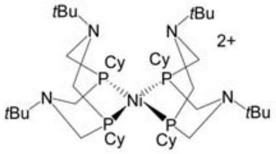
The solvent can have a large effect on hydricity, not only because removal of H^- increases the charge on the metal complex, but also because in some cases a solvent molecule, such as MeCN, will bind to the metal following hydride transfer.[28,29] Third-row metals exhibit higher thermodynamic hydricity compared to that of their first-row analogs. An example is $[HPt(dmpe)_2]^+$, which is 9 kcal/mol more hydridic than $[HNi(dmpe)_2]^+$ {dmpe = 1,2-bis(dimethylphosphanyl)ethane}.[22] Comparing substituent effects on the diphosphane ligand when the metal is kept the same also shows large changes: the hydricity of $[HNi(dmpe)_2]^+$ exceeds that of $[HNi(dppe)_2]^+$ {dppe = 1,2-bis(diphenylphosphanyl)ethane} by 12 kcal/mol, owing to the higher electron-donating ability of methyl groups relative to phenyl groups.[24] Studies of the hydricity of a series of $[HPd(diphosphane)_2]^+$ complexes showed a range of 27 kcal/mol in hydricity as the natural bite angle of the P–Pd–P changed by 33°.[27] Diphosphanes with sterically demanding groups can have a large effect on the dihedral angle between the planes defined by the two P atoms of each diphosphane and the metal, as shown by crystallographic studies.[27] The dihedral angle (which increases with the bulkiness of the attached group and generally increases with the natural bite angle) correlates very well with hydricity. Larger dihedral angles lead to better hydride acceptor ability of the metal cation.

The free energy for addition of H_2 [Equation (6); ΔG°_{H2}] determines the bias of a potential catalyst. When ΔG°_{H2} is negative, incorporation of H_2 into the metal complex is thermodynamically favorable, and those complexes are good candidates for oxidation of H_2 if kinetic requirements are also met. In contrast, a positive ΔG°_{H2} will be found in cases where expulsion of H_2 is favored, which will then lead to catalysts more suited for production of H_2. Hydrogenase enzymes catalyze the oxidation of H_2 as well as the production of H_2, and in principle it is possible to design synthetic catalysts that operate as catalysts in both directions. Designing catalysts that operate with high rates for both directions with low overpotentials will require low intrinsic barriers for addition/elimination of H_2. In practice, synthetic catalysts are usually biased toward one direction or the other, so that they are catalysts for oxidation of H_2 *or* for production of H_2, but not both.

Catalytic Oxidation of H_2 by Ni Complexes

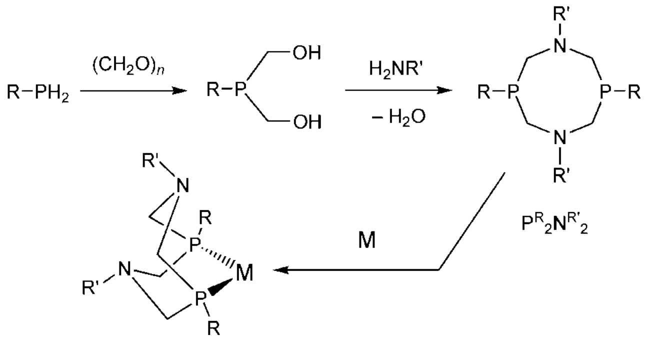
A Ni complex with two diphosphanes that have no proton relays, $[Ni(depp)_2]^{2+}$ {depp = 1,2-bis(diethylphosphanyl)propane; see first entry in Table 1} is an electrocatalyst for the oxidation of H_2 in the presence of added NEt_3,[30] but the reaction is slow. The cyclic voltammogram of the Ni^{II} hydride complex $[HNi(depp)_2]^{2+}$, with no proton relay, has an irreversible oxidation wave at 0.0 V. In striking contrast, the wave in the cyclic voltammogram for oxidation of $[HNi(PNP)_2]^{2+}$ (PNP = $Et_2PCH_2NMeCH_2PEt_2$) occurs at –0.62 V, a much more negative potential. Incorporation of a proton relay into the ligand structure in the PNP ligand leads to a much lower energy pathway for oxidation. Electrocatalytic oxidation of H_2 (1 atm) by $[Ni(PNP)_2]^{2+}$ has an overpotential of about 100 mV, a decrease of about 600 mV from that observed with $[Ni(depp)_2]^{2+}$.[30] The pendant amine in $[Ni(PNP)_2]^{2+}$ facilitates the transfer of protons from the metal to the external added base, without requiring large structural reorganization of the ligand, since the base is built into the ligand. The overall rate of catalysis is still slow, however, since binding/cleavage of H_2 is slow (Table 1).

