Published in final edited form as:

J Am Chem Soc. 2011 October 19; 133(41): 16366–16369. doi:10.1021/ja207003m.

Characterization of a Non-classical Dihydrogen Adduct of an $S = \frac{1}{2}$ Fe(I) Center

Yunho Lee^{†,‡}, R. Adam Kinney^{‡,‡}, Brian M. Hoffman^{‡,*}, and Jonas C. Peters^{†,*}

[†]Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125 (USA)

[‡]Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208 (USA)

Abstract

We have exploited the capacity of the '(SiPⁱPr₃)Fe(I)' scaffold to accommodate additional axial ligands and have characterized the mononuclear, $S = \frac{1}{2}$ H₂-adduct complex (SiPⁱPr₃)Fe^I(H₂). EPR and ENDOR data, in the context of X-ray structural results, reveal that this complex provides a highly unusual example of an open-shell metal complex that binds dihydrogen as a ligand. The H₂ ligand at 2 K dynamically reorients within the ligand-binding pocket, tunneling among the energy minima created by strong interactions with the three Fe-P bonds.

Low-valent iron is proposed to play a prominent role in the function of hydrogenase and nitrogenase enzymes, a hypothesis that has inspired the study of formally low-valent iron model complexes that afford access to N₂ and H₂ ligation.^{1,2,3} Whereas model systems have historically focused on iron(0) and iron(II) systems in this context, the coordination chemistry of iron(I) has more recently come into focus.⁴ This is in part due to its suggested intermediacy in enzymatic hydrogenase activity. Because iron(I) is a key formal oxidation state to consider with respect to both N₂ and H⁺ reduction cycles, understanding how small molecules such as N₂ and H₂ interact with formal iron(I) centers is essential.

In several recent studies using a tripodal tetradenate tris(phosphino)silyl ligand (e.g., SiPⁱPr₃ = [Si(*o*-C₆H₄ iPr₂)₃][−]),^{3c,4b,c,e} it has been established that 5-coordinate iron in a TBP geometry (XL₃-Fe-L') can accommodate a terminally bonded N₂ (or CO) ligand in the axial site across three formal oxidation states (XL₃Fe⁰-N₂[−]/XL₃Fe^I-N₂/XL₃Fe^{II}-N₂⁺). Noteworthy is that the spin states of these TBP systems vary such that an $S = 0$ state is favored for iron(0), an $S = \frac{1}{2}$ state for iron(I), and an $S = 1$ state for iron(II). These findings encouraged us to explore the affinity of dihydrogen for the axial site, particularly for the $S = \frac{1}{2}$ iron(I) or $S = 1$ iron(II) states. Whereas it is common that H₂ will occupy the same coordination site as N₂, thoroughly characterized dihydrogen adducts of open shell complexes for transition metals remain exceptionally rare.^{5,6} Oxidative addition to form a dihydride and heterolytic cleavage to form a mono-hydride are well-established alternatives.

*Corresponding Author: jcpeters@caltech.edu; bmh@northwestern.edu.

[†]Present Addresses

Department of Chemistry, School of Molecular Science, Korea Advanced Institute of Science and Technology, Daejeon, Rep of Korea.

[‡]These authors contributed equally.

Author Contributions

The manuscript was written through contributions of all authors./All authors have given approval to the final version of the manuscript./

SUPPORTING INFORMATION

Detailed experimentals and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

NMR techniques, including measurement of T_1 values and J_{HD} coupling constants, have provided the method of choice for characterizing closed-shell H_2 adducts and distinguishing between the dihydrogen/dihydride extrema on the H_2 bonding continuum.⁷ Open-shell H_2 -adduct complexes are not amenable to this approach owing to the extreme line-broadening of resonances expected for H-atoms directly coordinated to a metal center with spin $S > 0$. Because the non-integer $S = 1/2$ state is EPR active we reasoned that a combined EPR/ENDOR study might prove most effective in characterizing the product formed by reacting H_2 with the $S = 1/2$ iron(I). The present report provides the results of such a study and introduces an $S = 1/2$ $\text{Fe}^{\text{I}}(\text{H}_2)$ adduct complex. Evidence for its related but cationic $S = 1$ $\text{Fe}^{\text{II}}(\text{H}_2)^+$ analogue is also provided.

