INTRODUCTION

A hydrogen energy economy will require not only catalysts capable of \( \text{H}_2 \) oxidation but also those that can put it back together again. The design of these catalysts takes much inspiration from hydrogenase enzymes (H\text{2}ases) because they perform just such chemistry in nature (1–4). These enzymes come in three distinct varieties, as determined by the metals at their active sites: [NiFe] H\text{2}ases, [FeFe] H\text{2}ases, and [Fe] H\text{2}ases (Fig. 1) (5–7). The H\text{2}ases can be classified according to their reactivity differences, as well as their structural differences. [NiFe] H\text{2}ases are more useful for \( \text{H}_2 \) oxidation than evolution, while [FeFe] H\text{2}ases are more useful for \( \text{H}_2 \) evolution, and [Fe] H\text{2}ases can catalyze hydride (\( \text{H}^− \)) transfer (5). It is not surprising then that model studies have so far treated these three H\text{2}ases as different species.

[NiFe] H\text{2}ases have been of particular interest to us, owing to their potential application in fuel cells, and so we have produced a series of model compounds that successfully mimic H\text{2}ase chemical and catalytic behavior (8, 9). This series culminated in the production of a NiFe complex that is capable of performing electron (\( \text{e}^− \)) and \( \text{H}^− \) transfer from \( \text{H}_2 \) and \( \text{H}_2 \) evolution. This complex, [Ni\text{II}(Z)Fe\text{II}(MeCN)\{P(OEt)\text{3}\}\text{3}(\text{BPh}_4)\text{2} (Z = N,N'-diethyl-3,7-diazanonane-1,9-dithiolato, and Me, Et, and Ph indicate methyl, ethyl, and phenyl groups, respectively), is based on a central NiFe bimetallic core; flexible \( \mu \)-S bridges, which allow close approach of the two metal centers; a labile monodentate ligand (MeCN), which acts as a vacant site; and three P(OEt)\text{3} ligands, which can accept \( \pi \)-back donation from Fe (8). Despite its successes, however, this complex was only able to perform single turnover, meaning we still had some way to go.

Examining the three classes of H\text{2}ases more closely, we noticed the following relationships between the Fe ligands: In [NiFe] H\text{2}ase, the possible \( \text{H}_2 \) active site (X in Fig. 1) is between the Fe and Ni centers and trans to a CO ligand; in [FeFe] H\text{2}ase, the possible \( \text{H}_2 \) active site is both trans and cis to two CO ligands; and in [Fe] H\text{2}ase, the possible \( \text{H}_2 \) active site is cis to two CO ligands (5). It therefore occurred to us that creating this series of isomers of a [NiFe] H\text{2}ase model complex might provide important insights into the differing reactivity of the H\text{2}ases.

We settled on the following arrangement. First, the flexible \( \mu \)-S bridges and Ni environment remain. Second, the Fe labile ligand was changed from MeCN to Cl\text{−} because it is not only labile but also a weak Lewis base, meaning it is able to remove the proton generated during the reaction cycle. Last, to fix the coordination geometry as far as possible and maintain \( \pi \)-back donation, we settled on 1,2-bis(diphenylphosphino)ethane (L) and the CO ligand that determines, based on its relationship to the possible \( \text{H}_2 \) active site, the principle reactivity of the complex.

Here, we report that the different isomers of a [NiFe] H\text{2}ase model complex have the expected relationship in reactivity and their crystal structures. Furthermore, we report catalytic \( \text{e}^− \) transfer,
RESULTS AND DISCUSSION

Synthesis and structures of hydride isomers

Water-soluble Ni^{II}Fe^{II} complex [Ni^{II}(Z)Fe^{II}(Cl)(CO)(L)][Cl] ([1] (Cl)) was prepared from the reaction of [Ni^{II}(Z)] with [Fe^{II}(L)(Cl)] under a CO atmosphere and characterized by x-ray analysis (fig. S1); electrospray ionization–mass spectrometry (ESI-MS; fig. S2); proton nuclear magnetic resonance (^1H NMR; fig. S3), ^57Fe Mössbauer (fig. S4), infrared (IR; fig. S5), and electron spin resonance (ESR) spectroscopies; and elemental analysis. The Fe^{II} center is surrounded by L and CO as supporting ligands and Cl^- as a labile ligand.

An Oak Ridge thermal ellipsoid plot (ORTEP) drawing of 1 shows its framework based around the Ni(μ-S)Fe butterfly core, in which Ni and Fe atoms are tethered by the thiolato units of Z (fig. S1). The distance of Ni–Fe is 3.2685 Å (S), and the angles of Ni–S–Fe are 94.00(2)° and 92.92(2)°. Its structural parameters match well with those optimized by density functional theory (DFT) calculations (fig. S6 and tables S1 to S3). The Ni atom of 1 adopts a square planar geometry with the ligand Z, whereas the Fe atom of 1 adopts a distorted octahedral coordination, where it is surrounded by one CO, one Cl, one bidentate ligand L, and one [Ni^{II}(Z)]. The Ni^{II}Fe^{II} complex 1 is diamagnetic, which is evidenced by the appearance of ^1H NMR signals in the diamagnetic region (fig. S3) and the ESR silence at 128 K. The ^57Fe Mössbauer spectrum of 1 in the absence of a magnetic field shows an isomer shift of 0.12 mm s^{-1} and a quadrupole doublet of 0.46 mm s^{-1} (fig. S4), which is comparable to the low-spin Fe^{III} center in the P(OEt)3 ligands complex (10). The isomer shift of 1 is well reproduced by the DFT calculation at the meta-generalized gradient approximation (meta-GGA) level (table S4), which supports our assignment of the spin state and the oxidation state of 1.

Complex 1 reacted with H_2 (0.1 to 0.8 MPa) at room temperature in water to give three hydride isomers (Fig. 2): [Ni^{II}(Z)(μ-H)Fe^{II}(CO)(L)][Cl] ([2a][Cl]), [Ni^{II}(Z)Fe^{II}(CO)(L)(H)][Cl] ([2b][Cl]), and [Ni^{II}(Z)Fe^{III}(CO)(L)(H)][Cl] ([2c][Cl]). The reaction was followed by ^1H NMR spectroscopy (fig. S7) and ESI-MS (fig. S8). The ^1H NMR spectrum shows three hydride signals in the metal hydride region, which indicates formation of three structurally different hydride species (fig. S7). The three types of Ni^{II}Fe^{III} hydride complexes were characterized by x-ray analysis (Fig. 3) as well as ^1H NMR (figs. S9 to S11), IR (figs. S12 to S14), ^57Fe Mössbauer (figs. S15 to S17), and ESR spectroscopies. The hydride complexes 2a–2c are diamagnetic, as evidenced by the appearance of its ^1H NMR spectrum and the ESR silence at 128 K. The singlet spin states of 2a–2c are expected by the DFT calculations (table S2), in which the DFT-optimized structures (tables S5 to S7) match well with the x-ray structures (tables S8 to S10).