Table 1. Ni^{II} catalysts for oxidation of H_2.

	TOF [s^{-1}] (oxidation of H_2)	$\Delta G°(H_2)$ [kcal/mol] (Equation 6)
	< 0.2	–
	< 0.2	–6.0
	0.4	–4.0
	10	–3.1
	50	–5.0 (estimated)

While the incorporation of a pendant amine into the PNP ligand leads to a significant decrease in the overpotential for the electrocatalytic oxidation of H_2, the six-membered ring Ni-PNP undergoes chair/boat conversions as observed for cyclohexane-type ring structures. Consequently, the pendant amine is positioned optimally for interaction with a Ni–H bond only when it is in a boat configuration. A crystal structure of a derivative of $[Ni(PNP)_2]^{2+}$ (with an *n*Bu group on each N) shows that both six-membered rings are in the chair form,[30] so conversion to the boat conformation contributes to the barrier for oxidation of H_2 by $[Ni(PNP)_2]^{2+}$.

As shown in Equation (1), the six-membered ring structure proposed in the [FeFe] hydrogenase has a boat conformation, so that the pendant amine is properly positioned to facilitate the binding and cleavage of the H_2 ligand. Seeking to enforce a similar boat conformation in Ni complexes, we prepared a series of complexes with "P_2N_2" ligands. The cyclic P_2N_2 ligands are readily prepared in two steps, as shown in Scheme 3. The addition of a second six-membered ring into the P_2N_2 ligand structure of $M(P_2N_2)$ complexes usually causes at least one of the pendant amines to adopt a boat conformation, thus making it properly positioned for interaction with a hydride or H_2 ligand on the metal. Changes in the alkyl or aryl group bound to P or N allow tuning of the steric and electronic properties of the P_2N_2 ligands [Equation (6), Scheme 1].



Scheme 3.

Catalytic oxidation of H_2 (1 atm) by $[Ni(P^{Cy}{}_2N^{Bn}{}_2)_2]^{2+}$ (Cy = cyclohexyl; Bn = benzyl) has a turnover frequency of about 10 s^{-1}, a rate much higher than that observed with $[Ni(PNP)_2]^{2+}$. Having the pendant amine properly positioned in the P_2N_2 ligand structure accelerates the rate of the catalytic reaction. A related complex with only one P_2N_2 ligand, $[Ni(P^{Cy}{}_2N^{Bn}{}_2)(dppp)]^{2+}$ {dppp = 1,2-bis(diphenylphosphanyl)propane} catalyzes the oxidation of H_2 with a turnover frequency of 0.4 s^{-1}.[31] The turnover-limiting step of all of these reactions is binding/cleavage of H_2, so the higher turnover frequency found for $[Ni(P^{Cy}{}_2N^{Bn}{}_2)_2]^{2+}$, with two positioned pendant amines, relative to $[Ni(P^{Cy}{}_2N^{Bn}{}_2)(dppp)]^{2+}$, with just one pendant amine, has been attributed to a beneficial effect of the second positioned pendant amine. As shown in Table 1, the free energy for addition of H_2 to the Ni complexes is more favorable for $[Ni(P^{Cy}{}_2N^{Bn}{}_2)(dppp)]^{2+}$ than for $[Ni(P^{Cy}{}_2N^{Bn}{}_2)_2]^{2+}$, yet $[Ni(P^{Cy}{}_2N^{Bn}{}_2)_2]^{2+}$ has a faster rate. The turnover frequency increases with the number of *positioned* pendant amines in this example. Since the overall rate of these catalytic reactions correlates with the rate of addition/cleavage of H_2, the higher rate obtained with two positioned pendant amines suggests that the pendant amines assist in the binding of H_2, in addition to their role of facilitating intramolecular and intermolecular proton movement. Theoretical studies on $[Ni(P^{Me}{}_2N^{Me}{}_2)_2]^{2+}$, however, suggest that only one pendant amine is directly involved in the heterolytic binding/cleavage of H_2.[32] Additional experimental and theoretical studies are being carried out to further refine our understanding of the involvement of one vs. two pendant amines in these reactions.

