

Supporting Information for

## Synthesis of Iron Hydride Complexes Relevant to Hydrogen Isotope Exchange in Pharmaceuticals.

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## Experimental Section

**I. General Considerations.** All air- and moisture-sensitive manipulations were carried out using standard vacuum line, Schlenk, and cannula techniques or in an MBraun inert atmosphere drybox containing an atmosphere of purified nitrogen. Benzene- $d_6$  was purchased from Cambridge Isotope Laboratories and dried over sodium and stored over 4 Å molecular sieves. p-Xylene- $d_{10}$  was purchased from Aldrich, degassed with three freeze-pump-thaw cycles, and stored over 4 Å molecular sieves for at least 24 hours prior to use. THF- $d_8$  was also purchased from CIL, dried over sodium/benzophenone and freshly distilled before use. All other solvents for air- and moisture-sensitive materials were initially dried and deoxygenated using literature procedures.<sup>1</sup> The iron dinitrogen complex,  $(H_4\text{-}^{iPr}CNC)Fe(N_2)_2$  was prepared as described previously.<sup>2</sup>

$^1H$  NMR spectra were recorded on Bruker AVANCE 300 and Bruker AVANCE 500 spectrometers operating at 300.13 and 500.62 MHz, respectively. All  $^{13}C$  NMR spectra were recorded on a Bruker AVANCE 500 spectrometer equipped with a DCH cryoprobe optimized for  $^{13}C$  detection operating at 125.893 MHz. All chemical shifts are reported relative to  $SiMe_4$  using the  $^1H$  (residual) and  $^{13}C$  chemical shifts of the solvent as a secondary standard. All NMR spectra were collected at 25 °C unless otherwise specified.  $T_1$ (min) measurements were performed on a Varian Inova 400 operating at 399.78 MHz. All NMR spectra were recorded at 25 °C unless otherwise noted.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox, transferred to a nylon loop and then quickly transferred to the goniometer head. A Bruker APEX2 Duo diffractometer equipped with molybdenum and copper X-ray tubes ( $\lambda = 0.71073$  and  $1.54178$  Å, respectively) was used to collect data for  $(H_4\text{-}^{iPr}CNC)Fe(N_2)_2$  (Mo source),  $(H_4\text{-}^{iPr}CNC)FeH_4$  (Mo source) and  $(H_4\text{-}^{iPr}CNC)FeH_2(N_2)$  (Cu

source). The space group was identified and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SIR92) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures.

The toluene solution, zero-field  $^{57}\text{Fe}$  Mössbauer spectrum of  $(\text{H}_4\text{-}^{\text{iPr}}\text{CNC})\text{FeH}_4$  was recorded on a SEE Co. Mössbauer spectrometer (MS4) at 80 K in constant acceleration mode.  $^{57}\text{Co}/\text{Rh}$  was used as the radiation source. WMOSS software was used for the quantitative evaluation of the spectral parameters (least-squares fitting to Lorentzian peaks). The temperature of the sample was controlled by a Janis Research Co. CCS-850 He/N<sub>2</sub> cryostat within an accuracy of 0.3 K. Isomer shifts were determined relative to  $\alpha$ -iron at 298 K. The sample was prepared by exposing a saturated toluene solution of  $(\text{H}_4\text{-}^{\text{iPr}}\text{CNC})\text{Fe}(\text{N}_2)_2$  to 1 atm of H<sub>2</sub> for 36 h. During this time, the head space was removed and replenished twice with a fresh atmosphere of dihydrogen. The solution was then frozen in liquid nitrogen for analysis.

**Characterization of  $(\text{H}_4\text{-}^{\text{iPr}}\text{CNC})\text{Fe}(\text{H})_2(\text{N}_2)$ .** A 20 mL scintillation vial was charged with 0.030 g (0.046 mmol) of  $(\text{H}_4\text{-}^{\text{iPr}}\text{CNC})\text{Fe}(\text{N}_2)_2$ , 2 mL of pentane and a magnetic stir bar. The resulting mixture was stirred at room temperature for 5 minutes. The supernatant was filtered through a thin pad of celite and transferred into a thick-walled glass vessel equipped with a Teflon stopcock. The vessel was sealed and then transferred out of the drybox and attached to a high-vacuum manifold. The contents of the vessel were frozen in liquid nitrogen and the vessel evacuated. At 23 °C, 1 atm of H<sub>2</sub> was admitted and the reaction mixture allowed to stand for approximately 5 days over which time orange purple crystals formed. The crystals were collected (submerged under polyisobutylene oil) under an atmosphere of argon. Exposure of the compound to an N<sub>2</sub> atmosphere

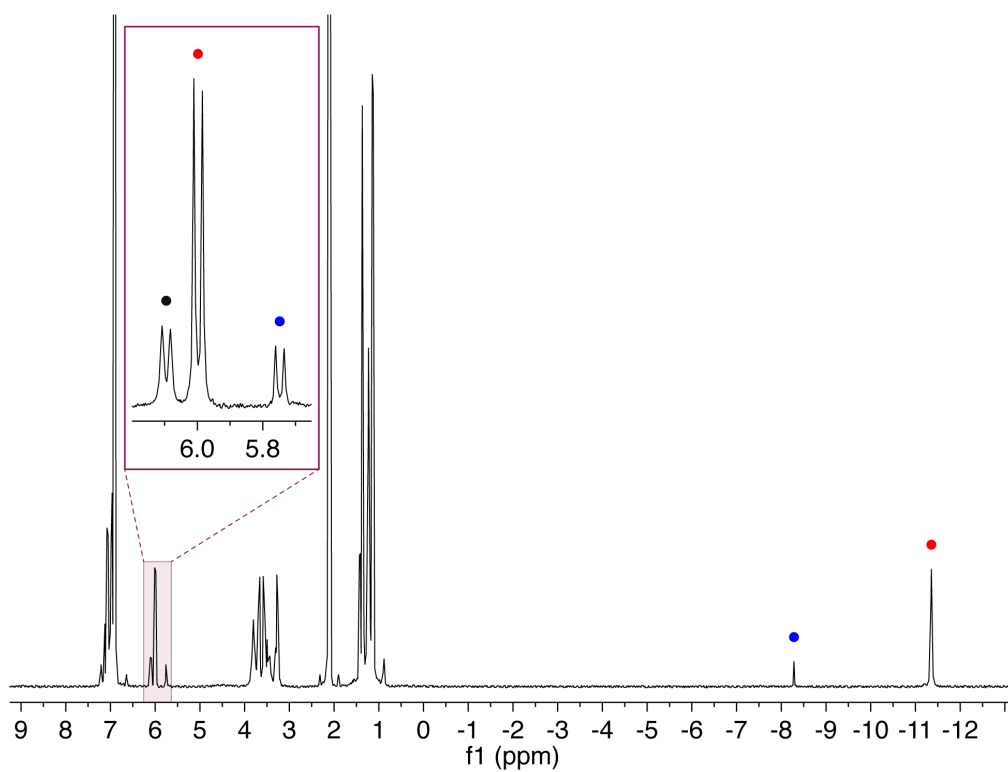
resulted in regeneration of  $(\text{H}_4\text{-}^i\text{PrCNC})\text{Fe}(\text{N}_2)_2$  and precludes collection of combustion analysis. Due to the equilibrium between the iron dinitrogen and iron hydride complexes,  $(\text{H}_4\text{-}^i\text{PrCNC})\text{FeH}_2(\text{N}_2)$  was always observed in the presence of  $(\text{H}_4\text{-}^i\text{PrCNC})\text{Fe}(\text{N}_2)_2$  or  $(\text{H}_4\text{-}^i\text{PrCNC})\text{FeH}_4$ . Integration of the all *meta*-pyridine resonances relative to the methyl resonance of co-crystallized toluene gave a ratio of 2:3, indicating the absence of paramagnetic or NMR silent impurities.  $^1\text{H}$  NMR (benzene- $d_6$ ):  $\delta$  -8.08 (s, 2H, Fe-H), 1.22 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 1.61 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 3.29-3.82 (m, 12H, imidazolidene backbone and  $\text{CH}(\text{CH}_3)_2$ ), 5.78 (d,  $^3J_{\text{HH}} = 7.89$  Hz, 2H, 3-*pyr*), 6.93-6.96 (m, 6H, *aryl*), 7.03 (t,  $^3J_{\text{HH}} = 7.89$  Hz, 1H, 4-*pyr*).  $^{13}\text{C}\{^1\text{H}\}$  NMR (benzene- $d_6$ ):  $\delta$  24.28 ( $\text{CH}(\text{CH}_3)_2$ ), 25.10 ( $\text{CH}(\text{CH}_3)_2$ ), 28.32 ( $\text{CH}(\text{CH}_3)_2$ ), 42.98 (*imidazolylidene backbone*), 55.72 (*imidazolylidene backbone*), 93.89 (3-*pyr*), 125.03 (*aryl*), 128.03 (*aryl*), 129.07 (4-*pyr*), 138.45 (*aryl*), 148.82 (*aryl*), 153.86 (2-*pyr*), 245.62(carbene).

