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# Hydrogen oxidation catalysis by a nickel diphosphine complex with pendant *tert*-butyl amines†‡

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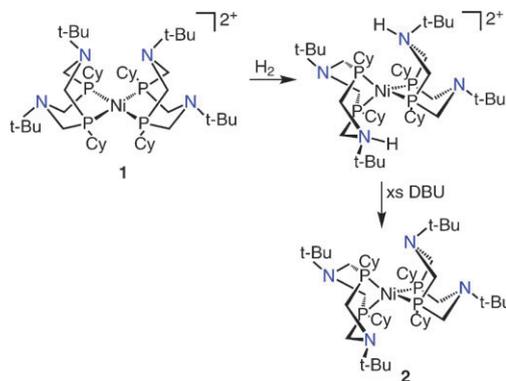
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A bis-diphosphine nickel complex with *tert*-butyl functionalized pendant amines  $[\text{Ni}(\text{P}^{\text{Cy}}_2\text{N}^{\text{t-Bu}}_2)_2]^{2+}$  has been synthesized. It is a highly active electrocatalyst for the oxidation of hydrogen in the presence of base. The turnover rate of  $50 \text{ s}^{-1}$  under 1.0 atm  $\text{H}_2$  at a potential of  $-0.77 \text{ V}$  vs. the ferrocene couple is 5 times faster than the rate reported heretofore for any other synthetic molecular  $\text{H}_2$  oxidation catalyst.

An important prerequisite for the expanded use of energy from renewable sources is the ability to store and recover the energy on demand. Chemical fuels are ideal in this context since chemical bonds have high energy density. Hydrogen has frequently been cited as a good candidate as a chemical fuel. To minimize energy requirements, efficient catalysts are necessary for both the production and utilization of hydrogen. Currently, the best catalyst for hydrogen production and oxidation is platinum, which is too costly for widespread use.

Such considerations have led to the development of molecular catalysts employing more abundant metals, and several complexes that contain nickel,<sup>1–5</sup> cobalt,<sup>5–9</sup> or iron<sup>10–14</sup> have been developed as electrocatalysts for the production of hydrogen. In contrast, there are few molecular complexes that perform hydrogen oxidation,<sup>15–20</sup> and even fewer have been studied for catalytic<sup>21–24</sup> or electrocatalytic activity.<sup>1,25–27</sup> We have previously reported that  $[\text{Ni}(\text{P}^{\text{Cy}}_2\text{N}^{\text{Bz}}_2)_2](\text{BF}_4)_2$  functions as an electrocatalyst for  $\text{H}_2$  oxidation with a turnover frequency of  $10 \text{ s}^{-1}$ .<sup>1</sup>  $\text{P}^{\text{R}}_2\text{N}^{\text{R}'_2}$  denotes cyclic diphosphine ligands that incorporate an amine base in each ligand chelate ring, where R and R' are substituents on the phosphorus and nitrogen atoms, respectively (e.g., see Scheme 1).

The non-coordinating pendant bases in these complexes have been found to contribute to high catalytic activity for both  $\text{H}_2$  formation and oxidation by stabilizing the binding of  $\text{H}_2$  to the metal center, assisting the heterolytic cleavage or formation of the H–H bond, facilitating intra- and intermolecular proton transfer, and coupling proton and electron



Scheme 1

transfer events.<sup>28,29</sup> In this communication we report a synthetic variant of the nickel complex. Replacement of the benzyl functionality on the pendant nitrogen base with a *tert*-butyl group increases its proton acceptor ability which leads to a greater driving force for hydrogen addition. The result is the most active molecular catalyst for hydrogen oxidation reported to date.

