DOI: 10.1002/anie.201104918

Preparation and Reactivity of a Nickel Dihydride Complex**

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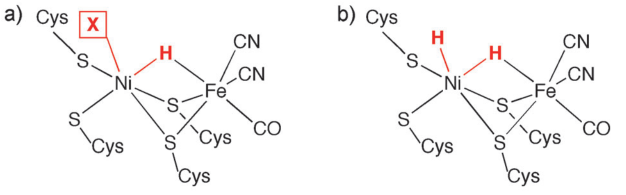
Hydrogen has the potential to provide clean, green energy for the 21st century.[1] One path to using hydrogen as an energy source is to develop catalysts based on the hydrogenase (H_2ase) class of enzymes.[2–5] In order to better understand and harness the properties of H_2ase, we previously constructed a robust H_2ase mimic based on a NiRu bis-μ-thiolato assembly.[6] In addition to successfully replicating the chemical features of the [NiFe]H_2ase, we were able to gain a number of crucial insights into their structural and mechanistic features. These findings have now been incorporated into the biological literature (Scheme 1).[7]

As part of our model study, we proposed the existence of a crucial bimetallic NiRu dihydride intermediate in the catalytic cycle.[6] Unfortunately, the dihydride could not be directly observed, but implicated by isotope labeling experiments. To provide further insights into the nature of the dihydride species, which is capable of acting as an electron donor, we have developed a remarkable dinuclear octahedral bis(μ-hydrido)dinickel(II) complex $[Ni^{II}_2(Me_2\text{-tpa})_2(\mu\text{-H})_2]Y_2$ ($\mathbf{1}Y_2$, Me_2-tpa = bis((6-methyl-2-pyridyl)methyl)(2-pyridylmethyl)amine, Y = NO_3, BF_4, or PF_6). Complex $\mathbf{1}(NO_3)_2$ can be derived from the reaction of a mononuclear complex $[Ni^{II}(Me_2\text{-tpa})(NO_3)](NO_3)$ ($\mathbf{2}(NO_3)$) with $NaBH_4$ in H_2O. Complex $\mathbf{2}(NO_3)$ was synthesized by the reaction of $Ni^{II}(NO_3)_2\cdot 6H_2O$ with Me_2-tpa in CH_3CN. The structure of **2** was characterized by X-ray analysis (Figure S1 in the Supporting Information), electrospray ionization mass spectrometry (ESI-MS; Figure S2), and IR spectroscopy (Figure S3).



Scheme 1. Proposed active-site structures of the active forms of [NiFe]H_2ase. a) Monohydride active form.[2,3c] X = vacant coordination site. b) Dihydride active form.[7]

We investigated the dinuclear complex $\mathbf{1}^{2+}$ by X-ray analysis and describe herein the first octahedral Ni^{II} dihydride complex reported to date (Figure 1).[8] Brown crystals of $\mathbf{1}(BF_4)_2$ suitable for X-ray diffraction were obtained from the substitution of NO_3^- in $\mathbf{1}(NO_3)_2$ to BF_4^- in CH_3OH at −40 °C. Complex **1** has a diamond $\{Ni^{II}_2(\mu\text{-H})_2\}$ core, in which the Ni atom adopts a distorted-octahedral coordination. The average bond lengths of Ni1–N2 and Ni1–N3 (2.189 Å) are longer than those of Ni1–N1 and Ni1–N4 (2.087 Å) because of the steric requirement of the 6-methyl groups bound to the pyridines. The distance of Ni1⋯Ni1* (2.6105(8) Å) is longer than that of a previously reported four-coordinated Ni^{II} dihydride complex (2.3939(6) Å).[8a]

Magnetic susceptibility measurements of $\mathbf{1}^{2+}$ in the solid state indicate the presence of an antiferromagnetic exchange interaction between two Ni^{II} centers. This interaction is also confirmed by ESR silence and signals in the diamagnetic region of ^1H NMR spectrum.