Oxidation of H_2 (1 atm) by $[Ni(P^{Cy}{}_2N^{tBu}{}_2)_2]^{2+}$, which has *tert*-butyl groups on the nitrogen atom of the pendant amines, occurs with a turnover frequency of 50 s^{-1} when NEt_3 is used as the base.[33] This is the fastest molecular electrocatalyst for oxidation of H_2 of which we are aware. The faster rate observed for this complex relative to that for $[Ni(P^{Cy}{}_2N^{Bn}{}_2)_2]^{2+}$ is due to the higher basicity of amine nitrogen atoms with *tert*-butyl groups than those with benzyl groups. Consequently, the driving force for addition of H_2 is more favorable, and the reaction occurs with a higher rate.

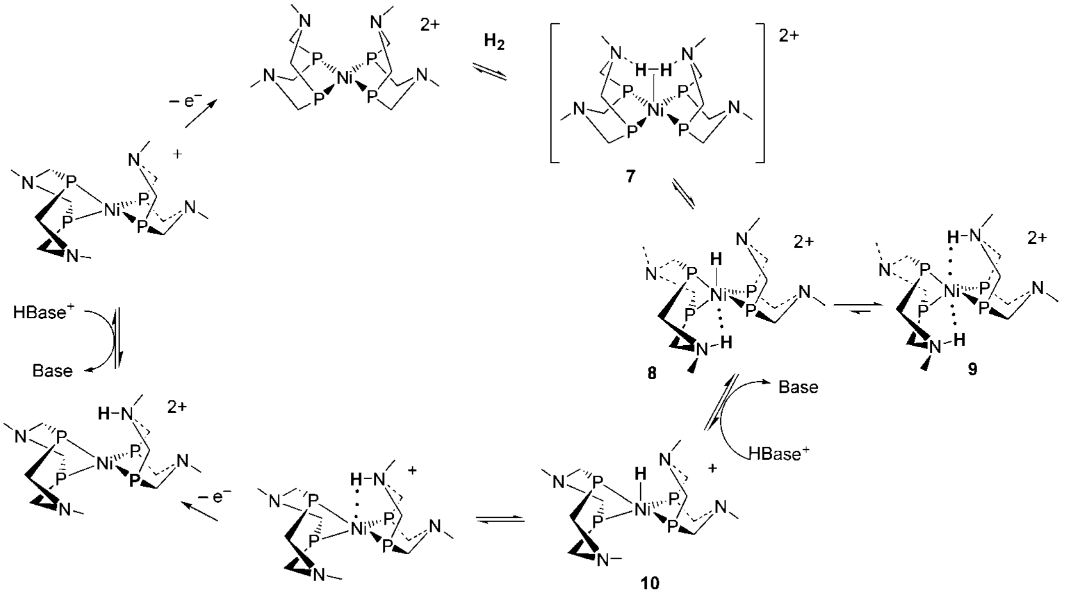
Mechanism of Catalytic Oxidation of H_2

The proposed mechanism for catalytic oxidation of H_2 by $[Ni(P^{R}_2N^{R'}_2)_2]^{2+}$ shown in Scheme 3 is based on spectroscopic and electrochemical measurements[31,34,35] as well as theoretical calculations.[32] Binding of H_2 to Ni to form an η^2-H_2 complex (compound **7**) is proposed as the first step. No direct experimental evidence has been obtained yet for this $Ni(H_2)^{2+}$ complex, but theoretical calculations[32] show that it exists in a shallow well, and thus may not be readily observed. In contrast to most other metals, dihydrogen complexes of Ni are very rare; Caulton has recently discovered a $Ni(H_2)$ complex, characterized by NMR spectroscopic measurements and DFT calculations.[36] Cleavage of the H–H bond leads to **9**, a Ni^0 complex with two protonated amine ligands that can be observed spectroscopically. The two electrons of H_2 have reduced the Ni^{II} to Ni^0, and the two protons have been transferred to the basic sites on the pendant amines. Intermediate **8**, which has one Ni–H and one N–H bond, may be on the pathway between dihydrogen complex **7** and Ni^0 complex **9**. Although **8** has not been detected spectroscopically, calculations on closely related complexes[32] support its involvement in the reaction. Deprotonation of **9** produces Ni hydride complex **10**. These reactions show that pendant amines play a key role related to the function of proton channels in enzymes, lowering the barrier for intramolecular proton mobility by moving the proton away from the metal, where it can then be readily transferred to an external base.