**Characterization of  $(\text{H}_4\text{-}^i\text{PrCNC})\text{FeH}_4$ .** A thick-walled glass vessel was charged with 0.030 g (0.046 mmol) of  $(\text{H}_4\text{-}^i\text{PrCNC})\text{Fe}(\text{N}_2)_2$  and 1 mL of toluene. The vessel was then transferred out of the drybox and attached to a high vacuum line and the contents of the vessel were frozen in liquid nitrogen. Following evacuation of the  $\text{N}_2$  atmosphere, 1 atm of  $\text{H}_2$  was admitted at -196 °C. The mixture was thawed, warmed to ambient temperature, and stirred at 23 °C for 1 hour. During this time, a color change from purple to clear orange was observed. The contents of the vessel were again frozen and the  $\text{H}_2$  atmosphere was removed under vacuum on the high vacuum line at -196 °C. While frozen, pentane was transferred into the vessel via vacuum distillation, and followed by readmission of 1 atm  $\text{H}_2$ . The resulting mixture was slowly warmed to room temperature, and allowed to stand at 23 °C over a period of 48 hours, and yielded bright orange crystals suitable for X-ray diffraction. The crystals were collected (submerged under

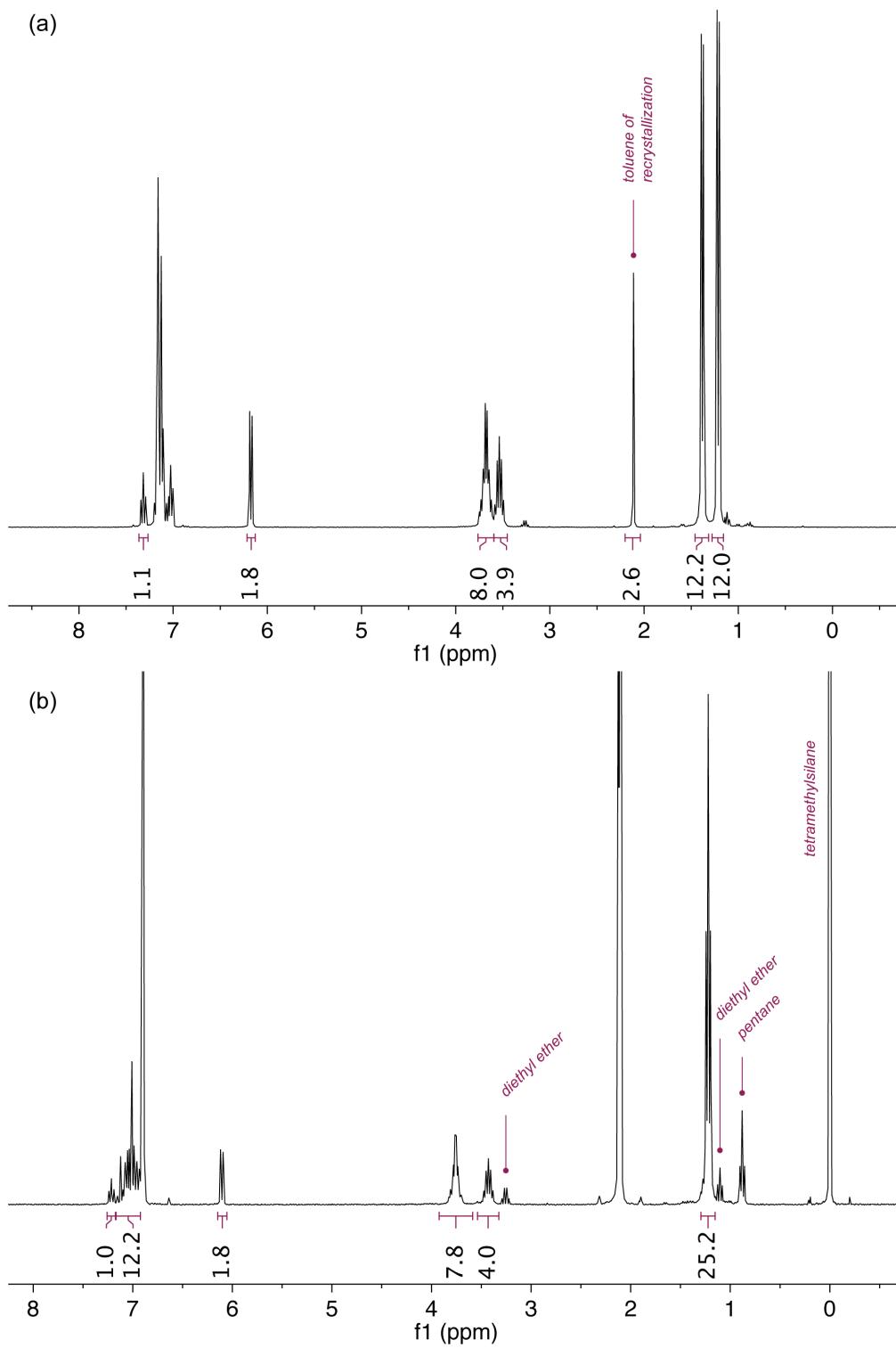


polyisobutylene oil) under an atmosphere of argon. The crystals are extremely sensitive to dinitrogen, rapidly reverting to  $(\text{H}_4\text{-}^{\text{iPr}}\text{CNC})\text{Fe}(\text{N}_2)_2$ , precluding combustion analysis. Purity