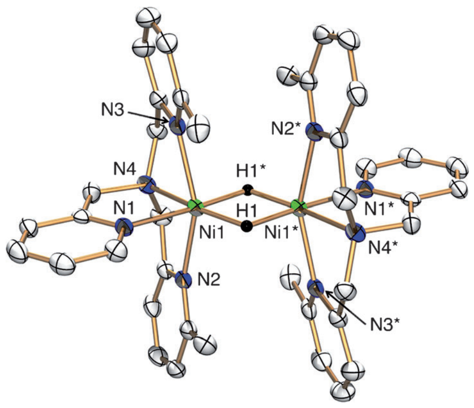


Figure 1. ORTEP drawing of $\mathbf{1}(BF_4)_2$ with ellipsoids at 50% probability. The counteranions, solvents (CH_3OH and H_2O), and hydrogen atoms of Me_2-tpa are omitted for clarity. Selected distances [Å]: Ni1⋯Ni1* 2.6105(8), Ni1–N1 2.075(3), Ni1–N2 2.191(4), Ni1–N3 2.186(4), Ni1–N4 2.098(4).

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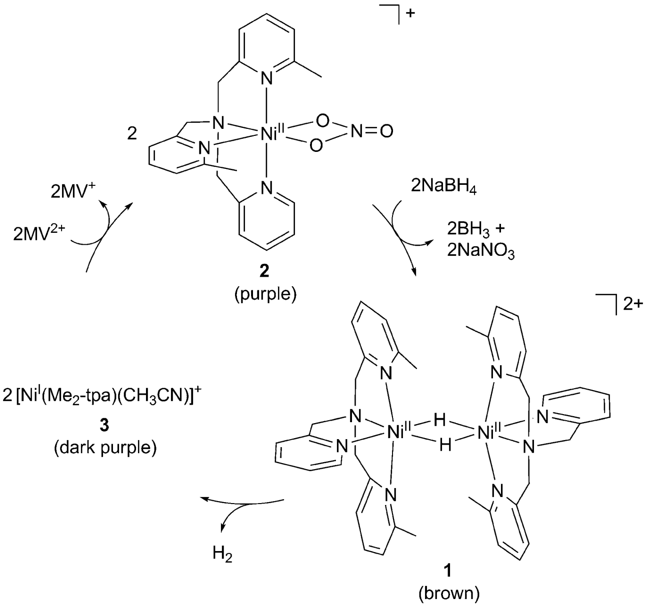
[**] This work was supported by the World Premier International Research Center Initiative (WPI Program), grants-in-aid: 18065017 (Chemistry of Concerto Catalysis), 19205009, and 23655053, the Global COE Program, "Science for Future Molecular Systems" from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) (Japan), and the Basic Research Programs CREST Type, "Development of the Foundation for Nano-Interface Technology" from JST (Japan).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201104918.

The positive-ion ESI mass spectrum of **1**$(PF_6)_2$ in CH_3OH shows a prominent signal at m/z 377.1 that corresponds to $\mathbf{1}^{2+}$, and a characteristic isotopic distribution that matches the calculated isotopic distribution (Figure S4 in the Supporting Information), thus indicating that $\mathbf{1}^{2+}$ has a dimeric structure in CH_3OH. To establish the origin of the hydrido ligands of $\mathbf{1}^{2+}$, $[Ni^{II}_2(Me_2\text{-tpa})_2(\mu\text{-}D)_2](PF_6)_2$ ($[D_2]$-**1**$(PF_6)_2$) was synthesized from $NaBD_4$. The mass spectrum showed the parent peak at m/z 378.1, thus demonstrating that the hydrido ligands originate from $NaBD_4$.

Of particular note is the observation that $\mathbf{1}^{2+}$ decomposes via reductive elimination to produce H_2 gas and leaves behind a low-valent Ni^I complex **3** in CH_3CN (Scheme 2). This decomposition is analogous to that proposed for the reductive elimination of H_2 from our NiRu model complex.[6]



Scheme 2. Proposed mechanism for the reaction cycle with the Ni-$(Me_2\text{-tpa})$ complexes **1**–**3**. The structures of **1** and **2** were determined by X-ray analysis. Complex **3** was characterized by ESR.