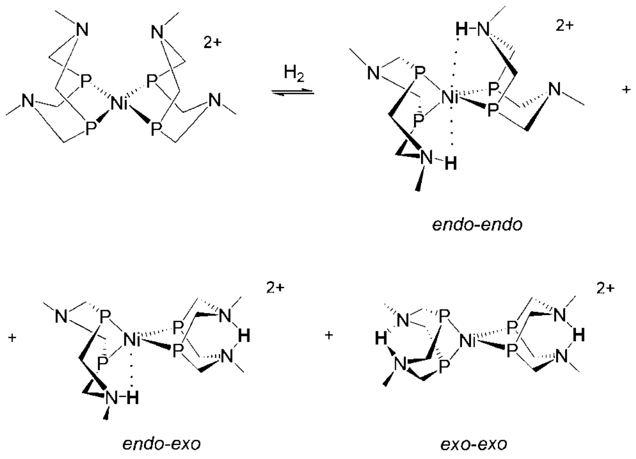
Completion of the catalytic cycle for oxidation of H_2 requires electrochemical oxidation of the Ni complex, followed by deprotonation and a second one-electron oxidation. As for many reactions involving movement of multiple electrons and protons, the question is which of these steps occur as separate steps of electron transfer and proton transfer. In some of these cases, the steps may be coupled in a proton-coupled electron transfer (PCET).[37] One-electron oxidation of transition metal hydrides can lead to large increases in acidity; changes of 15–21 pK_a units have been determined.[26,38] Considering the huge increase in acidity that occurs upon oxidation, the subsequent proton transfer may be coupled with the oxidation step without the actual participation of an intermediate. Some proton-coupled electron-transfer processes occur, but additional experimental and theoretical studies are needed to more fully define the precise mechanism of these reactions.

Evidence supporting the assignment of the initially observed product of addition of H_2 to $[Ni(P^{Cy}_2N^{Bn}_2)_2]^{2+}$ was obtained from ^1H and ^{31}P NMR experiments.[35] Addition of H_2 (1 atm) is reversible in acetonitrile; an equilibrium constant of $K = 190 \pm 20\ \text{atm}^{-1}$ was determined at 21 °C. The initially observed product is the *endo*-*endo* isomer shown in Scheme 5 (as well as **9** in Scheme 4). Two additional isomers, *endo*-*exo* and *exo*-*exo* (Scheme 5), were also identified. The isomers that have one or two N–H–N groups in an *exo* geometry are likely formed through intermolecular proton transfers.

Our studies[31] of the oxidation of H_2 by $[Ni(P^{Cy}_2N^{Bn}_2)(dppp)]^{2+}$ provided insights that had not been obtained from related complexes (Scheme 6). Experiments with D_2 show a kinetic isotope effect of $k_{H2}/k_{D2} = 1.7$ for $[Ni(P^{Cy}_2N^{Bn}_2)(dppp)]^{2+}$; this isotope effect is interpreted as a composite of the equilibrium isotope effect for binding of

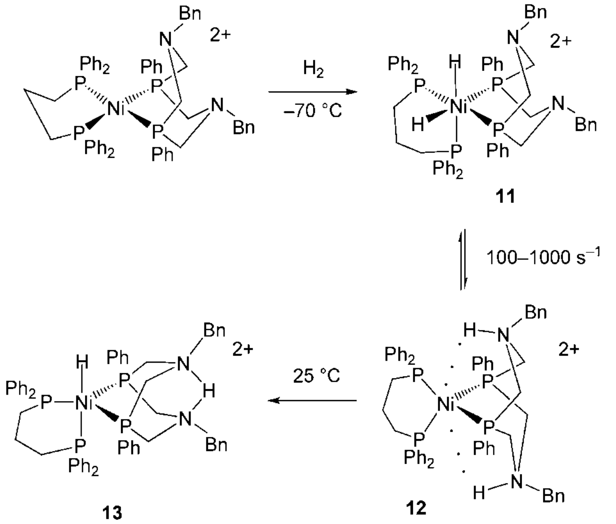


Scheme 4. (R groups on P and N not shown).



Scheme 5. (R groups on P and N not shown).