was established by monitoring the conversion of  $(\text{H}_4\text{-}^{\text{iPr}}\text{CNC})\text{Fe}(\text{N}_2)_2$  to  $(\text{H}_4\text{-}^{\text{iPr}}\text{CNC})\text{FeH}_4$  in benzene- $d_6$  by  $^1\text{H}$  NMR spectroscopy. The methyl resonance of co-crystallized toluene served as an internal standard. Integration of the *meta*-pyridine resonance of both starting material (Fig. S2a) and product (Fig. S3a) relative to toluene gave a ratio of 2:3, indicating the absence of paramagnetic or NMR silent impurities.  $^1\text{H}$  NMR (benzene- $d_6$ ):  $\delta$  -11.22 (s, 4H, Fe-H), 1.13 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 1.52 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 3.29-3.82 (m, 12H, imidazolidene backbone and  $\text{CH}(\text{CH}_3)_2$ ), 6.05 (d,  $^3J_{\text{HH}} = 7.89$  Hz, 2H, 3-*pyr*), 6.93-6.96 (m, 6H, *aryl*), 7.03 (t,  $^3J_{\text{HH}} = 7.89$  Hz, 1H, 4-*pyr*).  $^{13}\text{C}\{^1\text{H}\}$  NMR (benzene- $d_6$ ):  $\delta$  24.18 ( $\text{CH}(\text{CH}_3)_2$ ), 28.29 ( $\text{CH}(\text{CH}_3)_2$ ), 28.39 ( $\text{CH}(\text{CH}_3)_2$ ), 42.61 (*imidazolylidene backbone*), 56.65 (*imidazolylidene backbone*), 93.64 (3-*pyr*), 124.48 (*aryl*), 128.38 (*aryl*), 129.07 (4-*pyr*), 137.29 (*aryl*), 148.29 (*aryl*), 154.56 (2-*pyr*), 243.60 (carbene).

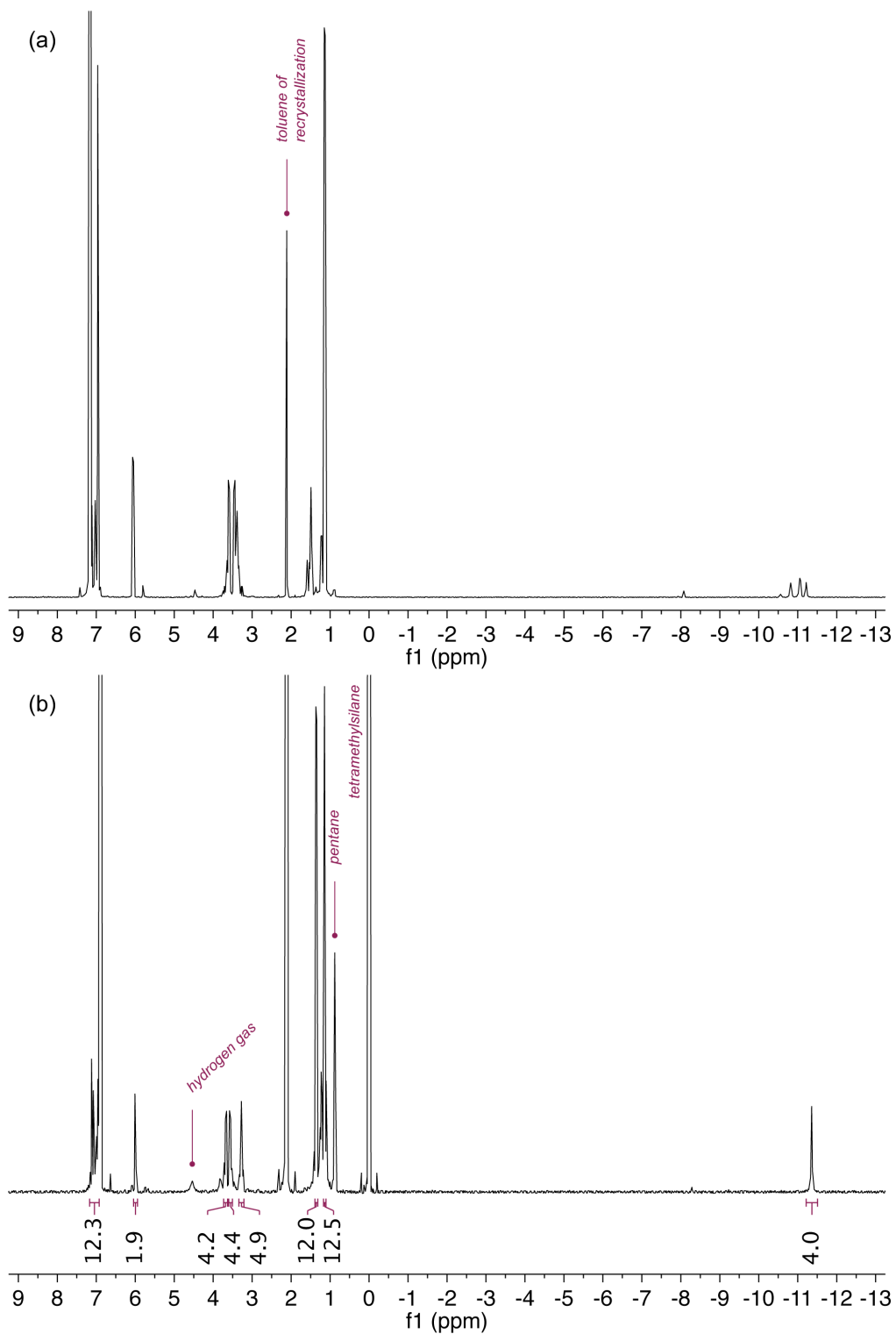
## II. Representative $^1\text{H}$ NMR Spectra.