The conditions for crystallization of 2a, 2b, and 2c were optimized by changing solvent, temperature, and counter anion, resulting in the successful isolation of the three Ni^{II}Fe^{II} hydride complexes (fig. S18). The isolation of 2a was performed by crystallization at room temperature (fig. S18, red part), while 2b and 2c were isolated by crystallization at −30°C to prevent their isomerizations (fig. S18, blue and green parts). The ORTEP drawings reveal one bridging hydride species, 2a, and two terminal hydride species, 2b and 2c (fig. 3). The position of the hydride ligand of 2b is trans to the CO bond, analogous to its position in [FeFe] H_2 ase. The hydride ligand of 2c is cis to the CO ligand, analogous to its position in [FeFe] H_2 ase. The Fe–H bond distance [1.47(2) Å] of 2a is much smaller than the Ni–H bond distance [2.04(2) Å], suggesting that the hydride ligand is located on the Fe center (Fig. 3A), analogous to its positions in Ni^{II}Fe^{II} H_2 ase (11). This structural conformation is similar to the previous Ni^{II}Fe^{II} hydride complex [Fe–D: 1.577(17) Å, Ni–D: 2.18(4) Å determined by neutron scattering analysis] (8) but is different to our Ni^{II}Ru^{II} hydride complex [Ru–D: 1.676(8) Å, Ni–D: 1.859(7) Å determined by neutron scattering analysis] (9). The Ni–Fe distance [2.6877(4) Å] of 2a is shorter than those in 2b [3.0534(6) Å; Fig. 3B] and 2c [2.8467(6) Å; Fig. 3C], probably due to the hydride ligand weakly interacting with the Ni atom. This shortened Ni–Fe distance of 2a is related to the Ni–S–Fe angles [72.006(18)° and 72.969(17)°] being shorter in 2a than in 2b [85.68(3)° and 85.70(3)°] and 2c [78.05(3)° and 77.09(3)°]. The Ni–Fe distance [2.6877(4) Å] of 2a is similar to those in the previous Ni^{II}Fe^{II} complex [2.7930(6) Å] and the Ni^{II}Ru^{II} complex [2.739(3) Å]. The Ni–S–Fe angles [72.006(18)° and 72.969(17)°] of 2a are also similar to those of our previous Ni^{II}Fe^{II} complex [75.76(3)° and 75.82(3)°] and the Ni^{II}Ru^{II} complex [70.4(2)° and 70.7(3)°].

The spectroscopic and electrochemical properties of 2a, 2b, and 2c (Table 1) were obtained in organic solvents because the ion pair with PF_6^- or BAr_4^-, necessary for isolation, was insoluble in water. The ^1H NMR spectra of the isolated 2a, 2b, and 2c (figs. S9 to S11) show that the hydride ligands are observed at −2.76 parts per million (ppm) for 2a as a double doublet resonance (fig. S9), −3.83 ppm for 2b as a triplet resonance (fig. S10), and −16.62 ppm for 2c as a double doublet resonance (fig. S11), respectively. The patterns are derived from the hydride ligand coupling with the nuclear spin of two P atoms. The results indicate that the hydride ligand of 2c is the most hydridic (i.e., has the highest electron density) and that of 2a is the least hydridic.

H_2 evolution, and H^- transfer in water using the [NiFe] H_2 ase model complex.

Fig. 2. Formation of three isomers of the hydride complexes, 2a, 2b, and 2c, by the reaction of 1 with H_2 in water.
Fig. 3. ORTEP drawings of the solid-state structures of [2a](PF₆), [2b](BAr₄), and [2c](PF₆) with ellipsoids at the 50% probability levels. (A) An ORTEP drawing of [2a](PF₆). H sits between the Fe and Ni centers. The hydrogen atoms (except for the hydride ligand), solvents, and counter anion (PF₆⁻) are omitted for clarity. Selected interatomic distances (Å) and angles (°/deg): Ni1—H1, 2.04(2); Fe1—H1, 1.47(2); Ni1—Fe1, 2.6877(4); Fe1—P1, 2.1757(6); Fe1—P2, 2.2562(6); Fe1—S1, 2.3413(5); Fe1—S2, 2.3680(6); Fe1—C1, 1.739(2); Ni1—S1, 2.173(5); Ni1—S2, 2.1983(6); Ni1—N1, 1.9973(18); Ni1—N2, 1.9864(18); C1—O1, 1.156(3); Ni1—S1—Fe1, 72.969(17); Ni1—S2—Fe1, 72.006(18). (B) An ORTEP drawing of [2b](BAr₄). H is trans to the CO ligand. The hydrogen atoms (except for the hydride ligand), solvents, and counter anion (BAr₄⁻) are omitted for clarity. Selected interatomic distances (Å) and angles (°/deg): Fe1—H1, 1.57(3); Ni1—Fe1, 3.0534(6); Fe1—P1, 2.1935(8); Fe1—P2, 2.1772(8); Fe1—S1, 2.3318(8); Fe1—C1, 1.777(3); Ni1—S1, 2.1544(7); Ni1—N1, 1.985(2); Ni1—N2, 1.998(2); C1—O1, 1.161(4); Ni1—S1—Fe1, 85.68(3); Ni1—S2—Fe1, 85.70(3). (C) An ORTEP drawing of [2c](PF₆). H is cis to the CO ligand. The hydrogen atoms (except for the hydride ligand) and counter anion (PF₆⁻) are omitted for clarity. Selected interatomic distances (Å) and angles (°/deg): Fe1—H1, 1.47(2); Ni1···Fe1, 2.687(2); Ni1—S1, 2.3413(5); Fe1—S1, 2.3318(8); Fe1—C1, 1.777(3); Ni1—S1—Fe1, 72.969(17); Ni1—S2—Fe1, 72.006(18).
The electrochemical properties of 2a, 2b, and 2c were investigated by cyclic voltammetry in acetonitrile (fig. S19). The redox potentials \(E_{1/2}\) of Fe\(^{II}/Fe\(^{I}\) are observed at \(-2.040, -2.044,\) and \(-2.063\) V versus \(Fc^-/Fc\) (ferrocenium/ferrocene) for 2a, 2b, and 2c, respectively. These results suggest that the geometry of the 2c ligand set results in the highest electron-donating ability, while that of 2a has the least electron-donating ability.

