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# H<sub>2</sub> Evolution from a Thiolate-Bound Ni(III) Hydride

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Supporting Information Placeholder

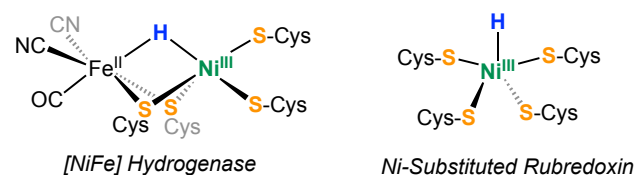
**ABSTRACT:** Terminal Ni<sup>III</sup> hydrides are proposed intermediates in proton reduction catalyzed by both molecular electrocatalysts and metalloenzymes, but well-defined examples of paramagnetic nickel hydride complexes are largely limited to bridging hydrides. Herein, we report the synthesis of an  $S = 1/2$ , terminally bound thiolate-Ni<sup>III</sup>-H complex. This species, and its terminal hydride ligand in particular, have been thoroughly characterized by vibrational and EPR techniques, including pulse EPR studies. Corresponding DFT calculations suggest appreciable spin leakage onto the thiolate ligand. The hyperfine coupling to the terminal hydride ligand of the thiolate-Ni<sup>III</sup>-H species is comparable to that of the hydride ligand proposed for the Ni-C hydrogenase intermediate (Ni<sup>III</sup>-H-Fe<sup>II</sup>). Upon warming, the featured thiolate-Ni<sup>III</sup>-H species undergoes bimolecular reductive elimination of H<sub>2</sub>. Associated kinetic studies are discussed and compared with a structurally related Fe<sup>III</sup>-H species that has been recently reported to also undergo bimolecular H-H coupling.

## INTRODUCTION

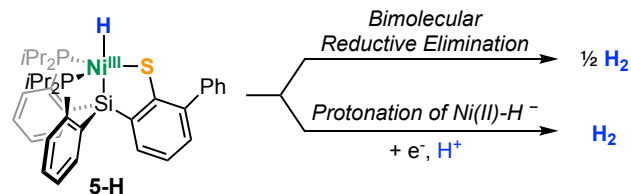
Hydrogen is a promising alternative to carbon-based fuel, and homogenous electrocatalysts for the H<sub>2</sub> evolution reaction (HER) have been scrutinized for possible practical applications and especially as well-defined systems for mechanistic studies.<sup>1</sup> Although metal hydrides may not be required intermediates of HER,<sup>2</sup> terminally bound Ni<sup>III</sup> hydride intermediates have been implicated in both stoichiometric<sup>3</sup> and catalytic<sup>4</sup> proton reduction<sup>5</sup> mediated by Ni-based systems. Additionally, paramagnetic Ni<sup>III</sup> hydride intermediates have been proposed in enzymatic H<sub>2</sub> evolution (Fig. 1, top). A bridging hydride has been identified in the  $S = 1/2$  [NiFe] hydrogenase intermediate (Ni<sup>III</sup>-H-Fe<sup>II</sup>) assigned as the Ni-C state,<sup>6</sup> and computational data suggest that the hydride is bound more tightly to Ni than to Fe (Ni-H: 1.61 Å, Fe-H: 1.72 Å).<sup>7,8</sup> Additionally, EPR data support an estimated Ni-H bond length of ~1.6 Å.<sup>6a</sup> The possible role of a [NiFe] hydrogenase state featuring a terminal Ni<sup>III</sup>-H has also been computationally investigated for the related case of

H<sub>2</sub> oxidation.<sup>9</sup> Furthermore, studies on Ni-substituted rubredoxin, a model enzyme for [NiFe] hydrogenase bearing a single Ni center in the active site, support the intermediacy of a terminal Ni<sup>III</sup>-H species in proton reduction catalysis.<sup>10</sup>

### Proposed Enzymatic Intermediates for H<sub>2</sub> Evolution



### This Work



**Figure 1.** (top) Proposed hydrogenase intermediates featuring a Ni<sup>III</sup> hydride motif (bottom) Accessible pathways for H<sub>2</sub> evolution from the Ni hydride complexes described in this work.

Owing to their posited role as intermediates in HER catalysis, well-characterized paramagnetic nickel hydride model complexes are needed for detailed study, but examples are lacking, whereas examples of related terminally bound Ni<sup>I/III</sup>-Me species are available.<sup>11</sup> For hydride cases, such species largely feature bridging hydrides bound to two metal centers (Ni-H-Ni),<sup>12</sup> three metal centers (Ni<sub>3</sub>-(H)),<sup>12d,13</sup> or as borohydride adducts (Ni-H-BR<sub>3</sub>).<sup>14</sup> Characterization data for *terminally* bound Ni<sup>I/III</sup> hydride complexes are scant. In previous work, irradiation of a matrix-isolated sample containing Ni(CO)<sub>4</sub> and HI yielded several EPR-active compounds, including a species assigned as H-Ni<sup>I</sup>(CO)<sub>4</sub>.<sup>15</sup> Related solid-state experiments employing Ni(CN)<sub>4</sub><sup>2-</sup> generated a [H-Ni(CN)<sub>n</sub>]<sup>x</sup> species as one of the EPR-active prod-

ucts.<sup>16</sup> Additionally, the Ni<sup>III</sup> hydride [(PS)<sub>3</sub>Ni<sup>III</sup>H][PPN] has been reported in solution by treatment of the analogous Ni<sup>III</sup>-O<sup>-</sup>Ph complex with pinacolborane.<sup>17,18</sup> Characterization data for this species was limited; in particular, the inferred hydride ligand was not confirmed by spectroscopic analysis (*vide infra*).