The new eight-membered cyclic ligand  $\text{P}^{\text{Cy}}_2\text{N}^{\text{t-Bu}}_2$  was synthesized by a procedure similar to that reported for other ligands in this class.<sup>1,3,30,31</sup> Two equivalents of the ligand were added to  $[\text{Ni}(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$  in acetonitrile to form the complex  $[\text{Ni}(\text{P}^{\text{Cy}}_2\text{N}^{\text{t-Bu}}_2)_2](\text{BF}_4)_2$  (**1**), isolated as a crystalline red solid.  $[\text{Ni}(\text{P}^{\text{Cy}}_2\text{N}^{\text{t-Bu}}_2)_2](\text{BF}_4)_2$  (**1**) in acetonitrile rapidly reacts with  $\text{H}_2$  (1 atm, RT) to form a colorless product which is identified by spectroscopic data as a Ni(0) complex with a protonated amine in each ligand, as shown in Scheme 1. In the  $^1\text{H}$  NMR spectrum a resonance at 4.9 ppm is assigned to the amine protons. No resonances are observed in the nickel hydride region ( $-5$  to  $-15$  ppm). Both the  $^1\text{H}$  and  $^{31}\text{P}$  chemical shifts (18.3 ppm) for the product are consistent with the isomer in which the protonated chelate rings of the ligand retain their boat conformations.<sup>2</sup> The Ni<sup>0</sup> complex  $\text{Ni}(\text{P}^{\text{Cy}}_2\text{N}^{\text{t-Bu}}_2)_2$  (**2**) can be synthesized from the hydrogen addition product by the addition of excess base (DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene), also shown in Scheme 1. Both complex **1** and **2** have been characterized by  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy, and elemental analysis, as detailed in the ESI.† All data are consistent with their formulations.

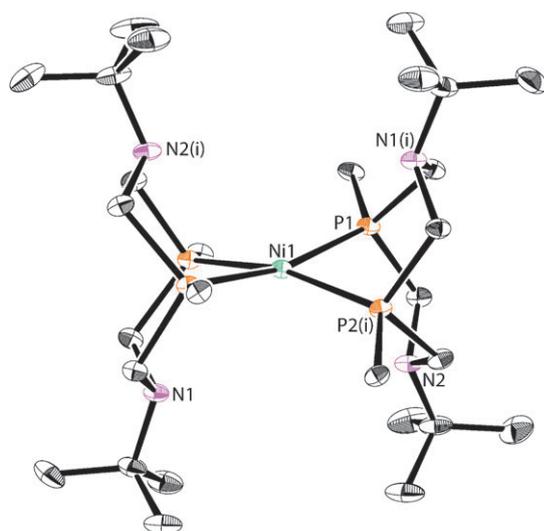
X-Ray diffraction studies have been carried out on crystals of **1** grown from a solution of acetonitrile and diethyl ether. The dication of **1** (Fig. 1) is a distorted square planar complex with a dihedral angle of  $22.61^\circ$ , between the two planes defined

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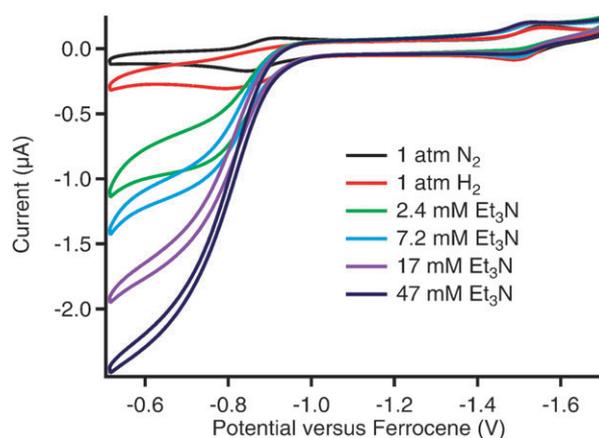


**Fig. 1** The crystallographic structure of the cation of  $[\text{Ni}(\text{P}^{\text{Cy}}_2\text{N}^{\text{t-Bu}}_2)](\text{BF}_4)_2$  (**1**). Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ):  $\text{Ni}(1)\text{--P}(1)$ , 2.2205(8);  $\text{Ni}(1)\text{--P}(2)$ , 2.2196(8);  $\text{P}(2)\text{--Ni}(1)\text{--P}(2)$ , 80.83(2). Thermal ellipsoids are shown at the 50% probability level. For clarity, only the carbons attached to the phosphorus atoms are shown.

by the phosphorus atoms of each ligand and nickel. This distortion from a planar geometry is likely the result of steric interactions between the cyclohexyl substituents on phosphorus. The small  $\text{P--Ni--P}$  bite angles for the cyclic diphosphine ligands ( $80.64^\circ$ ) are characteristic of first row metal complexes with these  $\text{P}^{\text{R}}_2\text{N}^{\text{R}'_2}$  ligands, and are attributed to constraints imposed by the second six-membered chelate ring in the backbone of the cyclic ligand.<sup>1,8,9,26,32</sup> From Fig. 1, it can be seen that all four six-membered rings formed upon coordination of the diphosphine ligands to the metal are in boat conformations, and the average non-bonding  $\text{Ni}\cdots\text{N}$  distance is 3.25  $\text{\AA}$ .