As previously reported, treatment of the methyl complex $(\text{SiP}^i\text{Pr}_3)\text{Fe}-\text{CH}_3$, **1**, with HCl followed by reduction generates the iron(I), $S = 1/2$ N_2 adduct $(\text{SiP}^i\text{Pr}_3)\text{Fe}(\text{N}_2)$, **2**.^{4b,c} The N_2 ligand is sufficiently labile to be displaced by H_2 in benzene to afford a yellow species formulated as $S = 1/2$ “ $(\text{SiP}^i\text{Pr}_3)\text{Fe}(\text{H}_2)$ ” or “ $(\text{SiP}^i\text{Pr}_3)\text{Fe}(\text{H})_2$ ”, **3** ($\mu_{\text{eff}} = 1.9 \mu_{\text{B}}$; Evans method; Scheme 1) in ca. quantitative yield. The optical spectrum of **3** (see SI) features a low-energy d-d transition at 1350 nm ($\epsilon \sim 100 \text{ cm}^{-1} \text{ M}^{-1}$), similar to that of **2** (1250 nm, $\epsilon \sim 300 \text{ cm}^{-1} \text{ M}^{-1}$).

Displacement of the N_2 ligand of **2** by H_2 can be conveniently monitored by ^1H NMR spectroscopy in C_6D_6 (Figure 1). Most of the paramagnetically shifted resonances are sufficiently well resolved at RT to easily distinguish between **2** and **3**. As shown in Figure 1, the H_2 -adduct **3** is stable to vacuum over prolonged periods (even at 60 °C over 12 hours), but converts back to **2** upon exposure to N_2 , which would be consistent with an associative exchange process proceeding through a formally 19-electron intermediate. Alternatively, and perhaps more likely, is a labile phosphine donor that exposes a site for N_2 binding via a 15-electron intermediate, followed by H_2 loss and re-coordination of the phosphine donor to provide **2**. We also prepared and similarly characterized the D_2 derivative of **3** (see SI). The ^1H NMR spectrum of **3**- D_2 is analogous to that for **3**, and a ^2H NMR spectrum does not reveal any deuterium resonances for **3**- D_2 (SI). This fact is consistent with deuterons that are directly bonded to an $S = 1/2$ iron center. Incubation of **2** under HD instead of H_2 gas at RT for 15 h caused no HD/ H_2 / D_2 scrambling, suggesting that **3** binds an intact H_2 ligand, rather than having undergone heterolytic activation, for example to generate an Si-H or P-H bond and an Fe-H.

The well-behaved NMR properties of **2** and **3** allow for the direct measurement of the equilibrium constant for H_2/N_2 exchange at the $S = 1/2$ iron center. Using sealed J-Young vessels with known N_2/H_2 gas mixtures, and exploiting the well-defined resonances from the SiP^iPr_3 ligand at ca. 10 and 8 ppm to integrate the respective concentrations of **2** and **3**, an equilibrium constant of 50 ± 20 in C_6D_6 at room temperature, in favor of H_2 binding, is estimated.

X-ray structures of the unusual H_2 -adduct species **3** were obtained from crystals under vacuum and under an atmosphere of H_2 . While both structures are of high quality, neither shows the positions of the H_2 /hydride. Nonetheless, it is clear that the two structures are essentially identical, and are likewise very similar to the N_2 adduct complex **2**^{4c} and its CO-adduct congener $(\text{SiP}^i\text{Pr}_3)\text{Fe}^{\text{I}}(\text{CO})$ ^{4e} (Figure 2; Table 1), except for the absence of an axially bound diatomic ligand for **3**. We attempted to gain insight into the hydrogenic ligand of **3** by IR spectroscopy, both in solution and in the solid-state, but were not able to unequivocally locate a vibration consistent with either an Fe-H or an Fe-(H-H) motif. Whereas terminal M-H vibrations are readily assigned, $\nu(\text{H-H})$ vibrations for H_2 -adduct complexes are not as reliably discerned.^{6a,7} The absence of $\nu(\text{Si-H})$ or $\nu(\text{P-H})$ stretches in the IR is likewise

inconsistent with heterolytic generation of Fe-H and Si-H/P-H bonds, but consistent with an intact H₂ ligand.