When $\mathbf{1}^{2+}$ was dissolved in CH_3CN under an N_2 atmosphere, the appearance of a strong absorption band around 590 nm, which corresponds to a gradual color change from brown to dark purple, was observed in the UV/Vis spectrum (Figure S5a, b in the Supporting Information). This color change is concurrent with the evolution of H_2 gas, where the yield of evolved H_2 is 94 % based on $\mathbf{1}^{2+}$, as determined by GC. Use of $[D_2]$-$\mathbf{1}^{2+}$ confirmed that the H_2 originated from the hydrido ligands. The dark-purple species **3** showed an ESR spectrum typical of Ni^I (Figure S6 in the Supporting Information). The ESR spectrum of a frozen solution of **3** in CH_3CN, measured at 7 K, exhibits a rhombic signal with g values of 2.28, 2.16, and 2.04, which are similar to those observed for some Ni^I complexes.[9]

The mechanism of reductive elimination was determined by means of products analysis of mixtures of $\mathbf{1}^{2+}$ and $[D_2]$-$\mathbf{1}^{2+}$. Mixing $\mathbf{1}^{2+}$ and $[D_2]$-$\mathbf{1}^{2+}$ in CH_3CN results in intermolecular H^+/D^+ exchange to produce $\mathbf{1}^{2+}$, $[Ni^{II}_2(Me_2\text{-tpa})_2(\mu\text{-}D)(\mu\text{-}H)]^{2+}$ ($[D]$-$\mathbf{1}^{2+}$), and $[D_2]$-$\mathbf{1}^{2+}$, as confirmed by ESI-MS. These three complexes can thereafter release the corresponding gas by means of intramolecular reductive elimination to give H_2, HD, and D_2, as determined by GC. The evidence for intramolecular reductive elimination was supported by the fact that decomposition of $\mathbf{1}^{2+}$ to $\mathbf{3}^{+}$ with evolution of H_2 followed first-order kinetics ($k_H = 1.0 \times 10^{-3}\ s^{-1}$; Figure S5c, d in the Supporting Information). Furthermore, the kinetic deuterium isotope effect value (k_H/k_D) was determined to be 2.4, which is consistent with that of reductive elimination of H_2 by the other metal hydride complex.[10]

We were also able to demonstrate that $\mathbf{3}^{+}$ acted as a reducing agent, in common with the reduced form of our NiRu H_2ase mimic. Complex $\mathbf{3}^{+}$ was able to reduce methyl viologen (MV^{2+}), the ferrocenium ion ($[Fe^{III}(C_5H_5)_2]^+$), and methylene blue. The quantitative reduction of MV^{2+} by $\mathbf{3}^{+}$ in CH_3CN under an N_2 atmosphere gave MV^+, as confirmed by UV/Vis spectroscopy (Figure S7). To the best of our knowledge, this is the first example of reduction of MV^{2+} by electrons from a metal hydride complex.[11] A cyclic voltammogram (CV) of $\mathbf{3}^{+}$ in CH_3CN showed a reversible redox couple at $E_{1/2} = -1.28$ V versus $Ag/AgNO_3$, which was assigned to the one-electron oxidation of the Ni^I to the Ni^{II} state (Figure S8).

Following these observations, we propose the following mechanism for the extraction of electrons from the nickel complexes (Scheme 2). In the first step, reaction of **2** with $NaBH_4$ produces the bis(μ-hydride) species $\mathbf{1}^{2+}$. This dihydride then undergoes reductive elimination to produce the low-valent Ni^I species $\mathbf{3}^{+}$. Complex $\mathbf{3}^{+}$ then reduces an electron acceptor to return to $\mathbf{2}^{+}$. We believe this is a mechanistic analogue for our NiRu H_2ase mimic and, by extension, for [NiFe]H_2ase itself.

In conclusion, we have synthesized a Ni^{II} dihydride complex as a model for the dihydride active form of our [NiFe]H_2ase mimic. While this complex is not a direct model for the core of hydrogenase itself, it mimics many of the essential structural and mechanistic aspects, that is, it involves a dihydride complex of an octahedral Ni center, which can evolve H_2 by reductive elimination. Rather than being the complete solution, this model provides us with a central piece of evidence and we can anticipate finally solving how [NiFe]H_2ase uses hydrogen as an energy source.