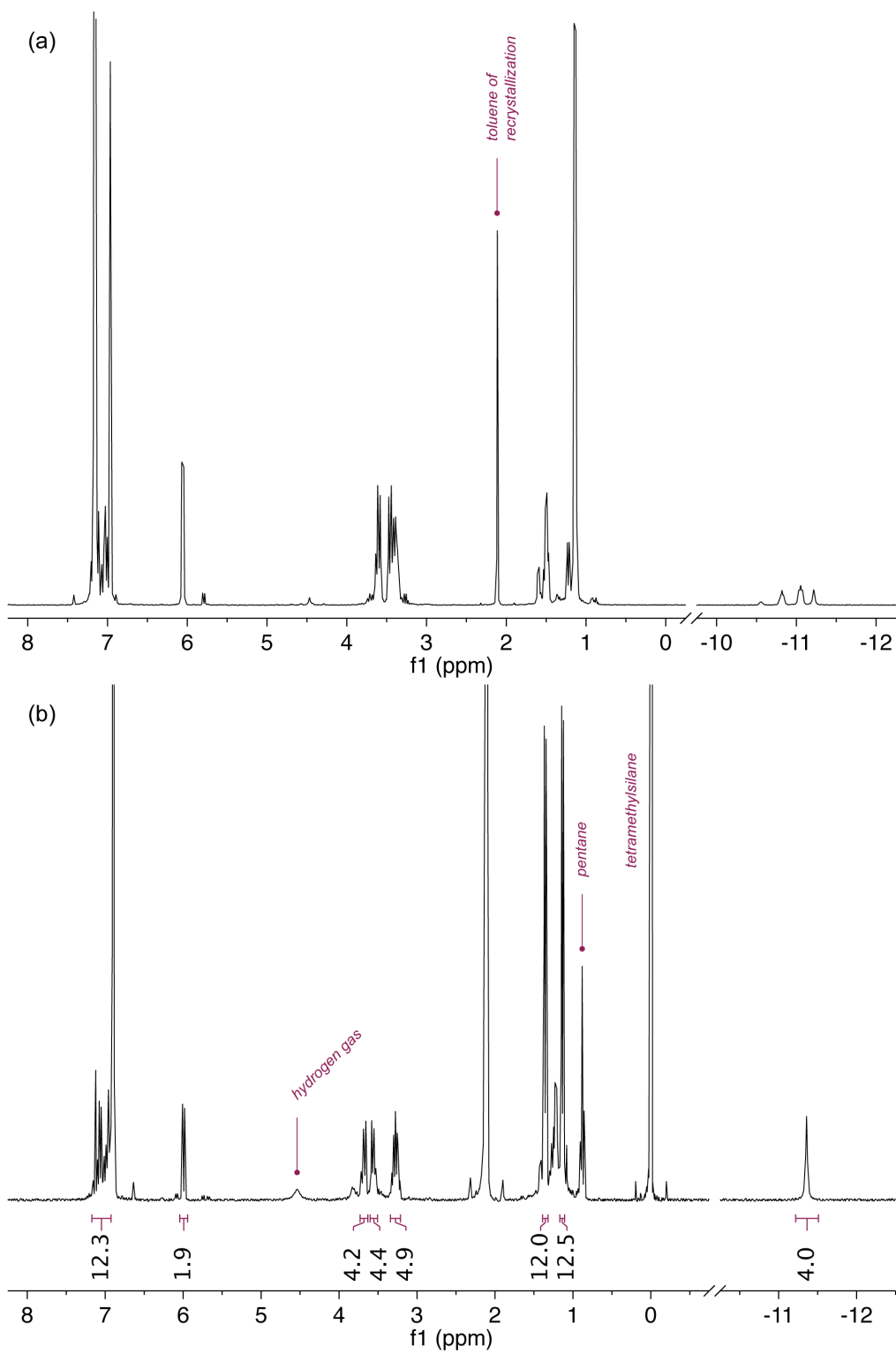
**Figure S1.** Representative  $^1\text{H}$  NMR spectrum of a mixture of  $(\text{H}_4\text{-}^i\text{PrCNC})\text{Fe}(\text{N}_2)_2$  (black circle),  $(\text{H}_4\text{-}^i\text{PrCNC})\text{FeH}_4$  (red circle) and  $(\text{H}_4\text{-}^i\text{PrCNC})\text{FeH}_2(\text{N}_2)$  (blue circle) in *p*-xylene- $d_{10}$  under 1 atm  $\text{H}_2$ . The inset is an expanded view of the diagnostic 3-pyridine region.



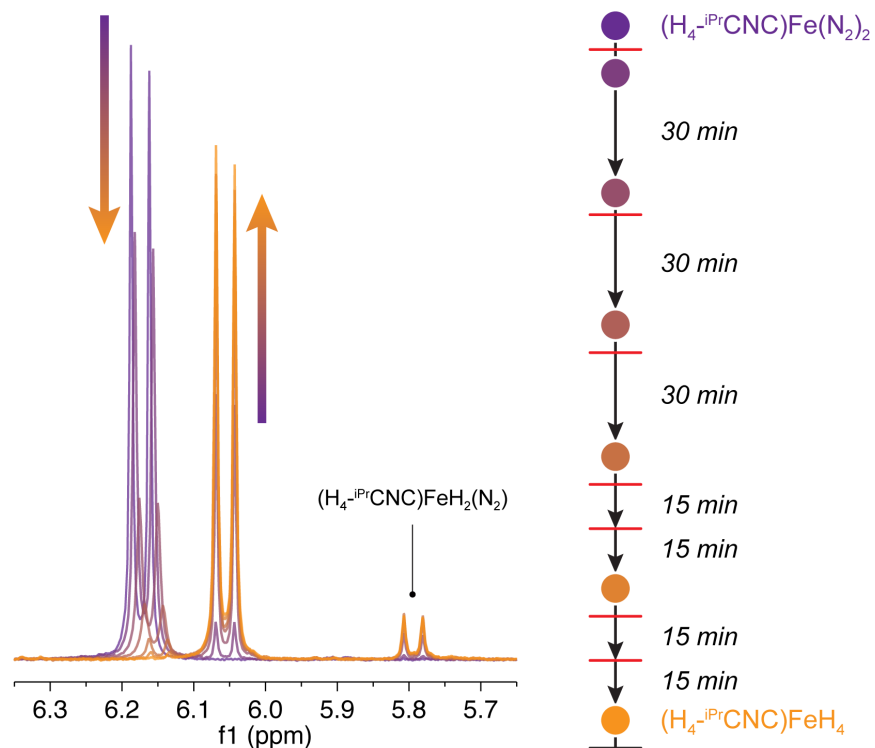
**Figure S2.**  $^1\text{H}$  NMR spectra of  $(\text{H}_4\text{-}^i\text{PrCNC})\text{Fe}(\text{N}_2)_2$  in (a) benzene- $d_6$  and (b)  $p$ -xylene- $d_{10}$ . Tetramethylsilane was added as an internal reference.