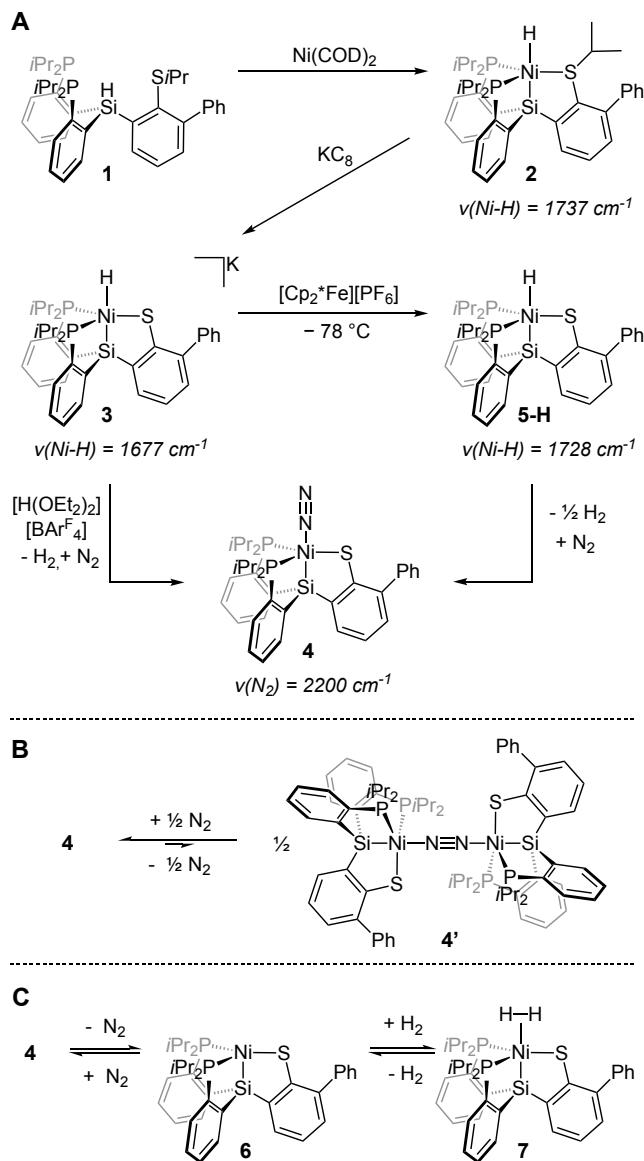
Herein, we generate and spectroscopically characterize a thiolate-supported, terminally-bound Ni<sup>III</sup>-H species at low temperature. Direct identification of the terminal hydride ligand is confirmed by both vibrational and pulse EPR data. Of note, bimolecular reductive elimination of H<sub>2</sub> proceeds upon warming this Ni<sup>III</sup>-H species, followed with N<sub>2</sub> binding to quantitatively generate a Ni<sup>II</sup>-N<sub>2</sub> product. Stoichiometric reactivity studies from the Ni<sup>II</sup>-H<sup>-</sup> and Ni<sup>III</sup>-H species featured herein demonstrate the viability of both a heterolytic and homolytic pathway for H<sub>2</sub> evolution.

## RESULTS AND DISCUSSION

### Synthesis and characterization of Ni precursors.

Following a recent study of a ferric Fe(H)(N<sub>2</sub>) species featuring a tetradentate bis(phosphine)(silyl)(thiolate) ligand (Scheme 1),<sup>19</sup> we targeted the generation of a trivalent Ni-H species supported by this ligand framework. Treatment of HSiP<sub>2</sub>S<sup>*i*Pr</sup> (**1**)<sup>19</sup> with Ni(COD)<sub>2</sub> (COD = 1,5-cyclooctadiene) yields a thioether-bound Ni(II) hydride, (SiP<sub>2</sub>S<sup>*i*Pr</sup>)Ni<sup>II</sup>H (**2**, Scheme 1a; see Fig. 2A for solid-state structure) with a Ni-H stretch at 1737 cm<sup>-1</sup> and a <sup>1</sup>H NMR hydride signal at -6.90 ppm (t, <sup>2</sup>J<sub>H,P</sub> = 46.3 Hz, in C<sub>6</sub>D<sub>6</sub>). Addition of KC<sub>8</sub> to **2** results in the reductive cleavage of the S-*i*Pr bond to furnish a thiolate-bound Ni(II) hydride, [(SiP<sub>2</sub>S)Ni<sup>II</sup>H]K (**3**, see Fig. 2B for solid-state structure; ν(Ni-H) at 1677 cm<sup>-1</sup>; hydridic resonance at -8.10 ppm (t, <sup>2</sup>J<sub>H,P</sub> = 43.0 Hz) in C<sub>6</sub>D<sub>6</sub>).

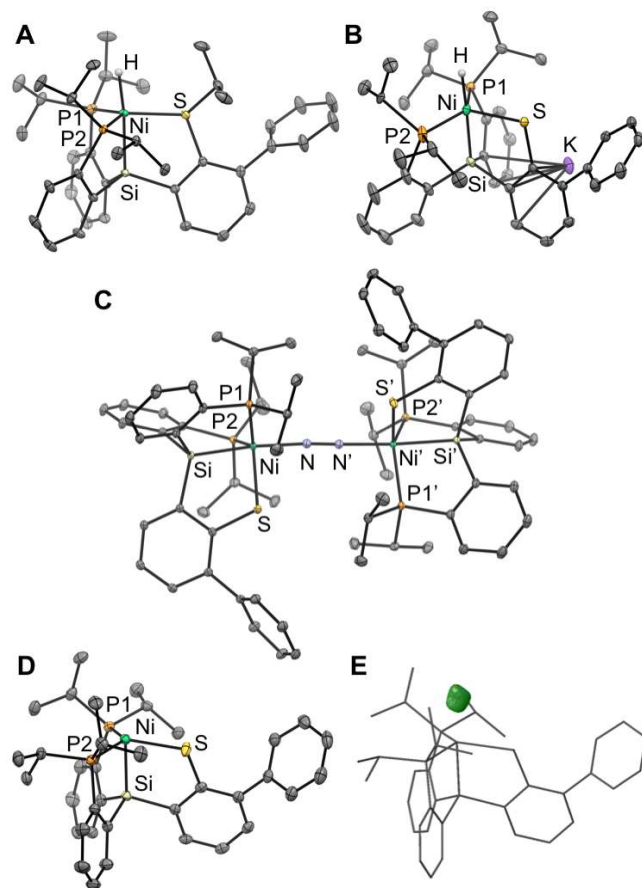
Protonation of hydride **3** with [H(OEt<sub>2</sub>)<sub>2</sub>][BAr<sup>F</sup><sub>4</sub>] under an N<sub>2</sub> atmosphere affords a nickel(II) complex, (SiP<sub>2</sub>S)Ni<sup>II</sup>(N<sub>2</sub>) (**4**), which crystallizes as the dimeric, dinitrogen-bridged species, [(SiP<sub>2</sub>S)Ni<sup>II</sup>]<sub>2</sub>(N<sub>2</sub>) (**4'**) (Scheme 1B). XRD data confirms the structure of **4'** (Fig. 2C; Table 1) and reveals an N-N bond length of 1.115(2) Å. Solid-state IR data of crystals of **4'** do not show an N<sub>2</sub> stretch, consistent with the inversion center gleaned in the solid-state structure. However, an intense N<sub>2</sub> stretch at 2200 cm<sup>-1</sup> is observed in solution under an N<sub>2</sub> atmosphere, indicating that **4'** dissociates to monomeric **4** in solution. Notably, a solid thin-film produced by concentration of a solution of **4** under an N<sub>2</sub> stream does not exhibit the N<sub>2</sub> stretch at 2200 cm<sup>-1</sup>, demonstrating that **4'** predominates upon concentration and is consistent with an equilibrium between **4** and **4'**.