The positive-ion ESI mass spectra of 2a, 2b, and 2c all show prominent signals at mass-to-charge ratio \((m/z)\) 789.1, 789.2, and 789.1, which correspond to [2a]\(^{+}\), [2b]\(^{+}\), and [2c]\(^{+}\), respectively. The spectra also showed characteristic isotopic distributions that match well with the calculated isotopic distributions (figs. S20 to S22). To establish the origins of the hydride ligands of 2a–2c, we synthesized D-labeled 2a–2c by using D\(_2\). The mass spectra show the signals at \(m/z\) 790.3, 790.3, and 790.2, demonstrating that the original hydride ligands are derived from H\(_2\).

The process of isomerization of the hydride complexes was observed by \(^1\)H NMR spectroscopy (figs. S23 to S25). The results indicate that 2b is the most thermally unstable, 2a is the most thermally stable, and 2c is metastable. The kinetic analysis of isomerization of three hydride complexes was conducted, which indicates that the conversion of 2c to 2a \((k_3 = 1.1 \times 10^{-4} \text{ s}^{-1})\) is the fastest, and the conversion of 2b to 2a \((k_1 = 5.0 \times 10^{-5} \text{ s}^{-1})\) is faster than that of 2b to 2c \((k_2 = 1.5 \times 10^{-5} \text{ s}^{-1})\) in acetone (fig. S23). The order of thermodynamic stability agrees with the DFT prediction (table S11).

**Reactivity of hydride isomers**

The three isomers were compared for reactivity in terms of yield over a given time period (Figs. 4 and 5, figs. S26 to S32, and Table 1). Specifically, e\(^-\) transfer, H\(_2\) evolution, and H\(^-\) transfer reactions of the isolated hydride complexes 2a, 2b, and 2c were performed in organic solvents for 1, 30, and 60 min using decamethylferrocenium ion \([\text{Fe}^{III}(\text{C}_5\text{Me}_5)_2]\)^\(^+\) as the e\(^-\) acceptor, aqueous acetic acid solution as the H\(^+\) source, and methylene blue \([\text{MB}]^+\) as the H\(^-\) acceptor, respectively. The processes were monitored with ultraviolet-visible (UV-vis) absorption spectroscopy and gas chromatography (GC). These results indicate not only that the position of the hydride ligand generates selective reactivity but also that the relative reactivity mimics the relative efficiencies of their natural counterparts, i.e., 2a is the most efficient isomer for e\(^-\) transfer, as for [NiFe] H\(_2\)ase; 2b is the most efficient isomer for H\(_2\) evolution, as for [FeFe] H\(_2\)ase; and 2c is the most efficient isomer for H\(^-\) transfer, as for [Fe] H\(_2\)ase.

The catalytic reaction of 1, free to convert between isomers, with H\(_2\) was studied in water. Control experiments, without 1 or H\(_2\), demonstrated that no reaction occurred in their absence. For the e\(^-\) transfer, \([\text{Fe}^{III}(\text{C}_5\text{Me}_5)_2]\)^\(^+\) was catalytically reduced to decamethylferrocene \([\text{Fe}^{II}(\text{C}_5\text{Me}_5)_2]\) by H\(_2\) (0.1 to 0.8 MPa), in the presence of catalytic amounts of 1, at 50°C for 12 hours in phosphate buffer solution at pH 6.0 (fig. S33) under catalytic conditions (1/[\text{Fe}^{III}(\text{C}_5\text{Me}_5)_2]\)^\(^+\) = 1/300). Significantly, this is the first example of catalytic e\(^-\) transfer to a substrate with a NiFe complex by using H\(_2\) as the e\(^-\) source in water. The turnover number (TON) was determined as 86 at pH 6.0 by using UV-vis absorption spectroscopy. For the H\(^+\) transfer, \([\text{MB}]^+\) was catalytically reduced to leucomethylene blue \([\text{MBH}]^-\) by H\(_2\) (0.1 to 0.8 MPa), in the presence of catalytic amounts of 1, at 30°C for 12 hours in phosphate buffer solution at pH 6.0 (1/[\text{MB}]^+ = 1/98). The TON was determined to be 23 (fig. S34) by using UV-vis absorption spectroscopy. Catalytic H\(_2\) evolution was observed using methyl viologen cation radical \([\text{MV}]^{+}\) as an e\(^-\) donor and acetate buffer solution (pH 4.0) as the H\(^-\) donor at 40°C in the presence of catalytic amounts of 1 (11 equivalents of \([\text{MV}]^{+}\)). The TON was determined as 2.67 by using GC. It was confirmed by GC that D\(_2\) was evolved from a CD\(_3\)COOD/D\(_2\)O solution of 1 and \([\text{MV}]^{+}\) at pH 4.0.