H_2/D_2, together with the kinetic isotope effect on the oxidative addition of H_2/D_2 to the metal. An unusual feature is the observation of a Ni^{IV} dihydride complex that forms by oxidative addition of H_2 to $[Ni(P^{Cy}{}_2N^{Bn}{}_2)(dppp)]^{2+}$. The dihydride, $[(H)_2Ni(dppp)(P^{Ph}{}_2N^{Bn}{}_2)]^{2+}$ (**11**), was characterized by ^1H and ^{31}P NMR at –70 °C; it exhibits inequivalent hydride resonances with ^{31}P coupling. To the best of our knowledge, **11** is the only known example of a Ni^{IV} dihydride complex.



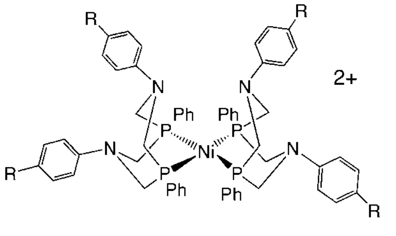
Scheme 6.

A second Ni complex observed at –70 °C from the reaction of H_2 with $[Ni(P^{Cy}{}_2N^{Bn}{}_2)(dppp)]^{2+}$ is assigned as $[Ni(dppp)(P^{Ph}{}_2N^{Bz}{}_2H_2)]^{2+}$ (**12**), a Ni^0 complex with two protonated amines. Dihydride **11** is in equilibrium with **12**, and conversion between them occurs with a rate constant of about 100–1000 s^{-1} at –20 °C. Two reversible proton transfers between Ni and N are required to convert between the two complexes. The ability to promote fast proton transfer between the metal and the pendant amine is a key feature that enables proton relays to enhance the rates of catalytic reactions. The final thermodynamically favored isomer that forms upon warming to room temperature is complex **13**, which has one Ni–H bond and one N–H–N bond, as shown in Scheme 6.

Ni Catalysts for Production of H_2 by Proton Reduction

While the Ni complexes discussed above with alkyl or benzyl substituents on the pendant amine are catalysts for the oxidation of H_2, a related class of $[Ni(P^{Ph}{}_2N^{R'}{}_2)_2]^{2+}$ complexes with aryl groups on both the P and N atoms are electrocatalysts for production of H_2 by reduction of protons. As discussed earlier, catalysts for production of H_2 will generally have a positive value of $\Delta G°_{H2}$ [Equation (6)], meaning that they will favor evolution of H_2 rather than addition/oxidation of H_2. Electrocatalytic reduction of a buffered solution of protonated dimethylformamide (H–DMF^+) in CH_3CN is achieved at 22 °C by using $[Ni(P^{Ph}{}_2N^{Ph}{}_2)_2]^{2+}$.[34] The reaction is second-order in acid concentration at low acid concentrations and independent of acid concentration at high acid concentrations. The mechanism is thought to be the same as that shown in Scheme 4, but proceeding in the opposite direction (clockwise as drawn for oxidation of H_2 and counterclockwise for H_2 production).

A series of related complexes were prepared in which the substituent on the *para* position of the aromatic group of the amine was varied.[39] This change systematically alters the basicity of the pendant amine, while exerting minimal changes in the sterics around the metal, since all the complexes studied had Ph groups on the phosphane of the P_2N_2 ligand.



R = OMe, Me, H, Br, CF_3

Reversible waves assigned to the Ni(II/I) and the Ni(I/0) couples were observed in the cyclic voltammograms of these complexes. For both the II/I and the I/0 couples, a more negative reduction potential was observed as the electron-donating ability of the *para* substituent increased. The $E_{1/2}$ values (vs. Cp_2Fe^+/Cp_2Fe) for the II/I couples ranged from –0.88 V (for R = OMe) to –0.74 V (for R = CF_3), and the $E_{1/2}$ values for the I/0 couples varied from –1.07 V (for R = OMe) to –0.89 V (for R = CF_3). The electronic effects are large enough for the II/I couple for the complex with R = OMe to occur at essentially the same potential as that for the I/0 couple of the Ni complex with R = CF_3. A plot of the $E_{1/2}$ values vs. the pK_a of the free anilinium (i.e., the pK_a of $RC_6H_4NH_3^+$) gives a straight line for both the II/I and the I/0 couples. The *para* substituent (R) on the aromatic group is eight bonds away from the Ni, yet this correlation shows that there is remarkably effective electronic communication between the pendant amine and the metal.