**Scheme 1.** Synthesis and numbering scheme of compounds discussed herein.

A degassed solution of diamagnetic **4** bears NMR features distinct from those acquired under an N<sub>2</sub> atmosphere, intimating the loss of N<sub>2</sub> to generate a diamagnetic four-coordinate Ni species, (SiP<sub>2</sub>S)Ni<sup>II</sup> (**6**), under vacuum (Scheme 1C). Exposure of **6** to an atmosphere of H<sub>2</sub> yields the five-coordinate Ni<sup>II</sup>-H<sub>2</sub> complex, (SiP<sub>2</sub>S)Ni<sup>II</sup>(H<sub>2</sub>) (**7**). XRD data obtained on crystals grown under an atmosphere of H<sub>2</sub> are consistent with the assignment of **7** (Fig. 2D). In particular, the structural similarity between **7** and **4'** suggests that **7** bears an intact H-H fragment in the solid state, which disfavors alternative assignments as the Ni(H<sub>2</sub>) or NiH(SH) species in the solid state (Table 1). While the H<sub>2</sub> unit could not be reliably identified from the XRD data, positive residual electron density located trans to the silyl group is consistent with a bound H<sub>2</sub> ligand (Fig. 2E), as has been previously observed in XRD data of related H<sub>2</sub>-bound complexes.<sup>20</sup> Additionally, the HD analogue, (SiP<sub>2</sub>S)Ni<sup>II</sup>(HD), exhibits a <sup>1</sup>J<sub>HD</sub> of 35 Hz (toluene-*d*<sub>8</sub>,

–80 °C), indicative of an intact dihydrogen unit in solution.<sup>21</sup> Examples of Ni(H<sub>2</sub>) complexes are rare,<sup>22,23</sup> and **7** is distinct by virtue of the thiolate donor ligand; H<sub>2</sub> activation across a Ni-thiolate bond has been invoked elsewhere.<sup>24</sup>



**Figure 2.** X-ray structures of **2** (A), **3** (B), **4'** (C), **7** (D), and the residual positive electron density plot of **7** (isovalue: 0.78) (E). C-H hydrogen atoms and solvent molecules are omitted for clarity. Ellipsoids are depicted at 50% probability.

**Table 1.** Bond lengths of **4'** and **7**.

	$d(\text{Ni-S})$	$d(\text{Ni-P})$	$\angle(\text{P-Ni-P})$	$\angle(\text{P-Ni-S})$
<b>4'</b>	2.3320(6)	2.2405(5) 2.2627(6)	129.82(3)	109.69(2) 116.49(2)
<b>7</b>	2.3089(9)	2.208(1) 2.2246(9)	129.12(4)	108.62(4) 119.77(4)

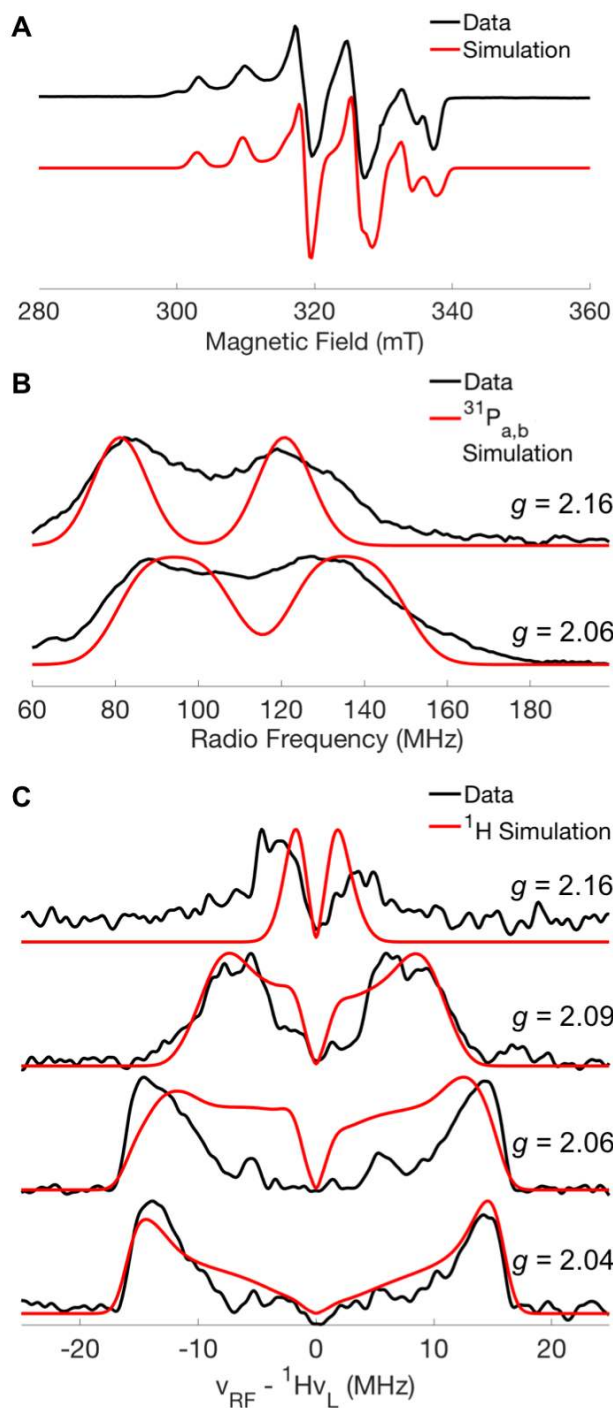
### Generation and characterization of a Ni<sup>III</sup>-H.