**CONCLUSION**

In conclusion, we have synthesized and characterized a [NiFe] H\(_2\)ase model complex, 1, that is capable of catalyzing e\(^-\) transfer, H\(_2\) evolution, and H\(^-\) transfer in water. Of particular note, 1 presents the first example of a NiFe complex that is capable of achieving catalytic e\(^-\) transfer from H\(_2\) in water. We have also isolated and characterized three hydride isomers, 2a, 2b, and 2c, and demonstrated that their relative catalytic efficiencies follow the same pattern as the efficiencies of their natural analogs. We believe that these studies will provide crucial insights into the mechanism of natural H\(_2\)ases.
MATERIALS AND METHODS
All experiments were carried out under an N₂ atmosphere using standard Schlenk techniques and a glovebox. Acetonitrile was distilled over CaH₂ under an N₂ atmosphere and dried with molecular sieves 3Å that was activated at 300°C for 6 hours under reduced pressure. H₂ (99.9999%), D₂ (99.5%), and CO (99.9%) were purchased from Sumitomo Seika Chemical Co. Ltd.; ultrapure water and methylene blue trihydrate (3,7-bis(dimethylamino)-5-phenothiazinium chloride trihydrate, [MB](Cl)·3H₂O) were purchased from FUJIFILM Corporation and used after purification by sublimation. [NiII(Z)(Cl)] (Z = 1,2-bis(diphenylphosphino)ethane), [NiII(Z)] (Z = 4,4′-bipyridinium dichloride, [MV](Cl)] was purchased from Tokyo Chemical Industry Co. Ltd.; NaBH₄ and benzaldehyde were purchased from Sigma-Aldrich; and CDCl₃, CD₂Cl₂, CD₃COCD₃, NaBD₄, D₂O, CD₃COOD, CD₃CN, and ¹³CO gas (99%) were added to the methanol/acetone solution of [FeII(L)(Cl)₂]. CO gas (99.9%) was added to the methanol solution (4 ml) of [NiII(Z)]. After stirring for 30 min, the solvents were removed by evaporation at −10°C to form dark red powders [yield: 92% based on [FeII(L)(Cl)]]. H NMR (400 MHz, in CDCl₃, referenced to TMS): δ 1.22 to 3.86 (m, 28H, N─C₆H₄─C₆H₄─C₆H₄─), 7.16 to 7.89 (m, 18H, P=C₆H₃), and 8.10 to 8.29 (m, 2H, P=C₆H₃). ³¹P NMR (202 MHz, in CDCl₃, referenced to external 85% H₃PO₄): δ 64.5 (s, 1P, Fe=P) and 72.9 (s, 1P, Fe=P). ESI-MS (in methanol): m/z 823.1 [[1]+, relative intensity (I) = 100% in the range of m/z 200 to 2000]. Anal. calcd for [1](Cl)·2H₂O: C₄₀H₈₀Cl₂Fe₅NiO₈P₂S₂: C, 51.97; H, 6.11; N, 3.03%. Found: C, 51.72; H, 6.24; N, 2.95%. IR (cm⁻¹): 1950 (νCO). UV-vis: 400 nm (ε = 4600 M⁻¹ cm⁻¹).

[NiII(Z)FeII(Cl)(13CO)(L)]([13CO-labeled 1](Cl))
¹¹CO-labeled complex [[¹³CO-labeled 1](Cl) was prepared by the same method as the synthesis of [1](Cl) except the use of ¹³CO instead of CO. ESI-MS (in methanol): m/z 824.3 [[¹³CO-labeled 1]+, I = 100% in the range of m/z 200 to 2000]. IR (ν(CO)): 1906 (ν13CO).

[NiII(Z)(μ-H)FeII(CO)(L)(PF₆)](2a)(PF₆) and [NiII(Z)(μ-H)FeII(CO)(L)(PF₆)](2b)(PF₆) were prepared under dark conditions. Method A: A 40 mM phosphate buffer solution (pH 7.0, 35 ml) of [1](Cl) (50 mg, 58 μmol) was stirred for 2 hours under an H₂ atmosphere (0.1 to 0.8 MPa) at room temperature. KPF₆ (16 mg, 87 μmol) was added to the resulting solution to afford red-purple precipitates, which were collected by filtration and dried in vacuo (yield of mixture of three isomers: 92% based on [1](Cl)). The red-purple precipitates were recrystallized in its acetone solution diffused by diethyl ether for 2 days at room temperature to yield the brown crystals, which were collected by filtration and dried in vacuo (yield: 66% based on [1](Cl)). Method B: A methanol solution (4 ml) of [1](Cl) (100 mg, 116 μmol) was added to NaBH₄ (100 mg, 2.64 mmol), and the resulting solution was kept standing until the H₂ bubble was diminished, to which KPF₆ (64 mg, 0.35 mmol) was added. Acetone (4 ml) was added to the suspension to dissolve remaining KPF₆, and the resulting solution diffused by diethyl ether was kept standing for 2 days at room temperature to form crystals, which were obtained and collected by filtration. Dichloromethane (15 ml) was added into the crystals, and the filtrate was collected by filtration to remove the residue. The solvent was removed under reduced pressure to afford the solid, which was recrystallized in acetone/methanol (1:1) solution diffused by diethyl ether for 2 days at room temperature. Brown crystals were collected by filtration and dried in vacuo (yield: 70% based on [1](Cl)). H NMR (400 MHz, in CD₃COCD₃/CDCl₃ (1:1), referenced to TMS): δ −2.76 [dd, 1H, Ni(H₂)] and 72.9 (s, 1P, Fe─P), −0.43 (d, 1H, S─CH₂─), 0.92 (t, 3H, N─CH₃─CH₃), 0.31 to 1.40, 1.78 to 1.99, 2.06 to 2.36, 2.45 to 2.57, 2.62 to 2.92, 3.04 to 3.73 (m, 2H, −CH₂─CH₂─), 2.72 to 7.63 (m, 18H, P=C₆H₃), and 8.19 to 8.25 (m, 2H, P=C₆H₃). ³¹P NMR (202 MHz, in CD₃COCD₃, referenced to external 85% H₃PO₄): δ 59.7 (s, 1P, Fe─P) and 95.3 (s, 1P, Fe=P). ESI-MS (in methanol): m/z 789.1 [[2a]+, I = 100% in the range of m/z 200 to 2000]. Anal. calcd for [2a](PF₆): C₃₈H₄₀Fe₂NiO₅P₂S₂: C, 48.79; H, 5.28; N, 2.99%. Found: C, 48.78; H, 5.38; N, 2.95%. IR (cm⁻¹): 1918 (νCO) and 1675 (ν(NO─Fe)). UV-vis: 410 nm (ε = 2940 M⁻¹ cm⁻¹).

[NiII(Z)FeII(CO)(L)(H)](2b)(PF₆) All procedures were conducted under dark conditions. A 40 mM phosphate buffer solution (pH 7.0, 35 ml) of [1](Cl) (50 mg, 58 μmol) was stirred for 2 hours under an H₂ atmosphere (0.1 to 0.8 MPa) at room temperature. KPF₆ (16 mg, 87 μmol) was added to the resulting...
solution to afford red-purple precipitates, which were collected by filtration and dried in vacuo. The red-purple precipitates were recrystallized in acetone/methanol (1:1) solution diffused by diethyl ether for 4 days at −30°C. The brown crystals were removed by decantation at −20°C, and the solvent was removed in vacuo to form the red-purple powders at low temperature of −20°C to prevent isomerization. The recrystallization was repeated for two to three times to remove 2a and 2c (yield: 54% based on [1](Cl)).

\[ \text{Anal. calcd for } [\text{Ni}^{II}(Z)\text{Fe}^{II}(CO)(L)(H)](PF_6) \] except the use of D_2 or NaBD_4 method as the synthesis of [D-labeled 2a](PF_6) and inorganic salts. The precipitates were removed by decantation, and the solvent was removed under reduced pressure. Dichloromethane (20 ml) was added into the residue, and the insoluble materials were removed by filtration. The solvent was removed under reduced pressure at low temperature. The residue (ca. 100 mg) was dissolved in acetone (1 ml), to which methanol (1 ml) was added. The resulting solution (2 ml) was diffused by cooled diethyl ether (20 ml) and was kept standing at −30°C for 2 days. Brown crystals (ca. 60 mg) were collected by filtration and were dissolved in acetone (6 ml). The acetone solution was evaporated, and the residue was dissolved in acetone (2 ml), to which methanol (1 ml) was added. The resulting solution (0.5 ml) was diffused by cooled diethyl ether (20 ml) and was kept standing at −30°C for 2 days. The brown solid was collected by filtration and dried in vacuo (yield: 7% based on [1](Cl)).