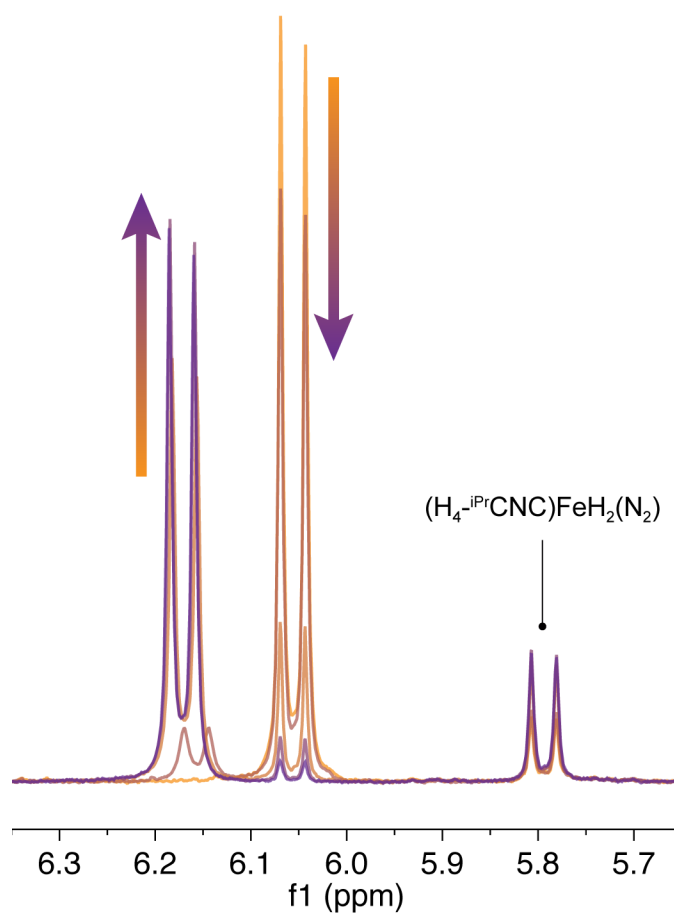
**Figure S3.**  $^1\text{H}$  NMR spectra of  $(\text{H}_4\text{-}^{i\text{Pr}}\text{CNC})\text{FeH}_4$  in (a) benzene- $d_6$  and (b)  $p$ -xylene- $d_{10}$  under a hydrogen atmosphere. Tetramethylsilane was added as an internal reference.



**Figure S4.** Selected regions of the  $^1\text{H}$  NMR spectra of  $(\text{H}_4\text{-iPrCNC})\text{FeH}_4$  in (a) benzene- $d_6$  and (b)  $p$ -xylene- $d_{10}$  under a hydrogen atmosphere. Tetramethylsilane was added as an internal reference.

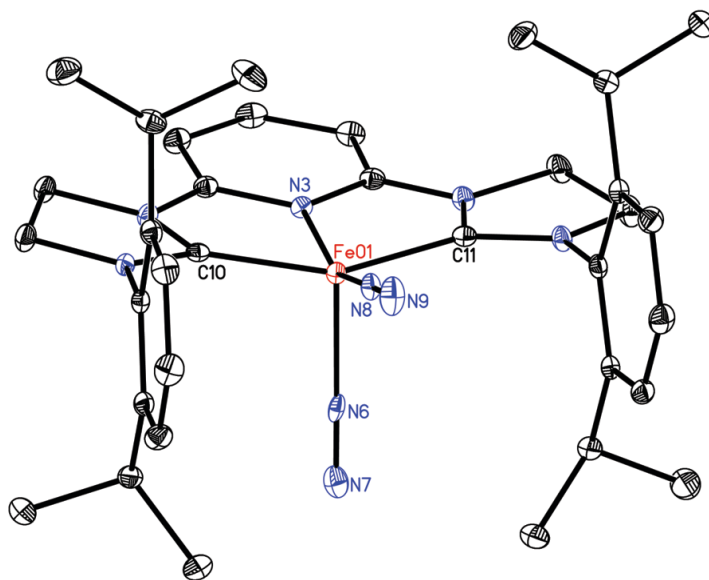


**Figure S5.**  $^1\text{H}$  NMR spectra of the 3-pyridine region (left) following addition of 1 atm  $\text{H}_2$  to  $(\text{H}_4\text{-iPrCNC})\text{Fe}(\text{N}_2)_2$  in benzene- $d_6$ . Experimental details are presented on the right. Circles represent spectra that are presented, and red lines represent freeze-pump- $\text{H}_2$  refresh cycles.



**Figure S6.**  $^1\text{H}$  NMR spectra of the 3-pyridine region following addition of 1 atm  $\text{N}_2$  to  $(\text{H}_4\text{-iPrCNC})\text{FeH}_4$  in benzene- $d_6$ .

### III. Selected Metrical Data

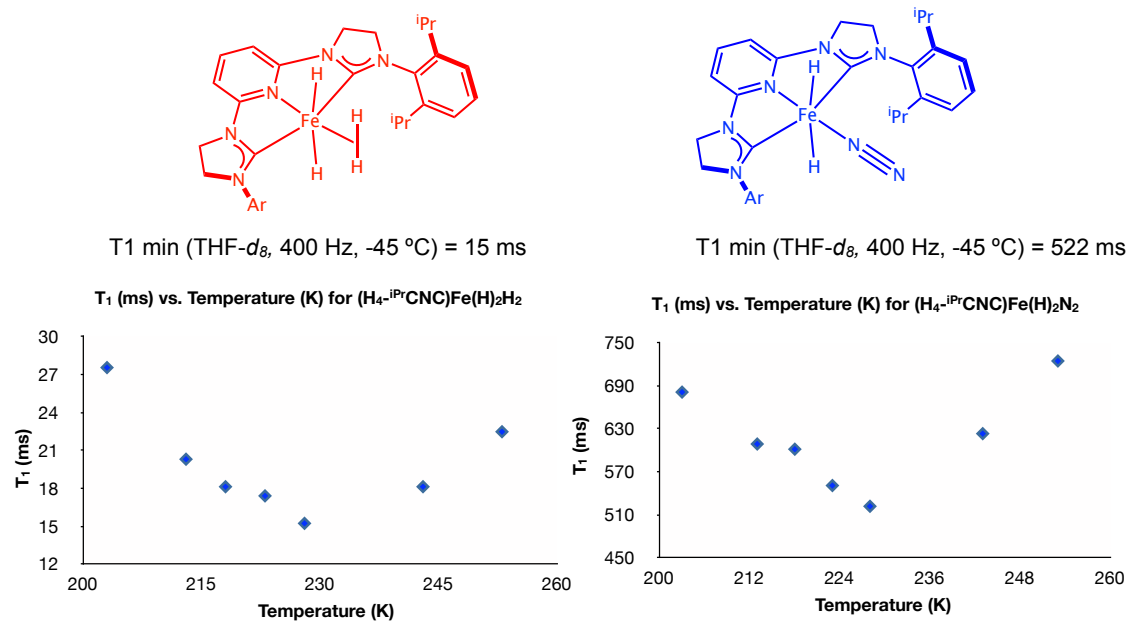


**Figure S7.** Solid state molecular structure of  $(\text{H}_4\text{-}^i\text{PrCNC})\text{Fe}(\text{N}_2)_2$  at 30% probability ellipsoids. Hydrogen atoms and one molecule of toluene are omitted for clarity.