All of these complexes are electrocatalysts for production of H_2 in acetonitrile solution, using organic acids as the proton source. These observed half-wave potentials occur within 50 mV of the II/I couple, consistent with an initial reduction of the Ni^{II} to Ni^{I}, followed by proton transfer to this complex, as shown by the mechanism in Scheme 4 (counterclockwise for H_2 production). Overpotentials varied in the range 220–370 mV.

The fastest rates were observed when protonated DMF ($H–DMF^+$) was used as the acid. This acid can be isolated as a crystalline solid[40] and has a pK_a of 6.1 in acetonitrile.[41] Turnover frequencies found for H_2 production with $H–DMF^+$ were fastest (740 s^{-1}) for R = Br and slower (590 s^{-1}) for R = H. A slower rate (310 s^{-1}) was found for R = OMe, and this is attributed to a lower driving force for elimination of H_2. Since the OMe substituent leads to the most basic amine, the elimination of H_2 is thermodynamically less favorable in this case. An even slower rate (95 s^{-1}) was found for the Ni catalyst with R = CF_3. The lower rate in this case is attributed to the pendant amine having too low basicity to be easily protonated. The fastest rates are found with the amine substituents of intermediate basicity, as too little or too much electron density at the nitrogen atom gives slower rates.

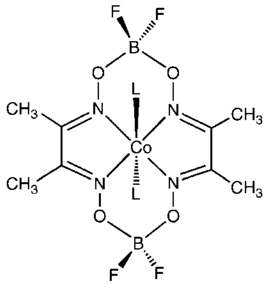
Relative to H_2 production experiments with $H–DMF^+$ as the acid, slower rates were found with protonated anilinium acids, 2,6-dichloroanilinium (pK_a 5.0 in CH_3CN)[42] and 4-cyanoanilinium (pK_a 7.0 in CH_3CN). The highest turnover frequency obtained with any anilinium acid was 36 s^{-1} for the Ni complex with R = Br, with 2,6-dichloroanilinium as the acid. With the exception of the Ni complex with R = CF_3, the turnover frequencies differed by less than a factor of two when using 2,6-dichloroanilinium or 4-cyanoanilinium as the acid. The turnover frequencies do not correlate with the acid strength, since $H–DMF^+$ (pK_a 6.1) gives faster rates in all cases than either the stronger acid 2,6-dichloroanilinium or the weaker acid 4-cyanoanilinium. Our hypothesis for this observation is that the different acids produce different distributions of products upon protonation. The acid giving the fastest catalytic rates, $H–DMF^+$, is smaller sterically than the anilinium acids, and is thought to more efficiently protonate the *endo* sites of the pendant amines (see Scheme 5 for *endo* and *exo* designations).

For all of the Ni complexes in this series, addition of H_2O gives higher turnover frequencies. Using $H–DMF^+$ as the acid, addition of H_2O (0.1–0.3 M) gave rates that were typically 20%–50% faster than those without added H_2O. The rates observed using anilinium acids were accelerated by larger amounts with added water. For the Ni complex with R = Br, the turnover frequency of 36 s^{-1} found with 2,6-dichloroanilinium as the acid in the absence of water increased sharply to 480 s^{-1} when the catalytic reaction was carried out with 0.25 M added H_2O. A possible role of water is to facilitate the conversion of *exo* isomers, which are not catalytically productive, to catalytically competent *endo* isomers. In addition, water might also stabilize the transition state for H_2 evolution. The extent of these and other possible roles of water in accelerating the reaction are not yet fully understood and are currently under investigation.

In the presence of water, the fastest rates were observed for a Ni complex that had a phosphonate bound to the *para* position of the aromatic ring [R = $CH_2P(=O)(OEt)_2$]. While this complex had a rate of 500 s^{-1} for H_2 production with $H–DMF^+$ as the acid, it exhibited a much higher rate when water was added, giving a turnover frequency of 1850 s^{-1}. As there are four phosphonate groups on this complex, it may experience additional hydrogen-bonding interactions with water. For comparison, H_2 production by [NiFe] hydrogenase is reported to have a rate of 700 s^{-1} at 30 °C, while the [FeFe] hydrogenase enzyme is much faster, at 6,000–9,000 s^{-1}.[43] The fastest molecular electrocatalysts for production of H_2 occur at rates exceeding those reported for [NiFe] hydrogenase, but the synthetic catalysts have a higher overpotential and are thus not as energy-efficient as the enzymes.

