SUPPLEMENTARY MATERIAL

[NiFe]-Hydrogenase synthetic models with redox-active ligands

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Figure S1. FT-IR spectrum ($\nu _{\text{CO}}$ region, CH$_2$Cl$_2$) of [1a(μ-H)]BF$_4$.

Figure S2. $^{31}$P{1H} NMR spectra (CD$_2$Cl$_2$, 202 MHz) of [1a(μ-H)]BF$_4$ recorded at room temperature (top) and at –28°C (bottom).
Figure S3. $^1$H NMR spectrum (CD$_2$Cl$_2$, 500 MHz) of [1a(μ-H)]BF$_4$. Resonances at 3.43 (Et$_2$O), 1.31 (pentane), 1.12 (Et$_2$O) and 0.89 ppm (pentane) are from impurities in the NMR solvent.

Figure S4. Positive ion ESI mass spectrum of [1a(μ-H)]BF$_4$. 
Brown single crystals of [1a(μ-H)]BF₄·CH₂Cl₂ formed upon slow diffusion of pentane vapor into a concentrated CH₂Cl₂ solution of [1a(μ-H)]BF₄. One crystal was subjected to X-ray diffraction at 173 K, its space group determined as monoclinic P2₁/c (Z = 4) with cell parameters: a 12.6528(6) Å, b 33.7738(18) Å, c 12.2942(6) Å, α 90°, β 90.373(4)°, γ 90°. While these preliminary data were of poor quality, they did confirm the atom connectivity within the complex. The Ni-Fe distance in [1a(μ-H)]⁺ (2.662 Å) is similar to that in the analogous triphosphine hydride [(dppe)Ni(pdt)HFe(CO)₂(PPh₃)]⁺ (2.643 Å), with the monophosphine occupying a basal coordination site trans to an S atom in both complexes. The H⁻ ligand was not resolved in the Fourier difference map. Rather, it was fixed at a distance from Fe₁ equivalent to that in the PPh₃ congener. Indirect evidence of the presence of H⁻ comes from the stereochemistry at the Fe₁ site: were the hydride not present, then the mppf ligand would likely occupy an apical position, as it does in the Ni(II)Fe(I) model complexes of the type [(dppe)Ni(pdt)Fe(CO)₂(PRAr₂)]⁺, including [2b]⁺. In this case, the π-accepting CO ligands are poised trans to the π-donating CO groups, no doubt a favorable situation. But this is not the case with [1a(μ-H)]⁺, in which mppf occupied a basal site, ceding its favorable apical position to CO, a ligand that prefers a strong donor trans to it, in this case H⁻. Lastly, it is noted that the bond distances are consistent with a Ni(II)(μ-H)Fe(II)Fe(II) description for this complex, in line with the CO stretching frequencies and the sharpness of the NMR data.

![Figure S5. X-ray structure of [1a(μ-H)]BF₄·CH₂Cl₂ with the H atoms, disordered BF₄⁻ anion and CH₂Cl₂ solvate molecule omitted for clarity. Disorder in the Cp ring and two Ph groups of the dppe ligand is also omitted for clarity. Selected distances (Å): Ni1-Fe1, 2.66; Ni1-P1, 2.17; Ni1-P2, 2.17; Ni1-S1, 2.21; Ni1-S2, 2.21; Fe1-S1, 2.31; Fe1-S2, 2.31; Fe1-H1, 1.49; Fe1-C30, 1.79; Fe1-C31, 1.78; Fe1-P3, 2.23; Fe2-C8(PPh₃(centroid), 1.64; Fe2-C3H₄PPh₃(centroid), 1.72.](image-url)
Figure S6. Cyclic voltammograms of [1α(μ-H)]BF₄ (1 mM) acquired in the presence of varying molar equivalents of CF₃CO₂H.

Figure S7. Analysis of the currents observed for reduction of [1α(μ-H)]BF₄ (1 mM). The quotient of the current in the presence ($i_c$) to that in the absence of the acid CF₃CO₂H ($i_p$) is plotted against the molar ratio of CF₃CO₂H to [1α(μ-H)]BF₄. At higher acid concentrations, the wave shifts to more negative potentials, in line with direct reduction of CF₃CO₂H at the glassy carbon electrode.

The turnover frequency $k$ for catalytic hydrogen evolution ($n = 2$) at a given scan rate $v$ and temperature $T$ can be determined using peak currents in the presence ($i_c$) and absence of acid ($i_p$). For catalysis at $E_{pc} = -1.37$ V (potential at $i_c/2 = E_{pc} = -1.33$ V):

$$\frac{i_c}{i_p} = \frac{n}{0.4463} \sqrt{\frac{RTk}{Fv}}$$

$$\frac{965 \mu A}{22.6 \mu A} = 2 \frac{0.4463}{\sqrt{(8.314 J K^{-1} mol^{-1})(298 K)(96485 \frac{C}{mol})(0.1 J C^{-1} s^{-1})}} \approx 350 \text{ s}^{-1}$$
Figure S8. FT-IR spectrum ($\nu_{\text{CO}}$ region, CH$_2$Cl$_2$) of [1a]BF$_4$.

Figure S9. Positive ion ESI mass spectrum of [1a]BF$_4$. 
Figure S10. Cyclic voltammogram of [1a]BF₄.

Figure S11: FT-IR spectrum (νCO region, CH₂Cl₂) of [1b]BF₄.
Figure S12: Positive ion ESI mass spectrum of [1b]BF₄⁻.

Figure S13: FT-IR spectrum ($\nu_{CO}$ region, CH₂Cl₂) of [1c]BF₄⁻.
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Figure S15. X-band EPR spectra of [1c]BF₄ in CH₂Cl₂/PhMe recorded at 110 K (top) and room temperature (bottom).

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Figure S17. FT-IR spectrum ($\nu_{\text{CO}}$ region, CH$_2$Cl$_2$) of [1c](BF$_4$)$_2$.

Figure S18. $^{31}$P {$^1$H} NMR spectrum (CD$_2$Cl$_2$, 202 MHz) of [1c](BF$_4$)$_2$. 
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Figure S23. Cyclic voltammogram of [2a]BF$_4$. 
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Figure S25. Positive ion ESI mass spectrum of [2b]BF$_4$. 
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Figure S27: FT-IR spectrum (νCO region, CH₂Cl₂) of [2c]BF₄.
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Figure S29. X-band EPR spectra of [2c]BF₄ in CH₂Cl₂/PhMe recorded at 110 K (top) and room temperature (bottom).

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Figure S34. Cyclic voltammogram of [3](BF₄)₂.