The cyclic voltammogram of **4** in THF reveals a reduction event at –2.33 V vs. Cp<sub>2</sub>Fe/Cp<sub>2</sub>Fe<sup>+</sup>, and **4** slowly catalyzes HER in the presence of PhOH as a weak acid source at a strongly cathodic potential (see Supporting Information for details).<sup>25</sup> Treatment of the Ni<sup>II</sup>-H<sup>–</sup> **3** with PhOH in THF results in quantitative generation of H<sub>2</sub> and (SiP<sub>2</sub>S)NiOph<sup>–</sup>, demonstrating a heterolytic

pathway for H-H bond formation within the system. For comparison, we also explored the viability of a homolytic pathway for H<sub>2</sub> generation from the corresponding Ni<sup>III</sup>-H species. Examples of M<sup>n/n+1</sup> hydride pairs that can access H<sub>2</sub> evolution via a homolytic pathway from one oxidation state and a heterolytic pathway from another are rare.<sup>27e,28a</sup> Whereas protonation of a metal hydride complex to release H<sub>2</sub> is commonly observed,<sup>1,26</sup> examples of bimolecular reductive elimination of H<sub>2</sub> from two well-defined M-H units is less precedent,<sup>19,27,28,29</sup> although such a pathway has been proposed in a number of HER electrocatalysts.<sup>1,4f,27e,30</sup>

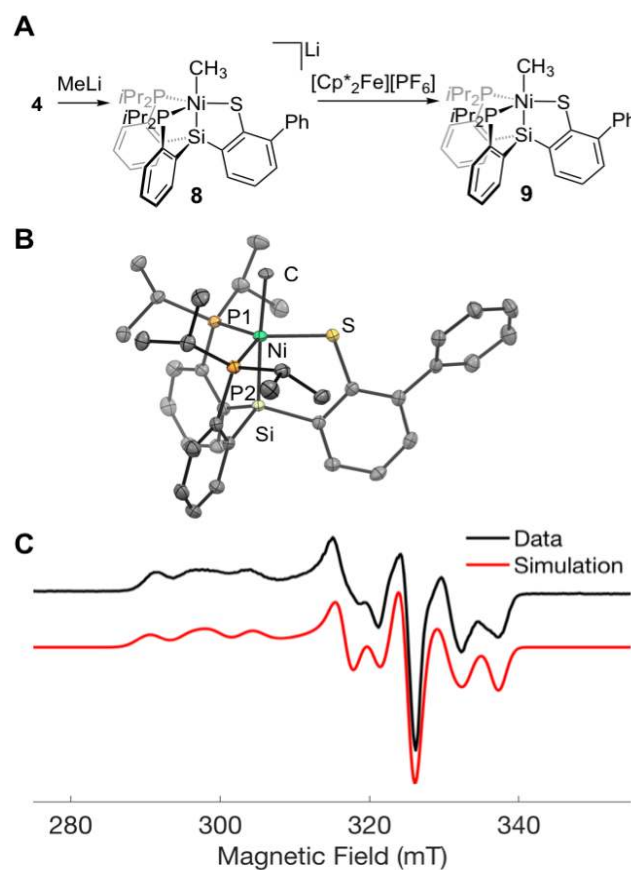
The cyclic voltammogram of the Ni<sup>II</sup>-H<sup>–</sup> species **3** exhibits a reversible feature at –1.26 V vs. Cp<sub>2</sub>Fe/Cp<sub>2</sub>Fe<sup>+</sup> in THF that corresponds to the formal Ni<sup>II/III</sup> couple, and chemical oxidation using [Cp\*<sub>2</sub>Fe][PF<sub>6</sub>] at –78 °C in THF yields a dark blue-green solution of the desired (SiP<sub>2</sub>S)Ni<sup>III</sup>H (**5-H**) species. Solutions of **5-H** are thermally sensitive (*vide infra*) and were therefore handled at low temperatures to obtain spectroscopic data. As expected for a Kramer's doublet species, **5-H** exhibits paramagnetically shifted peaks in its <sup>1</sup>H NMR spectrum (THF-*d*<sub>8</sub>, –40 °C). A characteristic terminal Ni-H stretch is observed in the IR spectrum at 1728 cm<sup>–1</sup> (THF solution, –78 °C) that vanishes upon deuteration via the analogue (SiP<sub>2</sub>S)Ni<sup>III</sup>D (**5-D**).<sup>31</sup> This Ni-H stretch is in good agreement with the DFT-predicted gas-phase value of 1720 cm<sup>–1</sup>.<sup>32</sup>