Cobalt Electrocatalysts for H_2 Production

Connolly and Espenson reported in 1986 that acidic solutions of Cr^{II} in the presence of the Co^{II} macrocyclic complex $Co(dmgBF_2)_2$ evolve H_2.[44] Studies of the kinetics provided evidence that Cr^{II} was an inner-sphere reducing agent, and $[(H_2O)_5Cr\text{-}Cl\text{-}Co(dmgBF_2)_2]^+$ was proposed as an intermediate. Dissociation of this complex would give $[Co(dmgBF_2)_2]^-$, which can be protonated to give the cobalt hydride $HCo(dmgBF_2)_2$, the precursor to the formation of H_2.



L = MeCN or H_2O

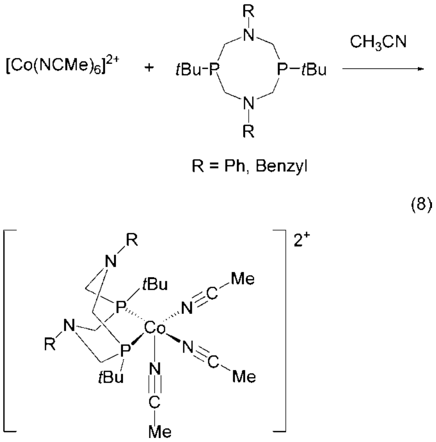
Peters,[45] Gray,[46] and co-workers found that H_2 can be electrocatalytically produced by using cobalt complexes, with CF_3CO_2H as the acid. Production of H_2 by $Co(dmgBF_2)_2(CH_3CN)_2$ occurred near the Co(II/I) couple, which was observed at –0.93 V vs. Cp_2Fe^+/Cp_2Fe (reported as –0.55 V vs. SCE). The overpotential for H_2 production was estimated to be 40 mV. The low overpotential suggested that this same catalyst might function in the opposite direction, oxidizing H_2. H_2 reacted with $Co(dmgBF_2)_2(CH_3CN)_2$ in the presence of $[Bu_4N][CF_3CO_2]$, but the reaction took several days.

Artero and co-workers reported studies of cobaloxime complexes and found that $[Co^{III}(dmgH)_2(py)Cl]$ is an electrocatalyst for H_2 production with $HNEt_3^+$ as the acid.[47] They found faster rates when electron-donating substituents were used on the pyridine ligand, and slower catalysis when electron-withdrawing pyridine ligands were used. Subsequent studies showed that a series of cobalt and nickel complexes with diimine/dioxime ligands were electrocatalysts for H_2 production with low overpotentials.[48]

We sought to determine whether pendant amines could enhance catalysis with cobalt complexes as they do for nickel complexes. The cobalt complex $[Co(P^{Ph}_2N^{Ph}_2)_2(CH_3CN)]^{2+}$ was prepared by reaction of two equivalents of $P^{Ph}_2N^{Ph}_2$ with $[Co(CH_3CN)_6]^{2+}$.[49] This cobalt complex has the same +2 charge as the Ni complexes discussed above, and thus is a paramagnetic d^7 Co^{II} complex compared to the diamagnetic d^8 Ni^{II} complexes. When HOTf was added to solutions of $[Co(P^{Ph}_2N^{Ph}_2)_2(CH_3CN)]^{2+}$ in CH_3CN, H_2 was produced in an electrocatalytic reaction, initially suggesting that the Ni^{II} and Co^{II} complexes had similar catalytic reactivity. But further studies showed significant differences between the two metals. The half-wave potential for electrocatalytic production of H_2 was observed at –1.00 V, whereas the Co(II/I) couple of $[Co(P^{Ph}_2N^{Ph}_2)_2(CH_3CN)]^{2+}$ occurs at –0.58 V. It became clear that the production of H_2 was *not* being catalyzed by $[Co(P^{Ph}_2N^{Ph}_2)_2(CH_3CN)]^{2+}$. Instead, the potential at which catalysis occurred corresponds to the Co(II/I) couple of $[Co(P^{Ph}_2N^{Ph}_2)(CH_3CN)_3]^{2+}$, which was synthesized by addition of just one equivalent of $P^{Ph}_2N^{Ph}_2$ to $[Co(CH_3CN)_6]^{2+}$. Addition of HOTf to $[Co(P^{Ph}_2N^{Ph}_2)_2(CH_3CN)]^{2+}$ leads to protonation and loss of one $P^{Ph}_2N^{Ph}_2$ ligand, producing $[Co(P^{Ph}_2N^{Ph}_2)(CH_3CN)_3]^{2+}$ under the conditions of the catalytic experiment.