The cyclic voltammogram of  $[\text{Ni}(\text{P}^{\text{Cy}}_2\text{N}^{\text{t-Bu}}_2)](\text{BF}_4)_2$  (**1**) recorded in benzonitrile displays two reversible one-electron reduction waves at  $-0.81$  V and  $-1.45$  V vs. the ferrocenium/ferrocene couple, which are assigned to the  $\text{Ni}^{\text{II/I}}$  and  $\text{Ni}^{\text{I/0}}$  couples ( $\Delta E_{\text{p}} = 82$  mV and 60 mV, respectively, at a scan rate of  $50$   $\text{mV s}^{-1}$ ). The corresponding cyclic voltammogram of the  $\text{Ni}^0$  complex,  $[\text{Ni}(\text{P}^{\text{Cy}}_2\text{N}^{\text{t-Bu}}_2)]$  (**2**), recorded in benzonitrile consists of two reversible one-electron oxidation waves ( $\Delta E_{\text{p}} = 63$  mV and 76 mV at a scan rate of  $50$   $\text{mV s}^{-1}$ ) at  $-1.49$  V and  $-0.87$  V vs. the ferrocenium/ferrocene couple (shown in black in Fig. 2).

Fig. 2 also displays the cyclic voltammogram of  $[\text{Ni}(\text{P}^{\text{Cy}}_2\text{N}^{\text{t-Bu}}_2)]$  (**2**) recorded in benzonitrile purged with hydrogen (red trace), and upon addition of aliquots of triethylamine (other colored traces). In the absence of base (red trace), **2** does not react with hydrogen until it is oxidized to the  $\text{Ni}^{2+}$  complex (**1**), upon which the oxidation wave at  $-0.87$  V is enhanced. Addition of triethylamine (up to 82 equivalents) results in an increase in the anodic current observed for the wave at  $-0.87$  V (colored scans). Higher concentrations of triethylamine did not result in any further increase in current. The oxidative current for the  $\text{Ni}^{\text{II/I}}$  couple in the presence of hydrogen plus triethylamine is 23 times larger than the current observed for the  $\text{Ni}^{\text{II/I}}$  couple in the absence of hydrogen and

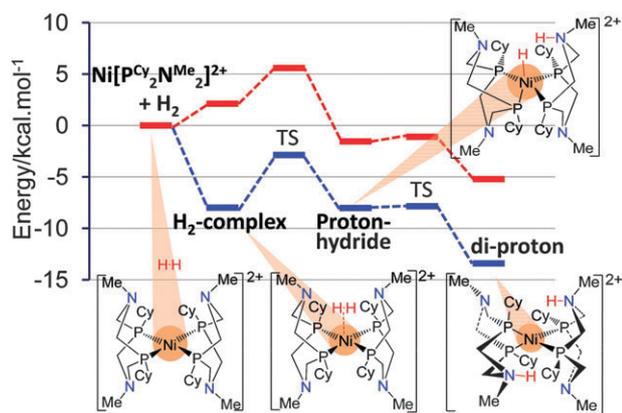


**Fig. 2** Cyclic voltammograms of a 0.57 mM  $[\text{Ni}(\text{P}^{\text{Cy}}_2\text{N}^{\text{t-Bu}}_2)_2]$  (**2**) solution under nitrogen (black), under hydrogen (red), and in increasing concentration of  $\text{Et}_3\text{N}$  (colored). Conditions: scan rate =  $50$   $\text{mV s}^{-1}$ , benzonitrile solvent,  $0.2$  M  $\text{Bu}_4\text{NPF}_6$  as supporting electrolyte, glassy carbon working electrode. Potentials are referenced to the ferrocenium/ferrocene couple.

base, indicating a catalytic reaction with a turnover frequency of  $50$   $\text{s}^{-1}$  under  $1.0$  atm  $\text{H}_2$ .<sup>33</sup>