The 77 K X-band CW EPR spectrum of **5-H** confirms the expected  $S = \frac{1}{2}$  spin state (Fig. 3) and is simulated with a rhombic  $g$  tensor of  $\mathbf{g} = [2.166, 2.056, 2.039]$  and hyperfine coupling to two equivalent <sup>31</sup>P nuclei ( $\mathbf{A}(\text{}^{31}\text{P}\alpha) = \mathbf{A}(\text{}^{31}\text{P}\beta) = \pm[200, 210, 260]$  MHz) and a Ni-H nucleus ( $\mathbf{A}(\text{}^1\text{H}) = \pm[1.63, 1.63, 31.9]$  MHz; for **5-D**,  $\mathbf{A}(\text{}^2\text{H}) = \pm[0.25, 0.25, 4.9]$  MHz). These simulation parameters are consistent with Q-band <sup>1</sup>H, <sup>31</sup>P Davies ENDOR and <sup>2</sup>H HYSCORE data for **5-H** and **5-D** (see Supporting Information). Notably, the <sup>1</sup>H dipolar tensor ( $\mathbf{T}$ ) of **5-H** is axially symmetric ( $\mathbf{A}(\text{}^1\text{H}) = a_{\text{iso}} + \mathbf{T}$ ;  $\mathbf{T} = \pm[-10.1, -10.1, 20.2]$  MHz), as can be anticipated for a terminally bound metal hydride (M–H), whereas a rhombic dipolar tensor would instead be expected for an approximately symmetric bridging hydride (M–H–M).<sup>33</sup> By scaling the isotropic component of the <sup>1</sup>H hyperfine coupling tensor ( $|a_{\text{iso}}(\text{}^1\text{H})| = 11.7$  MHz) by the  $a_{\text{iso}}$  value for a hydrogen atom (1420 MHz),<sup>34</sup> spin density localized at the hydride is estimated as  $\pm 0.008 e^-$ . The DFT-optimized structure in the gas phase for **5-H** (M06l) predicts a Mulliken spin density of  $-0.005 e^-$  on the hydride, consistent with the experimental data.



**Figure 3.** (a) X-band CW EPR spectrum of **5-H** in 2-MeTHF with simulation. Simulation parameters:  $g = [2.166, 2.056, 2.039]$ ;  $A(^{31}P\alpha) = A(^{31}P\beta) = [200, 210, 260]$  MHz;  $A(^1H) = [1.6, 1.6, 31.9]$  MHz.; Acquisition parameters: MW frequency = 9.371 GHz; temperature = 77 K; MW power = 2 mW; modulation amplitude = 2 G; conversion time = 82 ms. (b) Field-dependent <sup>31</sup>P Q-band Davies ENDOR spectra of **5-D**. (c) Field-dependent Q-band Davies ENDOR <sup>1</sup>H minus <sup>2</sup>H difference spectra of **5-H** and **5-D**; difference spectra were smoothed using a 5-point Savitzky-Golay filter. ENDOR samples were prepared in 2-MeTHF, and spectra are simulated with the same g-values and hyperfine coupling as Fig. 3A. Experimental conditions for Fig. 3B,

**3C:** microwave frequency = 34.040 GHz; MW  $\pi$  pulse length = 80 ns; interpulse delay  $\tau = 400$  ns;  $\pi_{RF}$  pulse length = 15  $\mu$ s;  $T_{RF}$  delay = 2  $\mu$ s; shot repetition time (srt) = 2 ms; temperature = 12 K.



**Figure 4.** (A) Synthetic route to access compound **9**. (B) X-ray structure of **9**. Hydrogen atoms and disordered components are omitted for clarity. Ellipsoids are depicted at 50% probability. (C) X-band CW EPR spectrum of **9** in 2-MeTHF with simulation. Simulation parameters:  $g = [2.255, 2.073, 2.037]$ ;  $A(^{31}P\alpha) = [170, 133, 330]$  MHz;  $A(^{31}P\beta) = [260, 257, 130]$  MHz.; Acquisition parameters: MW frequency = 9.388 GHz; temperature = 77 K; MW power = 0.5 mW; modulation amplitude = 2 G; conversion time = 82 ms.

**Table 2.** Bond lengths of **5-H** (DFT) and **9** (XRD).

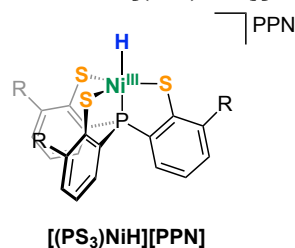
	$d(\text{Ni-X})$	$d(\text{Ni-S})$	$d(\text{Ni-P})_{\text{avg}}$	$d(\text{Ni-Si})$
<b>5-H</b>	1.55	2.22	2.25	2.25
<b>9</b>	2.047(5)	2.1972(6)	2.2428(6)	2.2541(6)

X = H (**5-H**), CH<sub>3</sub> (**9**)

Complex **5-H** could not be obtained in solid-state form due to its highly reactive nature. However, an analogous and more stable Ni<sup>III</sup>-Me species could be prepared, isolated, and crystallographically characterized. Accordingly, treatment of **4** with methyl lithium yields diamagnetic [(SiP<sub>2</sub>S)Ni<sup>III</sup>Me]Li (**8**), and its oxidation by [Cp\*<sub>2</sub>Fe][PF<sub>6</sub>] at -78 °C affords a dark blue-green solu-

tion of  $(\text{SiP}_2\text{S})\text{Ni}^{\text{III}}\text{Me}$  (**9**, Fig. 4).<sup>35</sup> Structural parameters for **9** compare favorably to the gas-phase, DFT-optimized parameters for **5-H** (Table 2). The 77 K X-band CW EPR spectrum exhibits a rhombic  $g$  tensor ( $\mathbf{g} = [2.255, 2.073, 2.037]$ ) and hyperfine coupling to two similar but distinct  $^{31}\text{P}$  nuclei ( $\mathbf{A}(^{31}\text{P}\alpha) = \pm[170, 133, 330]$  MHz;  $\mathbf{A}(^{31}\text{P}\beta) = \pm[260, 257, 130]$  MHz). Compared to that of **5-H**, the EPR spectrum of **9** exhibits slightly greater  $g$ -anisotropy and comparable  $|a_{\text{iso}}(^{31}\text{P})|$  values (**5-H**:  $|a_{\text{iso}}(^{31}\text{P}\alpha)| = |a_{\text{iso}}(^{31}\text{P}\beta)| = 223$  MHz; **9**:  $|a_{\text{iso}}(^{31}\text{P}\alpha)| = 211$  MHz,  $|a_{\text{iso}}(^{31}\text{P}\beta)| = 216$  MHz).

### EPR characterization of $[(\text{PS}_3)\text{NiH}][\text{PPN}]$ .



**Figure 5.** Structure of  $[(\text{PS}_3)\text{NiH}][\text{PPN}]$ . R =  $\text{SiMe}_3$ , PPN =  $(\text{Ph}_3\text{P})_2\text{N}^+$

Given the potential value for EPR data of model  $\text{Ni}^{\text{III}}\text{-H}$  species to guide reliable assignments of such intermediates in Ni-containing hydrogenases, we also undertook the generation of the previously reported  $[(\text{PS}_3)\text{NiH}][\text{PPN}]$  species<sup>17</sup> and the analogous nickel deuteride for related characterization by EPR techniques (Fig. 5). As noted above, previously reported vibrational and EPR data did not locate the presence of the terminal hydride moiety, though its chemical reactivity was consistent with such a formulation.