Electrocatalytic production of H_2 from $[Co(P^{Ph}_2N^{Ph}_2)(CH_3CN)_3]^{2+}$ with *p*-bromoanilinium as the acid was studied; a turnover frequency of 90 s^{-1} was found at 22 °C, with an overpotential of about 285 mV. As with the Ni complexes, a pendant amine substantially lowers the barrier for catalytic activity, as $[Co(dppp)(CH_3CN)_3]^{2+}$, which has no pendant amine, shows no significant catalytic activity under these conditions. Some catalytic production of H_2 was found with $[Co(CH_3CN)_6]^{2+}$ in the presence of the strong acid HBF_4, but the Co(II/I) couple occurs at –1.21 V so this reaction occurs with a much higher overpotential and slower rate than that with $[Co(P^{Ph}_2N^{Ph}_2)(CH_3CN)_3]^{2+}$.

Cobalt complexes with sterically demanding *tert*-butyl groups on the phosphorus and benzyl or phenyl groups on the nitrogen atom, as shown in Equation (8) were synthesized.[50]



(8)

The crystal structures of both $[Co(P^{tBu}_2N^{Ph}_2)(CH_3CN)_3]^{2+}$ and $[Co(P^{tBu}_2N^{Bn}_2)(CH_3CN)_3]^{2+}$ showed square pyramids, with CH_3CN in the axial position. Catalytic production of H_2 was observed by cyclic voltammetry with $[Co(P^{tBu}_2N^{Ph}_2)(CH_3CN)_3]^{2+}$ in the presence of *p*-bromoanilinium as the acid. The half-wave potential for the catalysis occurs at –0.88 V, corresponding to the Co(II/I) couple, with a turnover frequency of 160 s^{-1}. The overpotential is about 160 mV. The complex with *tert*-butyl groups on the phosphane is faster and has a lower overpotential than $[Co(P^{Ph}_2N^{Ph}_2)(CH_3CN)_3]^{2+}$. No catalysis was found with $[Co(P^{tBu}_2N^{Bn}_2)(CH_3CN)_3]^{2+}$, which has a more basic benzyl group on the nitrogen atom, and this is attributed to protonation of the nitrogen atom of the pendant amine and ligand loss before reduction of Co^{II} to Co^{I}.

Conclusions

Nature uses iron and nickel in hydrogenase enzymes to catalyze the oxidation of H_2 and the production of H_2. In these systems, a key feature is channels that regulate the precise delivery/removal of protons and H_2. In contrast to the use of abundant metal catalysts in Nature, low-temperature fuel cells rely on platinum, a precious metal of high cost and low abundance. Our efforts on functional models of hydrogenase enzymes have focused on complexes of nickel and cobalt. Pendant amines incorporated into the ligand structure serve as proton relays that accelerate intramolecular and intermolecular proton mobility. Thermodynamic values for the acidity of N–H bonds and the hydride donor ability of metal hydrides (and the hydride acceptor ability of metal cations) permit the determination of the thermodynamics of addition and heterolytic cleavage of H_2 in metal complexes. These thermodynamic values are critical components in the rational design of molecular catalysts for oxidation of H_2 and production of H_2. In addition to the role of accelerating proton transfer reactions, pendant amines also have additional beneficial effects, including enhancement of the binding of H_2 to a metal, lowering the barrier to heterolytic cleavage of H_2, and involvement in proton-coupled electron-transfer reactions. While the focus of this Microreview is limited to reactions involving H_2, we emphasize that *the concept of using proton relays to accelerate proton transfer reactions should be applicable to many other reactions* that involve the transfer of multiple protons and electrons, which includes many reactions of interest in the field of energy storage and utilization. Considering the large rate enhancements that can result from the incorporation of proton relays, we hope that the chemistry discussed here will encourage others to think broadly about the role of proton relays in a wide variety of reactions.

Acknowledgments

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