**Table S1.** Selected bond distances (Å) and angles (deg) for  $(\text{H}_4\text{-}^i\text{PrCNC})\text{Fe}(\text{N}_2)_2$ ,  $(\text{H}_4\text{-}^i\text{PrCNC})\text{FeH}_2(\text{N}_2)$  and  $(\text{H}_4\text{-}^i\text{PrCNC})\text{FeH}_4$ .

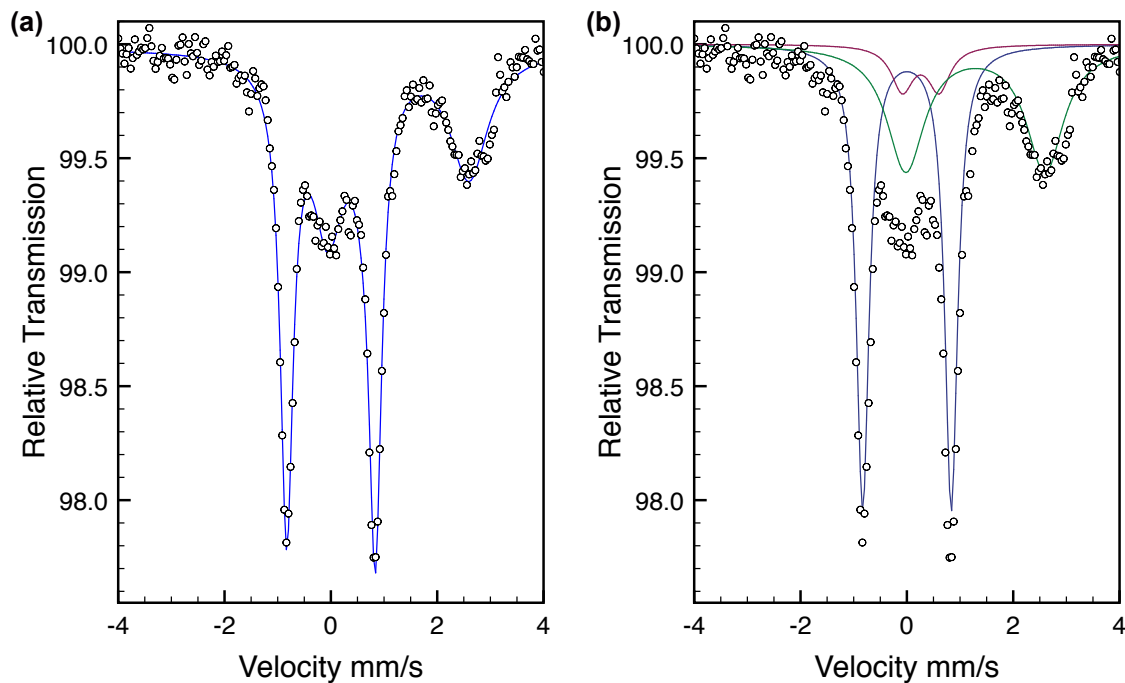
	$(\text{H}_4\text{-}^i\text{PrCNC})\text{Fe}(\text{N}_2)_2$	$(\text{H}_4\text{-}^i\text{PrCNC})\text{FeH}_2(\text{N}_2)$	$(\text{H}_4\text{-}^i\text{PrCNC})\text{FeH}_4$
Fe-N <sub>pyr</sub>	1.901(1)	1.879(2)	1.8731(2)
Fe-N <sub>equatorial</sub>	1.825(1)	1.728(5)	-
Fe-N <sub>axial</sub>	1.886(1)	-	-
Fe-C <sub>carbene</sub>	1.916(2)	1.891(2)	1.885(2)
	1.922(2)	1.891(2)	1.880(2)
Fe-H	-	1.48(4)	-
	-	1.61(3)	-
C <sub>carbene</sub> -Fe-N <sub>pyr</sub>	79.14(7)	80.38(9)	80.42(9)
	78.90(7)	80.45(9)	80.83(9)
C <sub>carbene</sub> -Fe-N <sub>eq</sub>	97.24(7)	98.1(2)	-
	97.46(7)	101.0(2)	-
C <sub>carbene</sub> -Fe-N <sub>ax</sub>	99.13(7)	-	-





**Figure S8.** T<sub>1</sub>(min) measurements of (H<sub>4</sub>-<sup>i</sup>PrCNC)FeH<sub>4</sub> (left) and (H<sub>4</sub>-<sup>i</sup>PrCNC)FeH<sub>2</sub>(N<sub>2</sub>) (right) in THF-*d*<sub>8</sub>. Both measurements were obtained from a single reaction mixture.

#### IV. Mössbauer Spectrum of in situ Generated $(\text{H}_4\text{-}^{\text{iPr}}\text{CNC})\text{FeH}_4$



**Figure S9.** Toluene solution, zero-field  $^{57}\text{Fe}$  Mössbauer spectrum containing  $(\text{H}_4\text{-}^{\text{iPr}}\text{CNC})\text{FeH}_4$  as the major species ( $\delta = 0.01$  mm/s;  $|\Delta E_Q| = 1.66$  mm/s) (a). The spectrum was fit as a three-component mixture (b):  $(\text{H}_4\text{-}^{\text{iPr}}\text{CNC})\text{FeH}_4$  (blue, 51%),  $(\text{H}_4\text{-}^{\text{iPr}}\text{CNC})\text{Fe}(\text{N}_2)_2$  (red, 9%) and a third impurity (green, 40%). Data collected at 80 K. The high concentration of impurity is due to oxidation arising from handling the solution Mössbauer capsule in a makeshift vessel to handle it under a hydrogen atmosphere.

## V. Analysis of FeH and Fe(H<sub>2</sub>) <sup>1</sup>H NMR Spectroscopic Data

**SOLVING FOR <sup>1</sup>J<sub>HD</sub>.** An equation to calculate the T<sub>1</sub><sup>H</sup>(obs) of the dihydrogen and hydride ligands of a MH(H<sub>2</sub>)L<sub>n</sub> complex in the fast exchange regime (*i.e.* no line-shape decoalescence) was reported by Morris (eq. 1).<sup>3</sup>

$$\frac{1}{T_{1,obs}^H} = \frac{2}{3T_1^{H_2}} + \frac{1}{3T_1^H} \quad (1)$$

Due to the additional hydride present in (H<sub>4</sub>-<sup>i</sup>PrCNC)FeH<sub>4</sub> (which was treated as a L<sub>3</sub>MH<sub>2</sub>(H<sub>2</sub>) system with the assumption that contribution to T<sub>1,obs</sub> by (H<sub>4</sub>-<sup>i</sup>PrCNC)Fe(H)<sub>4</sub> and (H<sub>4</sub>-<sup>i</sup>PrCNC)Fe(H<sub>2</sub>)<sub>2</sub> is negligible for the purposes of these calculations), the equation was modified (eq. 2):