Method B: A methanol solution (15 ml) of [1](Cl) (200 mg, 232 \mu mol) was added to NaBH_4 (400 mg, 10.6 mmol) at room temperature. The resulting solution was kept standing until H_2 gas diminished and was added to KPF_6 (128 mg, 695 \mu mol). Acetone (7 ml) was added to the resulting suspension to dissolve remaining KPF_6. The resulting solution diffused by diethyl ether (90 ml) was kept standing at −30°C for 1 day to form [2a](PF_6) and inorganic salts. The precipitates were removed by decantation, and the solvent was removed under reduced pressure. Dichloromethane (20 ml) was added into the residue, and the insoluble materials were removed by filtration. The solvent was removed under reduced pressure at low temperature. The residue (ca. 100 mg) was dissolved in acetone (1 ml), to which methanol (1 ml) was added. The resulting solution (2 ml) was diffused by cooled diethyl ether (20 ml) and was kept standing at −30°C for 3 days. Brown crystals (ca. 60 mg) were collected by filtration and were dissolved in acetone (6 ml). The acetone solution was diffused by cooled diethyl ether (60 ml) and was kept standing at −30°C for 2 days. Brown crystals were removed by decantation, and the solvent was removed under reduced pressure at low temperature.

The residue (ca. 25 mg) was dissolved into acetone (1 ml), to which methanol (0.7 ml) was added. The resulting solution (1.7 ml) was diffused by cooled diethyl ether (20 ml) and was kept standing at −30°C for 2 days. Brown crystals were collected by filtration and were dissolved in acetone (6 ml). The acetone solution was diffused by cooled diethyl ether (60 ml) and was kept standing at −30°C for 2 days. Brown crystals were removed by decantation, and the solvent was removed under reduced pressure at low temperature.

The residue (ca. 100 mg) was dissolved in acetone (1 ml), to which methanol (1 ml) was added. The resulting solution (1.7 ml) was diffused by cooled diethyl ether (20 ml) and was kept standing at −30°C for 2 days. Brown crystals were collected by filtration and were dissolved in acetone (6 ml). The acetone solution was diffused by cooled diethyl ether (60 ml) and was kept standing at −30°C for 2 days. Brown crystals were removed by decantation, and the solvent was removed under reduced pressure at low temperature.

The residue (ca. 25 mg) was dissolved into acetone (1 ml), to which methanol (0.7 ml) was added. The resulting solution (1.7 ml) was diffused by cooled diethyl ether (20 ml) and was kept standing at −30°C for 2 days. Brown crystals were collected by filtration and were dissolved in acetone (6 ml). The acetone solution was diffused by cooled diethyl ether (60 ml) and was kept standing at −30°C for 2 days. Brown crystals were removed by decantation, and the solvent was removed under reduced pressure at low temperature.

The residue (ca. 100 mg) was dissolved in acetone (1 ml), to which methanol (1 ml) was added. The resulting solution (1.7 ml) was diffused by cooled diethyl ether (20 ml) and was kept standing at −30°C for 2 days. Brown crystals were collected by filtration and were dissolved in acetone (6 ml). The acetone solution was diffused by cooled diethyl ether (60 ml) and was kept standing at −30°C for 2 days. Brown crystals were removed by decantation, and the solvent was removed under reduced pressure at low temperature.

The residue (ca. 100 mg) was dissolved in acetone (1 ml), to which methanol (1 ml) was added. The resulting solution (1.7 ml) was diffused by cooled diethyl ether (20 ml) and was kept standing at −30°C for 2 days. Brown crystals were collected by filtration and were dissolved in acetone (6 ml). The acetone solution was diffused by cooled diethyl ether (60 ml) and was kept standing at −30°C for 2 days. Brown crystals were removed by decantation, and the solvent was removed under reduced pressure at low temperature.

The residue (ca. 100 mg) was dissolved in acetone (1 ml), to which methanol (1 ml) was added. The resulting solution (1.7 ml) was diffused by cooled diethyl ether (20 ml) and was kept standing at −30°C for 2 days. Brown crystals were collected by filtration and were dissolved in acetone (6 ml). The acetone solution was diffused by cooled diethyl ether (60 ml) and was kept standing at −30°C for 2 days. Brown crystals were removed by decantation, and the solvent was removed under reduced pressure at low temperature.

The residue (ca. 100 mg) was dissolved in acetone (1 ml), to which methanol (1 ml) was added. The resulting solution (1.7 ml) was diffused by cooled diethyl ether (20 ml) and was kept standing at −30°C for 2 days. Brown crystals were collected by filtration and were dissolved in acetone (6 ml). The acetone solution was diffused by cooled diethyl ether (60 ml) and was kept standing at −30°C for 2 days. Brown crystals were removed by decantation, and the solvent was removed under reduced pressure at low temperature.

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The residue (ca. 100 mg) was dissolved in acetone (1 ml), to which methanol (1 ml) was added. The resulting solution (1.7 ml) was diffused by cooled diethyl ether (20 ml) and was kept standing at −30°C for 2 days. Brown crystals were collected by filtration and were dissolved in acetone (6 ml). The acetone solution was diffused by cooled diethyl ether (60 ml) and was kept standing at −30°C for 2 days. Brown crystals were removed by decantation, and the solvent was removed under reduced pressure at low temperature.
D$_2$ instead of H$_2$. ESI-MS (in methanol): m/z 790.2 ([D-labeled 2c]$^+$, I = 100% in the range of m/z 200 to 2000). IR (cm$^{-1}$): 1886 (v(CO)) and 1414 (v(Fe-D)).