Experimental Section

$[Ni^{II}_2(Me_2\text{-tpa})_2(\mu\text{-}H)_2](PF_6)_2$ (**1**$(PF_6)_2$): Method A: $NaBH_4$ (38 mg, 1.0 mmol) was added to an aqueous solution (4.0 mL) of **2**(NO_3) (0.10 g, 0.20 mmol) to precipitate a brown powder of **1**$(NO_3)_2$, which was collected by filtration. A solution of NH_4PF_6 (164 mg, 1.0 mmol) in CH_3OH (4.0 mL) was added to a solution of **1**$(NO_3)_2$ in CH_3OH (20 mL) and the resulting mixture was allowed to stand for 3 days at −40 °C to afford crystals of **1**$(PF_6)_2$, which were collected by filtration and dried in vacuo (yield: 40 % based on **2**(NO_3)). Method B: $NaBH_4$ (38 mg, 1.0 mmol) was added to a solution of **2**(NO_3) (0.10 g, 0.20 mmol) in CH_3OH (20 mL) to give a brown solution, to which was added NH_4PF_6 (164 mg, 1.0 mmol) in CH_3OH (4.0 mL). The resulting solution was allowed to stand for 3 days at −40 °C to afford brown crystals of **1**$(PF_6)_2$, which were collected by filtration and dried in vacuo (yield: 50 % based on **2**(NO_3)). ESI-MS (CH_3OH): *m/z* (% in the range *m/z* 200–2000): 377.1 (100) [$\mathbf{1}^{2+}$], 899.3 (16) [{**1**(PF_6)}$^+$]; elemental analysis calcd (%) for $C_{40}H_{46}N_8F_{12}Ni_2P_2$ (**1**(PF_6)$_2$): C 45.92 H, 4.43; N 10.71; found: C 46.02, H 4.21, N 10.56.

[Ni^{II}(Me_2-tpa)(NO_3)](NO_3) (**2**(NO_3)): $Ni^{II}(NO_3)_2\cdot 6H_2O$ (0.87 g, 3.0 mmol) was added to a solution of Me_2-tpa (1.0 g, 3.1 mmol) in CH_3CN (80 mL) to give a purple solution, to which diethyl ether (200 mL) was added. The resulting solution was allowed to stand for 3 days to afford purple crystals of **2**(NO_3), which were collected by filtration and dried in vacuo (yield: 83 % based on $Ni^{II}(NO_3)_2\cdot 6H_2O$). ESI-MS ($CH_3CN$): *m/z* (% in the range *m/z* 200–2000): 438.1 (100) [$\mathbf{2}^+$]; FT-IR (KBr disk): $\tilde{\nu} = 2873–3077$ (m, aliphatic C−H), 1607 (s, aromatic C=C), 1576 (s, aromatic C=C), 1281–1496 cm^{-1} (m, NO_3^-); elemental analysis calcd (%) for $C_{19}H_{22}N_6NiO_7$ (**2**(NO_3)·H_2O): C 46.27, H 4.66, N 16.19; found: C 46.12, H 4.62, N 16.10.

[Ni^{I}(Me_2-tpa)(CH_3CN)](PF_6) (**3**(PF_6)): **1**(PF_6)$_2$ (10 mg, 9.6 μmol) was dissolved in CH_3CN (1.0 mL) and the resulting solution was allowed to stand for 3 h to give a dark-purple solution of **3**(PF_6) with evolution of H_2. The solvent of the dark purple-solution was removed under reduced pressure to leave a dark purple powder of **3**(PF_6), which is very air- and moisture-sensitive (yield: 99 % based on **1**(PF_6)$_2$). UV/Vis (CH_3CN): λ_{max} (ε) = 670 (3540), 347 (2640); elemental analysis calcd (%) for $C_{22}H_{25}N_5F_6NiP$ (**3**(PF_6)): C 46.92, H 4.47, N 12.44; found: C 46.82, H 4.11, N 12.36.

X-ray crystallographic analysis: Crystals of **1**(BF_4)$_2$ suitable for X-ray diffraction were prepared by substituting of the NO_3^- counterion in **1**(NO_3)$_2$ with BF_4^- by adding a solution of $NaBF_4$ in CH_3OH to a solution of **1**(NO_3)$_2$ in CH_3OH at −40 °C. Crystals of **2**(NO_3) suitable for X-ray diffraction were prepared by recrystallization from an CH_3CN/diethyl ether solution of **2**(NO_3). Measurements were made on a Rigaku/MSC Saturn CCD diffractometer with confocal monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.7107$ Å). Data were collected and processed using the CrystalClear program (Rigaku). All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation. CCDC 825133 (**1**(BF_4)$_2$) and 825134 (**2**(NO_3)) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: July 14, 2011

Keywords: bimetallic complexes · dihydrides · hydrogenases · nickel

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