$$\frac{1}{T_{1,obs}^H} = \frac{2}{4T_1^{H_2}} + \frac{2}{4T_1^H} \quad (2)$$

The experimentally determined T<sub>1</sub><sup>H</sup>(obs) (15 ms) and T<sub>1</sub><sup>H</sup> (510 ms) allowed for the calculation of a 7.6 ms T<sub>1</sub><sup>H<sub>2</sub></sup>. This is consistent with the slow Fe(H<sub>2</sub>) rotation regime, allowing for the calculation of the dihydrogen distance, d<sub>HH</sub>, using equation 3.<sup>3</sup>

$$d_{HH} = 5.81 \sqrt[6]{\frac{T_1^{min}(slow)}{\nu}} \quad (3)$$

The dihydrogen distance (0.95 Å) was obtained from the calculated T<sub>1</sub><sup>min</sup> (0.0076 s) and spectrometer frequency (ν, 400 MHz). The <sup>1</sup>J<sub>HD</sub> was calculated using this value and equation 4.<sup>3</sup>

$$d_{HH} = -0.0167(J_{HD}) + 1.42 \quad (4)$$

A <sup>1</sup>J(HD) of 28 Hz for the H<sub>2</sub> ligand (δ<sup>H<sub>2</sub></sup>) was obtained.

**SOLVING FOR δ<sup>H<sub>2</sub></sup>.** The non-averaged chemical shift of the H<sub>2</sub> ligand (δ<sup>H<sub>2</sub></sup>) was calculated from the chemical shift of the *trans*-dihydride, (H<sub>4</sub>-<sup>i</sup>PrCNC)FeH<sub>2</sub>(N<sub>2</sub>) (-8.08 ppm) using equation 5,<sup>4</sup> which accounts for both hydride ligands.

$$\delta_{avg}^{H_2} = \frac{2\delta^{H_2}}{4} + \frac{2\delta^H}{4} \quad (5)$$

$$-11.22 \text{ ppm} = \frac{2\delta^{H_2}}{4} + \frac{2 \times (-8.08 \text{ ppm})}{4}$$

A chemical shift of -14.36 ppm was obtained.

**CALCULATING THE AVERAGE CHEMICAL SHIFT OF THE DEUTERATED ISOTOPOLOGUES.** To calculate the average chemical shift of the deuterated isotopologues, the average population of each isotopomer was approximated based on statistical distributions and preference for deuterium to be in the purported H–D ligand.<sup>3,4</sup> The isotopomers of the associated isotopologues of (H<sub>4</sub>-<sup>i</sup>PrCNC)FeH<sub>4</sub> are presented in Table S2. Calculated distributions were optimized to give the most accurate values of  $\delta^H_{avg}$  (*vide infra*), and used for the calculation of  $J_{HD,avg}$ .

**Table S2.** Isotopomer distribution of observed (H<sub>4</sub>-<sup>i</sup>PrCNC)FeH<sub>4</sub> *d*<sub>1–3</sub>-isotopologues.

ISOTOPOMER	STATISTICAL DISTRIBUTION	ADJUSTED DISTRIBUTION	CALCULATED DISTRIBUTIONS <sup>a</sup>
<b><i>d</i><sub>1</sub>-ISOTOPOLOGUE</b>			
FeH <sub>2</sub> (HD)	50%	>50%	58%
FeHD(H <sub>2</sub> )	50%	<50%	42%
<b><i>d</i><sub>2</sub>-ISOTOPOLOGUE</b>			
FeHD(HD)	66%	<66%	60%
FeH <sub>2</sub> (D <sub>2</sub> )	16.7%	>16.7%	26.5%
FeD <sub>2</sub> (H <sub>2</sub> )	16.7%	<16.7%	13.5%
<b><i>d</i><sub>3</sub>-ISOTOPOLOGUE</b>			
FeHD(D <sub>2</sub> )	50%	>50%	60.5%
FeD <sub>2</sub> (HD)	50%	<50%	39.5%

<sup>a</sup> Values used for the calculation of  $\delta^H_{avg}$  and  $J_{HD,avg}$ .

To calculate the average chemical shift, equation 6 was used, which was derived from the work of Morris and coworkers.<sup>4</sup>

$$\delta^H_{avg} = \sum_{i=1}^{N_I} \alpha_i \left( \frac{n_{i,H_2} \delta^{H_2} + n_{i,H} \delta^H}{n_{i,H_2} + n_{i,H}} \right) \quad (6)$$

In this equation,  $N_I$  is the number of isotopomers,  $\alpha_i$  is the weighted statistical probability of the isotopomer,  $n_{i,H_2}$  is the number of hydrogen atoms in the dihydrogen ligand of the isotopomer, and  $n_{i,H}$  is the number of hydrogen atoms in the dihydride positions of the isotopomer.

***d*<sub>1</sub>-Isotopologue.**

$$\delta^H_{avg} = 0.58 \left( \frac{\delta^{H_2} + 2\delta^H}{3} \right) + 0.42 \left( \frac{2\delta^{H_2} + \delta^H}{3} \right) \quad (7)$$

$$\delta^H_{avg} = 0.58 \left( \frac{-14.36 \text{ ppm} + (2 \times -8.08 \text{ ppm})}{3} \right) + 0.42 \left( \frac{(2 \times -14.36 \text{ ppm}) + (-8.08 \text{ ppm})}{3} \right)$$

$$\delta^H_{avg} = -11.05 \text{ ppm}$$

***d*<sub>2</sub>-Isotopologue.**

$$\delta_{avg}^H = 0.60 \left( \frac{\delta^{H_2} + \delta^H}{2} \right) + 0.265 \left( \frac{2\delta^H}{2} \right) + 0.135 \left( \frac{2\delta^{H_2}}{2} \right) \quad (8)$$

$$\delta_{avg}^H = 0.60 \left( \frac{-14.36 \text{ ppm} + (-8.08 \text{ ppm})}{2} \right) + 0.265 \left( \frac{2 \times (-8.08 \text{ ppm})}{2} \right) + 0.135 \left( \frac{2 \times (-14.36 \text{ ppm})}{2} \right)$$

$$\delta_{avg}^H = -10.81 \text{ ppm}$$

***d*<sub>3</sub>-Isotopologue.**

$$\delta_{avg}^H = 0.605 \left( \frac{\delta^H}{1} \right) + 0.395 \left( \frac{\delta^{H_2}}{1} \right) \quad (9)$$

$$\delta_{avg}^H = (0.605 \times -8.08 \text{ ppm}) + (0.395 \times -14.36 \text{ ppm})$$

$$\delta_{avg}^H = -10.56 \text{ ppm}$$

**CALCULATING THE AVERAGE  $J_{HD,avg}$  OF THE DEUTERATED ISOTOPOLOGUES.**

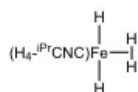
To calculate the average  $J_{HD,avg}$  for each isotopologue, equation 10 was used, which was derived from the work of Morris and coworkers.<sup>4</sup>

$$J_{HD,avg} = \sum_{i=1}^{N_I} \alpha_i \left( \frac{n_{i,1J} {}^1J_{HD} + n_{i,2J} {}^2J(H,D)}{n_{i,1J} + n_{i,2J}} \right) \quad (10)$$