**H$_2$ activation by 1 in water to form three hydride isomers monitored by ESI-MS**

All procedures were conducted under dark conditions. A 40 mM phosphate buffer solution (pH 7.0, 10 ml) of [1](Cl) (1.2 mg, 1.4 µmol) was stirred for 2 hours under an H$_2$ atmosphere (0.1 MPa) at room temperature. A portion (200 µl) of the resulting aqueous solution was diluted by methanol (1 ml), which was analyzed by ESI-MS.

**H$_2$ activation by 1 in water to form three hydride isomers monitored by $^1$H NMR spectroscopy**

All procedures were conducted under dark conditions. A 40 mM phosphate buffer solution (pH 6.0, 35 ml) of [1](Cl) (50 mg, 58 µmol) was stirred for 4 hours under an H$_2$ atmosphere (0.8 MPa) at room temperature. KPF$_6$ (32 mg, 0.174 mmol) was added to the resulting solution to afford red-purple precipitates of [2a](PF$_6$), [2b](PF$_6$), and [2c](PF$_6$), which were collected by filtration and dried in vacuo. The precipitates (5 mg) were dissolved into CD$_3$COCD$_3$ (480 µl), which was analyzed by $^1$H NMR spectroscopy.

**Time profiles for the ratios of isomers 2a, 2b, and 2c monitored by $^1$H NMR spectroscopy**

Hydride complex [2a](PF$_6$), [2b](PF$_6$), or [2c](PF$_6$) (3.0 mg, 3.21 µmol) was dissolved into CD$_3$COCD$_3$ (480 µl), whose isomerization at room temperature was monitored by $^1$H NMR spectroscopy to follow each hydride peak. Kinetic analyses were conducted by least-square curve fittings based on the data and selected rate equations of figs. S23 and S25.

**[MV]$_2$(ZnCl$_4$)**

Zinc powder (50 mg, 0.76 mmol) was added to an aqueous solution of methyl viologen [1,1’-dimethyl-4,4’-bipyridinium dichloride, [MV](Cl)$_2$] (300 mg, 1.17 mmol). The resulting suspension was stirred for 15 min, and the insoluble materials were removed by filtration. The filtrate was added to a saturated NaCl aqueous solution (10 ml) to form purple precipitates, which were collected by filtration and dried in vacuo (yield: 43% based on [MV](Cl)$_2$). Anal. calc’d for [MV]$_2$(ZnCl$_4$)-1.2H$_2$O: C$_{24}$H$_{30}$Cl$_2$N$_2$O$_4$Zn: C, 47.94; H, 5.10; N, 9.32%. Found: C, 47.84; H, 4.89; N, 9.29%. The [MV]$^+$ was confirmed by UV-vis spectroscopy (19).

**[MB](OTf)**

Methylene blue trihydrate (3.7-bis(dimethylamino)-5-phenothiazinium chloride trihydrate, [MB](Cl)-3H$_2$O) (300 mg, 0.802 mmol) was dissolved into water (100 ml), and the insoluble materials were removed by filtration. The filtrate, sodium trifluoromethanesulfonate (414 mg, 2.41 mmol) was added. Dark blue solids were collected by filtration and dried under reduced pressure (yield: 68% based on [MB](Cl)-3H$_2$O). Anal. calc’d for [MB](OTf)·1.5H$_2$O: C$_{17}$H$_{23}$F$_3$N$_3$O$_5$S$_2$: C, 44.34; H, 4.60; N, 9.13%. Found: C, 44.36; H, 4.33; N, 9.11%.

Decamethylferrocenium nitrate ([Fe$^{III}$(C$_5$Me$_5$)$_2$](NO$_3$))

[Fe$^{III}$(C$_5$Me$_5$)$_2$](NO$_3$) was synthesized by using the modified literature method (17). Ag(NO$_3$) (161 mg, 0.948 mmol) in water (20 ml) was added to an acetonitrile (100 ml) solution of decamethylferrocene [Fe$^{III}$(C$_5$Me$_5$)$_2$] (311 mg, 0.953 mmol), and the resulting solution was stirred for 4 hours at room temperature. Gray precipitates were removed by filtration, and the filtrate was evaporated up to 10 ml. Insoluble materials were removed by filtration, and the solvent was removed from the filtrate under reduced pressure. Dichloromethane was added into the residue, and the insoluble materials were removed by filtration. The solvent was evaporated to obtain green powder (yield: 73% based on [Fe$^{III}$(C$_5$Me$_5$)$_2$]). Anal. calc’d for [Fe$^{III}$(C$_5$Me$_5$)$_2$](NO$_3$): C$_{20}$H$_{30}$FeNO$_3$: C, 61.86; H, 7.79; N, 3.61%. Found: C, 61.63; H, 7.82; N, 3.59%.

**Stoichiometric reduction of [Fe$^{III}$(C$_5$Me$_5$)$_2$]$^+$ with 2a, 2b, or 2c in the absence of H$_2$**

An acetonitrile solution (50 µl) of [2a](PF$_6$), [2b](PF$_6$), or [2c](PF$_6$) (1.0 mg, 1.07 µmol) was added to an acetonitrile solution (50 µl) of [Fe$^{III}$(C$_5$Me$_5$)$_2$](NO$_3$) (0.83 mg, 2.14 µmol). The resulting solution was kept standing for 1 min at room temperature, which results in the reduction of [Fe$^{III}$(C$_5$Me$_5$)$_2$]$.^+$ The resulting solution was diluted to 300 µl by acetonitrile, which was monitored by UV-vis absorption spectroscopy (absorption band at 778 nm derived from [Fe$^{III}$(C$_5$Me$_5$)$_2$]$^+$) to confirm the reduction of [Fe$^{III}$(C$_5$Me$_5$)$_2$]$^+$ to form [Fe$^{II}$(C$_5$Me$_5$)$_2$]. The yields of [Fe$^{III}$(C$_5$Me$_5$)$_2$] were determined as 57% for 2a, 27% for 2b, and 33% for 2c based on 2a, 2b, and 2c by UV-vis absorption spectroscopy (yield = (mol of [Fe$^{II}$(C$_5$Me$_5$)$_2$])/mol of 2a, 2b, or 2c)/2 × 100% because of two-electron donor of 2a, 2b, and 2c and one-electron acceptor of [Fe$^{III}$(C$_5$Me$_5$)$_2$]$^+$, respectively. No reduction of [Fe$^{III}$(C$_5$Me$_5$)$_2$]$^+$ occurred without 2a, 2b, or 2c, which was confirmed by UV-vis absorption spectroscopy.