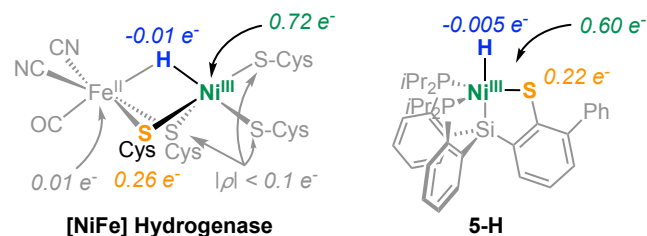
Through X-band HYSCORE experiments, the  $^2\text{H}$  hyperfine coupling for  $[(\text{PS}_3)\text{NiD}][\text{PPN}]$  could be detected:  $\mathbf{A}(^2\text{H}) = \pm[1.6, 9.3, 9.3]$  MHz (See Supporting Information for more details). Scaling  $\mathbf{A}(^2\text{H})$  by the ratio of the  $^1\text{H}/^2\text{H}$  gyromagnetic ratios ( $^1\text{H}\gamma/^2\text{H}\gamma = 6.514$ ) approximates a  $^1\text{H}$  hyperfine coupling of  $\mathbf{A}(^1\text{H}) = \pm[10.4, 60.6, 60.6]$  MHz in  $[(\text{PS}_3)\text{NiH}][\text{PPN}]$ , with  $|a_{\text{iso}}(^1\text{H})| = 43.9$  MHz and  $\mathbf{T} = \pm[-33.5, 16.7, 16.7]$  MHz. The  $|a_{\text{iso}}(^1\text{H})|$  value corresponds to approximately  $\pm 0.03$  e- of spin density localized on the hydride of  $[(\text{PS}_3)\text{NiH}][\text{PPN}]$ , in agreement with a DFT-estimated value of  $-0.05$  e- (gas phase, M06L; see SI). There hence appears to be greater spin delocalization onto the hydride ligand of  $[(\text{PS}_3)\text{NiH}][\text{PPN}]$  compared to **5-H**. This difference presumably arises from an increased metal-ligand covalency in **5-H**; a Mulliken spin density of  $0.73$  e- is calculated on Ni in  $[(\text{PS}_3)\text{NiH}][\text{PPN}]$ , compared to  $0.60$  e- in **5-H**.

### Comparison of $\text{Ni}^{\text{III}}\text{-H}$ species with the Ni-C hydrogenase state.

In both systems, spin delocalization onto the ligand framework likely stabilizes the  $\text{Ni}^{\text{III}}\text{-H}$  species. Consistent with this idea, DFT-calculated Mulliken spin densities (M06-L functional: def2tzvp [Ni] and def2svp [all other atoms] basis sets) suggests that there is considera-

ble spin leakage onto the supporting thiolate ligands of **5-H** ( $0.22$  e-) and  $[(\text{PS}_3)\text{NiH}][\text{PPN}]$  ( $0.07, 0.07, 0.16$  e-). For comparison, in the case of the Ni-C hydrogenase state, DFT calculations suggest the presence of significant spin delocalization onto one of the bridging cysteine groups (Fig. 6, BP86 functional),<sup>36</sup> with the majority of spin localized on Ni ( $0.72$  e-) rather than Fe ( $0.01$  e-). Additionally, a spin density of  $-0.01$  e- is calculated on the hydride bridging the Ni and Fe centers; experimental data support  $|a_{\text{iso}}(^1\text{H})| = ca. 11$  MHz for the hydride ligand in *D. gigas* hydrogenase,<sup>6c</sup> and a value of  $|a_{\text{iso}}(^1\text{H})| = 3.5$  MHz is measured for both *Ralstonia eutropha*<sup>6a</sup> and *D. vulgaris* Miyazaki F hydrogenases.<sup>6d</sup>

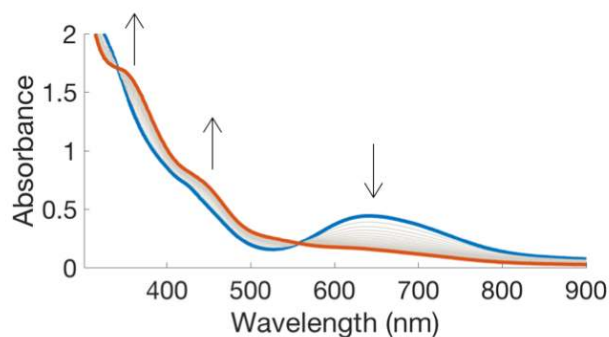
It has been noted that the  $|a_{\text{iso}}(^1\text{H})|$  value for the hydride of the Ni-C hydrogenase state is significantly smaller than that anticipated for a hydride covalently bound to Ni,<sup>6a,b,c</sup> given that  $|a_{\text{iso}}(^1\text{H})|$  for  $\text{H-Ni}^{\text{I}}(\text{CO})_3$  was reported to be  $293$  MHz,<sup>15,37</sup> and that of  $[\text{H-Ni}(\text{CN})_n]^x$  was estimated to be  $ca. 427$  MHz.<sup>16</sup> Assuming these assignments are reliable, one suggested explanation for the discrepancy is the presence of a proximal iron center in the Ni-C state, which may in turn perturb the spin distribution.<sup>6a</sup> However, it has been observed that the spin density on Fe is very low in the Ni-C state,<sup>38</sup> corroborated by DFT calculations.<sup>36</sup> In this context, it is therefore significant that **5-H** and  $[(\text{PS}_3)\text{NiH}][\text{PPN}]$  are measured to have  $|a_{\text{iso}}(^1\text{H})|$  values quite comparable to that of the Ni-C hydride. The data presented here demonstrates that hydrides covalently bound to a paramagnetic Ni center can exhibit comparatively small  $|a_{\text{iso}}(^1\text{H})|$  values. We attribute the small  $|a_{\text{iso}}(^1\text{H})|$  of these complexes in part to the significant spin delocalization onto the thiolate ligands of **5-H** and  $[(\text{PS}_3)\text{NiH}][\text{PPN}]$ , and by extension suggest that the bridging cysteine in the Ni-C state mitigates the magnitude of  $|a_{\text{iso}}(^1\text{H})|$  in the Ni-C state hydride, likely more so than the proximal Fe center.<sup>39</sup> Furthermore, although DFT-calculated EPR parameters for the hydrogenase structure featuring a bridging hydride between  $\text{Ni}^{\text{III}}$  and  $\text{Fe}^{\text{II}}$  provide a satisfactory fit to experimental data for the Ni-C state,<sup>6f,g</sup> the present study demonstrates that terminally bound  $\text{Ni}^{\text{III}}$  hydrides can bear  $|a_{\text{iso}}(^1\text{H})|$  values comparable to that measured for the Ni-C state.