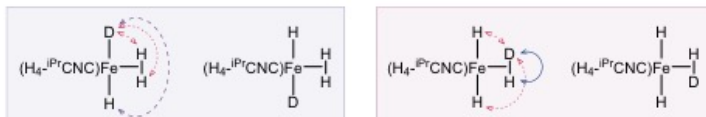
In this equation,  $N_I$  is the number of isotopomers,  $\alpha_i$  is the weighted statistical probability of the isotopomer,  $n_{i,1J}$  is the number of  ${}^1J_{HD}$  couplings in the isotopomer, and  $n_{i,2J}$  is the number of *cis*- and *trans*- ${}^2J_{H,D}$  couplings in the isotopomer. The  ${}^1J_{HD}$  and  ${}^2J_{H,D}$  couplings of all of the isotopomers are presented in Figure S10.

In previous studies by Morris and coworkers, both *cis*- and *trans*- ${}^2J_{H,D}$  couplings are negligible (approximated as 0 Hz).<sup>4</sup> However, observation of (H<sub>4</sub>-<sup>i</sup>PrCNC)FeHD(N<sub>2</sub>) allowed for the direct measurement of a *trans*- ${}^2J_{H,D}$  coupling (5.7 Hz). Both extremes of *trans*- ${}^2J_{H,D}$  coupling were therefore investigated.

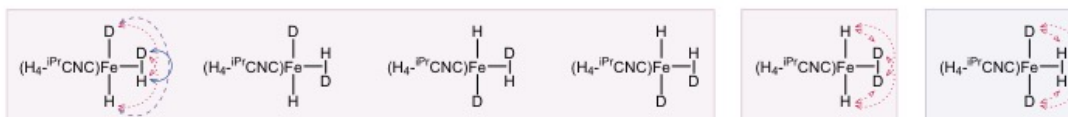
***d<sub>0</sub>-Isotopologue***



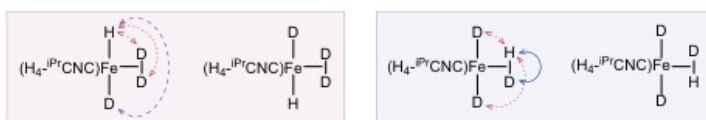
***d<sub>1</sub>-Isotopologue***



***d<sub>2</sub>-Isotopologue***



***d<sub>3</sub>-Isotopologue***



**Figure S10.** Isotopomers of the observed  $(H_4\text{-}^{iPr}CNC)FeH_4$   $d_{1-3}$ -isotopologues, and their associated  $^1J_{HD}$  and  $^2J_{H,D}$  couplings.

***d<sub>1</sub>-Isotopologue.***

If  $trans\text{-}^2J_{H,D} = 0$  Hz:

$$J_{HD,avg} = 0.58 \left( \frac{^1J_{HD} + (2 \times ^2J_{H,D})}{3} \right) + 0.42 \left( \frac{3 \times ^2J_{H,D}}{3} \right) \quad (11)$$

$$J_{HD,avg} = 0.58 \left( \frac{^1J_{HD}}{3} \right)$$

$$J_{HD,avg} = 5.4 \text{ Hz}$$

If  $trans\text{-}^2J_{H,D} = 5.7$  Hz:

$$J_{HD,avg} = 0.58 \left( \frac{^1J_{HD}}{3} \right) + 0.42 \left( \frac{^2J_{H,D}}{3} \right) \quad (12)$$

$$J_{HD,avg} = 6.2 \text{ Hz}$$

***d<sub>2</sub>-Isotopologue.***

If  $trans\text{-}^2J_{H,D} = 0$  Hz:

$$J_{HD,avg} = 0.60 \left( \frac{{}^1J_{HD} + (3 \times {}^2J_{H,D})}{4} \right) + 0.265 \left( \frac{4 \times {}^2J_{H,D}}{4} \right) + 0.135 \left( \frac{4 \times {}^2J_{H,D}}{4} \right) \quad (13)$$

$$J_{HD,avg} = 0.60 \left( \frac{{}^1J_{HD}}{4} \right)$$

$$J_{HD,avg} = 4.2 \text{ Hz}$$

If  $trans\text{-}^2J_{H,D} = 5.7 \text{ Hz}$ :

$$J_{HD,avg} = 0.60 \left( \frac{{}^1J_{HD} + {}^2J_{H,D}}{4} \right) \quad (14)$$

$$J_{HD,avg} = 5.1 \text{ Hz}$$

### ***d*<sub>3</sub>-Isotopologue.**

If  $trans\text{-}^2J_{H,D} = 0 \text{ Hz}$ :

$$J_{HD,avg} = 0.605 \left( \frac{3 \times {}^2J_{H,D}}{3} \right) + 0.395 \left( \frac{{}^1J_{HD} + (2 \times {}^2J_{H,D})}{3} \right) \quad (15)$$

$$J_{HD,avg} = 0.395 \left( \frac{{}^1J_{HD}}{3} \right)$$

$$J_{HD,avg} = 3.7 \text{ Hz}$$

If  $trans\text{-}^2J_{H,D} = 5.7 \text{ Hz}$ :

$$J_{HD,avg} = 0.605 \left( \frac{{}^2J_{H,D}}{3} \right) + 0.395 \left( \frac{{}^1J_{HD}}{3} \right) \quad (16)$$

$$J_{HD,avg} = 4.9 \text{ Hz}$$

**SUMMARY OF RESULTS.** A summary of the experimentally measured and calculated averaged chemical shifts and  $J_{HD,avg}$  couplings for the  $d_{1-3}$ -isotopologues of ( $H_4\text{-}^{iPr}\text{CNC})\text{FeH}_4$  are presented in the table below.

**Table S3.** Summary of the computed results.

ISOTOPOLOGUE	$\delta_{avg}$ (ppm)		$J_{HD,avg}$ (Hz)	
	OBSERVED	CALCULATED	OBSERVED	CALCULATED <sup>a</sup>
$d_1$	-11.05	-11.05	6.3	5.4 (6.2)
$d_2$	-10.82	-10.81	5.1	4.2 (5.1)
$d_3$	-10.56	-10.56	4.1	3.7 (4.9)

<sup>a</sup> Assume a  $cis\text{-}^2J_{H,D}$  of ~0 Hz. Values in parentheses indicate calculated  $J_{HD,avg}$  values incorporating a  $trans\text{-}^2J_{H,D}$  of 5.7 Hz.

## VI. References

- <sup>1</sup> Pangborn, A. B., Giardello, M. A., Grubbs, R. H., Rosen, R. K. & Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.
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- <sup>4</sup> Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155–284.