**Stoichiometric H$_2$ evolution from the reaction of 2a, 2b, or 2c with proton of acetic acid**

In 2.0-ml vial capped with septum, an aqueous acetic acid solution (0.1 M, 300 µl) was added to an acetonitrile solution (330 µl) of [2a](PF$_6$), [2b](PF$_6$), or [2c](PF$_6$) (1.0 mg, 1.07 µmol), and the resulting solution was standing for 30 min at room temperature. The evolved H$_2$ in the gas phase of the vial was sampled by a gas-tight syringe and quantified by GC. The yields were determined to be 16% for 2a, 55% for 2b, and 9% for 2c based on [2a](PF$_6$), [2b](PF$_6$), and [2c](PF$_6$) (yield = (mol of H$_2$/mol of 2a, 2b, or 2c) × 100%), respectively. No H$_2$ was formed without 2a, 2b, 2c, or acetic acid, which was confirmed by GC as blank experiment.

**Stoichiometric reduction of [MB]$^+$ with 2a in the absence of H$_2$**

An acetonitrile solution (98 µl, 21.5 mM) of [MB](OTf) was added to [2a](PF$_6$) (0.98 mg, 1.05 µmol), and the resulting solution was kept standing for 60 min at room temperature, which results in the reduction of [MB]$^+$ to MBH. Dichloromethane (2.0 ml) was added to a portion (10 µl) of the solution, which was measured by UV-vis absorption spectroscopy (absorption band at 654 nm derived from [MB]$^+$). The yield of MBH was determined as 4% based on 2a by UV-vis absorption spectroscopy (yield = (mol of MBH/mol of 2a) × 100%). No reduction of [MB]$^+$ occurred without 2a, which was confirmed by UV-vis absorption spectroscopy as blank experiment.

**Stoichiometric reduction of [MB]$^+$ with 2b in the absence of H$_2$**

An acetonitrile solution (121 µl, 21.5 mM) of [MB](OTf) was added to [2b](PF$_6$) (1.21 mg, 1.29 µmol), and the resulting solution was...
kept standing for 60 min at room temperature, which results in the reduction of [MB]⁺ to MBH. Dichloromethane (2.0 mL) was added to a portion (10 μL) of the solution, which was measured by UV-vis absorption spectroscopy (absorption band at 654 nm derived from [MB]⁺). The yield of MBH was determined as 14% based on 2b by UV-vis absorption spectroscopy [yield = (mol of MBH/mol of 2b) × 100%]. No reduction of [MB]⁺ occurred without 2b, which was confirmed by UV-vis absorption spectroscopy as blank experiment.

Stoichiometric reduction of [MB]⁺ with 2c in the absence of H₂
An acetonitrile solution (111 μL, 21.5 mM) of [MB](OTf) was added to [2c](PF₆) (1.11 mg, 1.19 μmol), and the resulting solution was kept standing for 60 min at room temperature, which results in the reduction of [MB]⁺ to MBH. Dichloromethane (2.0 mL) was added to a portion (10 μL) of the solution, which was measured by UV-vis absorption spectroscopy (absorption band at 654 nm derived from [MB]⁺). The yield of MBH was determined as 31% based on 2c by UV-vis absorption spectroscopy [yield = (mol of MBH/mol of 2c) × 100%]. No reduction of [MB]⁺ occurred without 2c, which was confirmed by UV-vis absorption spectroscopy as blank experiment.

Time profiles for isomerization of 2b to 2a and 2c with or without proton from acetic acid monitored by ¹H NMR spectroscopy
Hydride complex [2b](PF₆) (2.0 mg, 2.14 μmol) was dissolved into the mixture of CD₃CN (160 μL) and aqueous acetic acid solution (0.8 M, 50 μL). The isomerization process at room temperature was monitored by ¹H NMR spectroscopy based on each hydride peak. A sealed capillary tube within benzaldehyde (10 mM) in CD₃CN as a standard reference material was set in an NMR tube. The isomerization process of 2b without acid-derived proton in CD₃CN/H₂O was monitored by ¹H NMR spectroscopy in the mixture solution of CD₃CN (80 μL) and H₂O (25 μL) containing [2b](PF₆) (1.0 mg, 1.07 μmol). On the basis of the data and selected rate equations of figs. S24 and S25, kinetic analyses were conducted by least-square curve fittings.

Time profiles for isomerization of 2c to 2a with or without [MB]⁺ monitored by ¹H NMR spectroscopy
An CD₃CN (200 μL) solution of [MB](OTf) (1.86 mg, 4.28 μmol) was added into the hydride complex [2c](PF₆) (2.0 mg, 2.14 μmol). The isomerization process at room temperature was monitored by ¹H NMR spectroscopy based on each hydride peak. A sealed capillary tube within benzaldehyde (10 mM) in CD₃CN as a standard reference material was set in an NMR tube. The isomerization process of 2c without [MB]⁺ in CD₃CN was monitored by ¹H NMR spectroscopy in the CD₃CN solution (100 μL) of [2c](PF₆) (1.0 mg, 1.07 μmol). The rate constants were determined by least-square curve fittings based on the data and selected rate equations of figs. S24 and S25.

Catalytic H₂ evolution with 1 in the presence of [MV]⁺ as an electron source
All procedures were conducted under dark conditions. In 3.0-ml vial capped with septum, a 100 mM acetate buffer solution (pH 4.0, 2.0 mL) of [1](Cl) (1.0 mg, 0.58 mM) and [MV]₂(ZnCl₄) (7.7 mg, 6.64 mM) was kept standing for 6 hours at 40°C. The evolved H₂ in the gas phase of the vial was sampled by a gas-tight syringe and quantified by GC. The TON of the H₂ evolution was determined as 2.67 by GC (TON = mol of H₂/mol of 1). No catalytic evolution of H₂ occurred without 1 or [MV]₂(ZnCl₄), which was confirmed by GC as blank experiment. It was confirmed that 1 was stable under the conducted conditions by ESI-MS.

D₂ evolution with 1 in the presence of [MV]⁺ as an electron source
All procedures were conducted under dark conditions. In 3.0-ml vial capped with septum, a CD₃COOD solution in D₂O (pD 4.0, 2.0 mL) of [1](Cl) (1.0 mg, 0.58 mM) and [MV]₂(ZnCl₄) (7.7 mg, 6.64 mM) was kept standing for 5 hours at 40°C. The evolved D₂ in the gas phase of the vial was sampled by a gas-tight syringe by GC. No D₂ was formed without 1 or [MV]₂(ZnCl₄), which was confirmed by GC as blank experiment.