Previous kinetic studies of  $\text{H}_2$  oxidation catalysts by nickel diphosphine complexes with pendant amines have shown that the rate-limiting step is the addition/cleavage of  $\text{H}_2$  to the  $\text{Ni}^{\text{II}}$  complex. We have investigated the thermodynamic factors that govern this reaction, and these studies guided the design of the new catalyst reported here. The thermodynamic driving force for hydrogen addition can be tuned by modifying the phosphorus and nitrogen functionalities. A large substituent on phosphorus, such as the cyclohexyl group, results in a tetrahedral distortion of the complex. In a series of  $[\text{Ni}(\text{diphosphine})_2]^{2+}$  derivatives this distortion was found to lead to a decrease in the energy of the lowest unoccupied molecular orbital, resulting from a decrease in the sigma antibonding interaction between nickel and phosphorus. This lower energy enhances the hydride acceptor abilities of the  $\text{Ni}^{\text{II}}$  complexes<sup>34,35</sup> and favors the addition of  $\text{H}_2$ . The free energy for hydrogen addition is also favored by increasing the proton acceptor ability of the pendant amine. The use of the *tert*-butyl substituent on the nitrogen increases the basicity of the pendant amine compared to the previously studied benzyl derivative,  $[\text{Ni}(\text{P}^{\text{Cy}}_2\text{N}^{\text{Bz}}_2)]^{2+}$ . As a result, the catalyst  $[\text{Ni}(\text{P}^{\text{Cy}}_2\text{N}^{\text{t-Bu}}_2)](\text{BF}_4)_2$  has a greater driving force for hydrogen addition. The catalytic rate of  $50$   $\text{s}^{-1}$  is the fastest reported for a molecular hydrogen oxidation catalyst.

In conjunction with our experimental studies, we have performed a computational electronic structure study (see ESI† for relevant details) of the mechanism for  $\text{H}_2$  addition to the nickel catalyst. The symmetric all boat conformer of  $[\text{Ni}(\text{P}^{\text{Cy}}_2\text{N}^{\text{Me}}_2)]^{2+}$  is used in place of the *N*'Bu derivative to reduce the computational complexity. As shown in Fig. 3, the  $\text{H}_2$  molecule forms an adduct with the Ni complex with a relative free energy of  $+2$   $\text{kcal mol}^{-1}$  at  $T = 300$  K. The positive free energy arises from the loss of translational entropy of  $\text{H}_2$  ( $\sim 10$   $\text{kcal mol}^{-1}$ ) as it binds to the complex, a loss partially offset by a  $8$   $\text{kcal mol}^{-1}$  binding energy of  $\text{H}_2$  to the Ni center. The  $\text{H}_2$  adduct then undergoes heterolytic  $\text{H}_2$



**Fig. 3** Calculated reaction profile for all boat conformer of  $[\text{Ni}(\text{P}^{\text{Cy}}_2\text{N}^{\text{Me}}_2)_2]^{2+} + \text{H}_2$ . Blue lines: energy; red lines: free energy. Dashed lines are only a guide to the eye.

cleavage resulting in a  $\text{Ni}^{2+}$  hydride species and a protonated pendant amine. The transition state free energy for this step is calculated to be  $+3.5 \text{ kcal mol}^{-1}$  higher than the free energy of the adduct. A homolytic cleavage of the  $\text{H}_2$  adduct to form a dihydride intermediate (not shown) was also characterized and found to have a free energy barrier about twice as large ( $\sim 7 \text{ kcal mol}^{-1}$ ) as the heterolytic cleavage. The proton-hydride complex converts to the experimentally observed  $\text{Ni}(0)$  species with two protonated pendant amines with a free energy barrier of only  $\sim 1 \text{ kcal mol}^{-1}$ . The rate-determining barrier to the overall mechanism of  $\text{H}_2$  oxidation is thus the barrier associated with the heterolytic  $\text{H}_2$  bond cleavage step in addition to the free energy (translational entropy) loss due to the coordination of  $\text{H}_2$  to the complex. A detailed account of the computational study will be given in a future publication.<sup>36</sup>

In summary, a new derivative in the class of  $[\text{Ni}(\text{P}^{\text{R}}_2\text{N}^{\text{R}'})_2](\text{BF}_4)_2$  complexes has been synthesized. The incorporation of the *tert*-butyl amine into the cyclohexyl phosphine framework was designed to lower the free energy of hydrogen addition/cleavage, the rate-determining step for catalysis. This has led to an electrocatalyst that is 5 times faster than the best molecular  $\text{H}_2$  oxidation catalyst previously reported, the analogous nickel diphosphine derivative with benzyl substituents on the nitrogens.<sup>1</sup>

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