**Figure 6.** Calculated Mulliken spin densities of the Ni-C hydrogenase state and **5-H**.

### Bimolecular $\text{H}_2$ release from thiolate- $\text{Ni}^{\text{III}}\text{-H}$ and comparison with $\text{H}_2$ release from thiolate- $\text{Fe}^{\text{III}}\text{-H}$ .

Our ability to generate and reliably characterize the  $\text{Ni}^{\text{III}}\text{-H}$  species **5-H** enabled us to evaluate its propensity to undergo a bimolecular homocoupling process to generate  $\text{H}_2$ .<sup>40</sup> Accordingly, dark blue-green solutions of **5-H** prepared *in situ* at  $-78\text{ }^\circ\text{C}$  quantitatively convert to orange solutions of **4** upon warming to  $25\text{ }^\circ\text{C}$  under  $\text{N}_2$ .  $\text{H}_2$  production was confirmed by GC analysis (98%). The decay of **5-H** to **4** monitored by UV-Vis spectroscopy exhibits isosbestic behavior and is second-order with respect to **5-H** (Fig. 7,  $k = 20\text{ M}^{-1}\cdot\text{min}^{-1}$  at  $25\text{ }^\circ\text{C}$ ). A kinetic isotope effect is observed ( $k_{\text{H}}/k_{\text{D}} = 1.6$  at  $25\text{ }^\circ\text{C}$ ), suggesting that the hydride ligand is present in the rate-determining transition state, and Eyring analysis reveals activation parameters of  $\Delta S^\ddagger = -30(7)\text{ cal}/(\text{mol}\cdot\text{K})$  and  $\Delta H^\ddagger = 9(2)\text{ kcal/mol}$ . The large and negative entropic activation term is consistent with an ordered rate-determining transition state, and these data support the bimolecular reductive elimination of  $\text{H}_2$  between two  $\text{Ni}^{\text{III}}\text{-H}$  fragments. Metal hydrides with BDFE(M-H) less than half the BDFE of  $\text{H}_2$  (BDFE(M-H) < *ca.* 52 kcal/mol in MeCN)<sup>41</sup> are thermodynamically favored to undergo bimolecular reductive elimination of  $\text{H}_2$  ( $2\text{ M-H} \rightarrow 2\text{ M} + \text{H}_2$ ). Under static vacuum, a THF solution of **5-H** reacts to form the vacant species **6**, which is consistent with the DFT-estimated Ni-H gas-phase BDFE of 57 kcal/mol (**5-H**  $\rightarrow$   $\text{H}^\cdot$  + **6**).

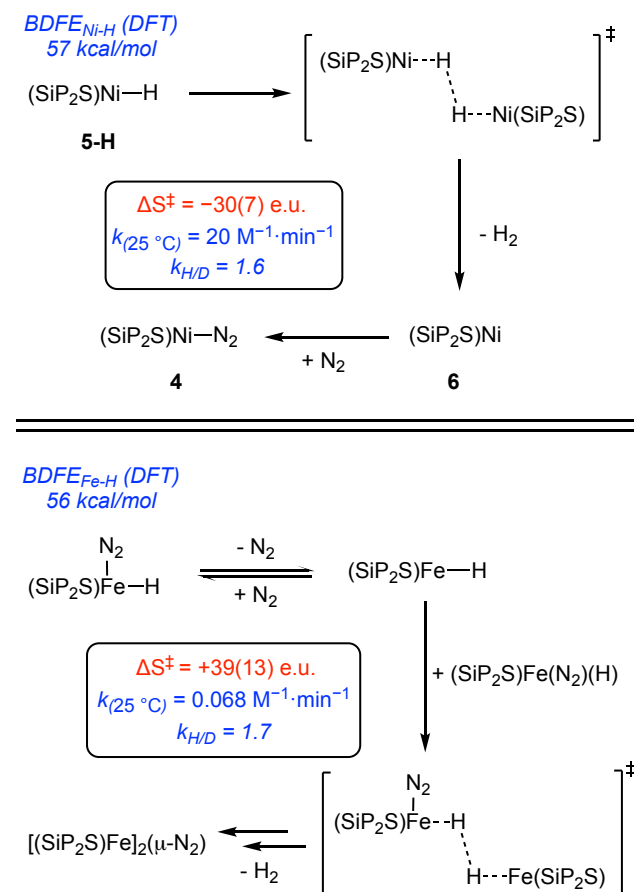


**Figure 7.** UV-Vis spectra depicting the decay of **5-H** to **4** at  $25\text{ }^\circ\text{C}$  in THF. Spectra collected in 20 min intervals.