Electrochemical analysis
Electrochemical measurements were conducted in an acetonitrile solution of each hydride complex [2a](PF₆), [2b](PF₆), or [2c](PF₆) (1.0 mM) with nBu₄NPF₆ (nBu = normal butyl) (0.1 M) as a supporting electrolyte on a BAS660A electrochemical analyzer using a carbon working electrode at room temperature. The cyclic voltammograms were collected using a scan rate of 100 mV s⁻¹. Potentials are referenced to a Fc⁺/Fc (ferrocenium/ferrocene) couple.

pH adjustment
pH values of aqueous solutions were adjusted by using acetate buffer solution for pH 4.0 and by using phosphate buffer solution for pH
6.0 to 7.0. In a pH range of 4.0 to 7.0, the pH values of the solutions were determined by a pH meter (IQ Scientific Instruments Inc., IQ200) equipped with a stainless steel micro pH probe (IQ Scientific Instruments Inc., PH15-SS). Values of pH were corrected by adding 0.4 to the observed pH values (pD = pH meter reading + 0.4) (20, 21).

**Computational details**

Geometry optimizations and potential energy calculations were performed for experimentally trapped four complexes, 1, 2a, 2b, and 2c, using the Gaussian 09 program (22). The experimentally determined oxidation states on the Ni and Fe species are both $^{2+}$ for all four complexes, indicating that the orbital occupancies are $d^8$ for Ni and $d^6$ for Fe, respectively. Therefore, we considered four spin multiplicities ($S = 0$ to $3$) to determine the ground-state spin multiplicity. All the structures were fully optimized without any constraints using the Becke-Perdew 1986 (BP86) (23, 24) functional with Grimme’s (D3) dispersion correction (25). The BP86 functional has been used to model biomimetic NiFe complexes (26–29). Furthermore, in our previously studied analogical NiFe complexes, the BP86 functional correctly described the ground-state spin multiplicity, while two hybrid functionals, B3LYP-D3 (D3-corrected Becke three-parameter Lee-Yang-Parr functional) (23, 30) and TPSSH (Tao-Perdew-Staroverov-Scuseria) (31), failed to predict (32, 33). Thus, the choice of BP86 functional is appropriate. The Stuttgart-Dresden (SDD) (34) basis set and the associated effective core potential were used for Ni and Fe, and the def2-SVP(split valence polarization) basis sets (35) were applied for other atoms (BS1). The potential energies were calculated at the level of BP86-D3/BS2 (BS2 = SDD for Ni and Fe, and def2-TZVP for the other atoms). Solvation effects were considered using the solvent model density implicit solvation model (36) with acetone as the solvent ($\epsilon = 20.493$) in both geometry optimizations and potential energy calculations. Vibrational frequency calculations were performed at the same level of theory to confirm minima and to obtain zero-point vibrational energy corrections. Thermal corrections were computed at the reaction conditions, that is, 298.15 K (room temperature) and 1 atm pressure. Integrals were evaluated using the pruned grid consisting of 99 radial shells and 590 angular points per shell. The wave function stability was checked for all complexes.

The $^{57}$Fe Mössbauer isomer shift and quadrupole splitting were calculated using the ORCA 4.0.1 program package (37). The isomer shift shows the linear relationship with electron density at the Fe nucleus (38).

Isomer shift $= \alpha(\rho - C) + \beta$

where $\rho$ is the electron density, and $\alpha$, $\beta$, and $C$ are parameters for the linear fits. The Mössbauer parameters were calculated based on the x-ray structures. We used the CP(PPP) basis set for Fe (39, 40), which performs reliably for Fe complexes (41), and the def2-TZVP basis set was used for the remaining atoms. As the hybrid density functionals give more reliable results, the TPSSH functional (31) was used. Increased integration accuracy (Grid7 for Fe and Grid6 for the reset of atoms in ORCA convention) was applied. The parameters used to drive the isomer shift, $\alpha$, $\beta$, and $C$, are $-0.376$, $4.130$, and $11810$, respectively (41).

**X-ray crystallographic analyses of 1, 2a, 2b, and 2c**

A single crystal of [1](Cl) was obtained from its methanol solution diffused with diethyl ether at $-30^\circ$C. A single crystal of [2a](PF$_6$) was obtained from its methanol/acetone (3:1) solution diffused with diethyl ether at room temperature. A single crystal of [2b](BAR$_4$) was obtained from its acetone solution diffused with diethyl ether at $-30^\circ$C. A single crystal of [2c](PF$_6$) was obtained from its methanol/acetone (3:1) solution diffused with diethyl ether at $-30^\circ$C.

Measurements were made on Rigaku XtaLAB P200 with confocal monochromated Mo-Kα radiation ($\lambda = 0.7107$ Å). Data were collected and processed using the CrystalClear program. All calculations were performed using the CrystalStructure crystallographic software package.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/6/24/eaaz8181/DC1

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Acknowledgments
Funding: This work was supported by JST CREST grant number JPMJCR18R2, Japan; JSPS KAKENHI grant numbers JP26000008 (Specially Promoted Research), JP18H02091, JP19K05503, and JP18K05297; and the World Premier International Research Center Initiative (WPI), Japan. Author contributions: S.O. conceived the project and wrote the manuscript. T.K., T.Y., K.M., R.Y., T.A., and M.K. performed experiments. T.M. and K.-S.Y. performed kinetic spectra measurements. Competing interests: The authors declare that they have no competing interests. Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors. Crystallographic data for (1)Cl·(2a)PF6, (2b)BF4, and (2c)PF6 have been deposited with the Cambridge Crystallographic Data Centre under reference numbers CCDC-1952766 (1), 1952767 (2a), 1952768 (2b), and 1952769 (2c), respectively.

Submitted 11 October 2019
Accepted 8 April 2020
Published 10 June 2020
10.1126/sciadv.aaz8181

Citation: S. Ogo, T. Kishima, T. Yatabe, K. Miyazawa, R. Yamasaki, T. Matsumoto, T. Ando, M. Kikkawa, M. Isegawa, K.-S. Yoon, S. Hayami, [NiFe], [FeFe], and [Fe] hydrogenase models from isomers. Sci. Adv. 6, eaaz8181 (2020).