A related  $S = \frac{1}{2}$  ferric hydride,  $(\text{SiP}_2\text{S})\text{Fe}^{\text{III}}(\text{H})(\text{N}_2)$ , that we have previously reported,<sup>19</sup> has a DFT-estimated gas phase Fe-H BDFE of 56 kcal/mol ( $(\text{SiP}_2\text{S})\text{Fe}(\text{H})(\text{N}_2) \rightarrow \text{H}^\cdot + (\text{SiP}_2\text{S})\text{Fe}(\text{N}_2)$ ) and also undergoes bimolecular reductive elimination of  $\text{H}_2$  upon warming to yield the  $\text{N}_2$ -bridged species  $[(\text{SiP}_2\text{S})\text{Fe}^{\text{II}}]_2(\text{N}_2)$ . Compared to the Ni system, there is a greater degree of spin delocalization onto the hydride ligand in the Fe system, evidenced by a greater  $|a_{\text{iso}}(^1\text{H})|$  value of 43 MHz. However, HER from the ferric hydride proceeds with a significantly smaller second-order rate constant at  $25\text{ }^\circ\text{C}$  compared to the Ni system ( $[\text{Fe}]$ :  $k = 0.068\text{ M}^{-1}\cdot\text{min}^{-1}$ , Scheme 2). Additionally, the bimolecular transformation of the ferric hydride bears a large and positive  $\Delta S^\ddagger$  of 39(13) cal/(mol·K) that we hypothesized to arise from  $\text{N}_2$  dissociation prior to H-H bond formation (e.g.  $\{\text{N}_2(\text{g}) +$

$[\text{Fe}^{\text{III}}]\text{-H}\cdots\text{H}-[\text{Fe}^{\text{III}}(\text{N}_2)]\}^\ddagger$ ). Such a scenario contrasts with the negative  $\Delta S^\ddagger$  determined for the present Ni system, which is consistent with an ordered rate-determining transition state (e.g.  $\{[\text{Ni}^{\text{III}}]\text{-H}\cdots\text{H}-[\text{Ni}^{\text{III}}]\}^\ddagger$ ).

The unobserved,  $\text{N}_2$ -dissociated ferric hydride  $(\text{SiP}_2\text{S})\text{Fe}^{\text{III}}(\text{H})$  would be an electron-deficient  $15\text{ e}^-$  species, favoring  $\text{N}_2$  binding to yield a  $17\text{ e}^-$  species  $(\text{SiP}_2\text{S})\text{Fe}^{\text{III}}(\text{H})(\text{N}_2)$ . In contrast, the Ni(III) hydride **5-H** is a  $17\text{ e}^-$  species, and  $\text{N}_2$  binding to form the  $19\text{ e}^-$  species  $(\text{SiP}_2\text{S})\text{Ni}^{\text{III}}(\text{H})(\text{N}_2)$  is thus disfavored. Pre-dissociation of  $\text{N}_2$  hence does not play a role in the  $\text{H}_2$  evolution chemistry of the Ni system, whereas it does in the Fe system. This is likely a significant factor in the dramatically enhanced rate of  $\text{H}_2$  formation in the Ni system compared to Fe. Additionally, because the terminal product is an  $\text{N}_2$ -bound species, thermodynamic stabilization afforded by  $\text{N}_2$  binding may also contribute to the relative rates of  $\text{H}_2$  elimination.



**Scheme 2.** Comparison of **5-H** and  $(\text{SiP}_2\text{S})\text{Fe}(\text{H})(\text{N}_2)$ , which both undergo bimolecular reductive elimination of  $\text{H}_2$  upon warming but with different rates and activation parameters in accord with the presented pathways. Gas-phase BDFEs were calculated with the M06-L functional (def2tzvp [Fe or Ni], def2svp [all other atoms]).

## CONCLUSION

In closing, we have reported the synthesis and spectroscopic characterization of an unusual  $S = 1/2$ , terminal  $\text{Ni}^{\text{III}}\text{-H}$  species, **5-H**, and its propensity to undergo homolytic bimolecular H-H coupling to release  $\text{H}_2$ . Heterolytic  $\text{H}_2$  evolution via protonation of its 1-electron reduced state,  $\text{Ni}^{\text{II}}\text{-H}^-$ , has also been demonstrated. For the  $\text{Ni}^{\text{III}}\text{-H}$  of most interest, the sulfur donor bears a considerable amount of spin density ( $0.22 e^-$ ) based on DFT calculations, stabilizing the system and allowing for the first time direct measurement of salient spectroscopic parameters, including a terminal Ni-H vibration ( $1728 \text{ cm}^{-1}$  in THF) and hyperfine coupling to the terminal hydride ligand ( $|a_{\text{iso}}(^1\text{H})| = 11.7 \text{ MHz}$ ), as detected via pulse EPR studies. Importantly, this isotropic hyperfine coupling value is similar to that of the hydride ligand in the Ni-C hydrogenase state.<sup>6a,c,d</sup> In contrast, significantly larger  $|a_{\text{iso}}(^1\text{H})|$  values, on the order of  $10^2 \text{ MHz}$ , were reported for  $\text{H-Ni}^{\text{I}}(\text{CO})_4$ <sup>15</sup> and  $[\text{H-Ni}(\text{CN})_n]^x$ <sup>16</sup> (via generation and detection in a solid matrix), the only previous examples of terminal Ni-H species with reported  $|a_{\text{iso}}(^1\text{H})|$  values.

The discrepancy between the significantly smaller  $|a_{\text{iso}}(^1\text{H})|$  measured for the assigned Ni-H-Fe moiety of the Ni-C hydrogenase state, compared to previously reported paramagnetic nickel hydride species, has been highlighted previously.<sup>6a,b,c</sup> The EPR data for the well-defined  $\text{Ni}^{\text{III}}\text{-H}$  species featured herein demonstrates that smaller  $|a_{\text{iso}}(^1\text{H})|$  values are compatible with a nickel hydride ligand assignment, especially when covalently bound to a spin active nickel center with one (or more) sulfur donors, as is suggested for the Ni-C hydrogenase state. Thus, the  $\text{Ni}^{\text{III}}\text{-H}$  species reported here, as well as related structures in future studies, can provide valuable platforms for constraining spectroscopic assignments in enzymatic systems and identifying specific reactivity patterns, including H-H bond formation to generate  $\text{H}_2$ .

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at <http://pubs.acs.org>.

Experimental procedures and compound characterization data (PDF)

X-ray data (CIF)

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## Notes

The authors declare no competing financial interests.

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1 the Ni-C hydrogenase state, which is measured to have a hydride  
2  $|a_{\text{iso}}(^1\text{H})|$  value of comparable magnitude as **5-H**.

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## TOC Graphic