To characterize the hydrogenic ligands of **3** and obtain more conclusive structural information for the “Fe(H₂)/Fe(H)₂” complex, we examined its EPR spectrum in both the solid-state and as a frozen glass. Treatment of **2** ($g = [2.364, 2.036, 2.003]$) with H₂ gas leads to complete loss of the starting material and the appearance of **3** with an $S = 1/2$ EPR signal ($g = [2.275, 2.064, 2.015]$), as measured for frozen solutions (9:1 THF:Me-THF) and pure powders (see SI). The unique magnetic direction ($g_1 = 2.275$) is assigned to the pseudo- C_3 symmetry axis of the molecule. These low-temperature measurements of **3** in frozen solution and as a pure solid, combined with the NMR Evans method studies of **3** in fluid solution at ambient temperature (Table 1), show that the coordination sphere and low-spin d^7 character of the Fe(I) center is maintained under all conditions.

The g values of **3** (and **2**) can be described in terms of a ‘pseudo Jahn-Teller effect’ (PJT), wherein spin-orbit coupling competes with vibronic coupling to lower the energy of the molecule by a distortion from a C_3 -symmetric structure.⁸ The idealized trigonal Fe(I) geometry, created by the [SiP^{*i*Pr}₃][−] ligand, leads to a doubly-degenerate ²E ground state in which the $d(xy)$, $d(x^2-y^2)$ orbital doublet is triply occupied, and therefore is subject to a Jahn-Teller distortion. The most obvious distortion in the X-ray structure of **3** (and **2**) is in the P-Fe-P angles, with an increase in one angle from the symmetric value of 120° and a decrease in the other two: for **3**, P2-Fe-P3 = 123.2°; P1-Fe-P3 ≈ P1-Fe-P2 ≈ 115.4°.

Although the hydrogenic ligand(s) of **3** is not visible by X-ray diffraction, we have directly characterized this ligand by ^{1,2}H ENDOR spectroscopy. Figure 3 displays a partial 2D field-frequency ¹H ENDOR pattern comprised of spectra collected across the EPR envelope of **3**. The spectrum collected at g_3 (Figure 3) shows a doublet centered at the ¹H Larmor frequency that is split by the hyperfine interaction $|A_3(^1H)| = 37.8$ MHz. The equivalent ²H ENDOR spectrum from [SiP^{*i*Pr}₃]Fe(²H₂) (**3'**) shows a corresponding doublet; its splitting, $|A_3(^2H)| = 5.6$ MHz, matches that of the ¹H doublet when scaled by the respective nuclear g -values (with a small isotope-effect correction). Likewise, the 2D field-frequency pattern of ²H ENDOR spectra corresponds to the ¹H pattern of Figure 3 (See SI). This correspondence demonstrates that the ENDOR response is associated with an Fe-bound hydrogenic ligand arising from dihydrogen. The complete 2D pattern is exceptionally well simulated by hyperfine coupling to a *single type* of ¹H, with coupling tensor, $\mathbf{A} = +[2.3, -40.6, -37.8]$ MHz, isotropic coupling, $a_{iso} = -25.4$ MHz, and anisotropic dipolar hyperfine coupling, $\mathbf{T} = +[27.7, -15.2, -12.4]$ MHz; the tensor orientation relative to $\mathbf{g}$ given by the rotation angles, $(\alpha, \beta, \gamma) = (0, 6, 0)$. The absolute sign of the ^{1,2}H hyperfine coupling has been experimentally determined with the PESTRE technique (see SI).⁹

The simplest chemical species compatible with a single type of interacting ¹H whose Fe-¹H vector lies close to g_1 is a neutral Fe(I) complex in which a terminal hydride bound to Fe(I) is generated by heterolytic cleavage of the H₂ molecule with delivery of the proton to the Si of the SiP^{*i*Pr}₃ ligand. However, this model can be rejected because it requires cleavage of the Fe-Si bond, with rearrangement of the geometry at Si and a substantial increase in $r(\text{FeSi})$ relative to **2**, whereas the crystal structure of **3** reveals a negligible change in $r(\text{FeSi})$ relative to **2** (see above).¹⁰ This conclusion is experimentally corroborated by EPR measurements that show that the solution, polycrystalline powder (SI), and single-crystal form of **3** have the same g -tensor,¹¹ and thus the same structure. The ENDOR pattern of Figure 3 must therefore arise from a neutral complex that has been generated by the *addition* of H₂, either in the form of an Fe(I)-H₂ complex or via oxidative addition to form an Fe(III)-dihydride that features two magnetically equivalent hydrogens, as depicted in Figure 4A.

The observed g -values provide a powerful argument against formulation of **3** as an Fe(III)-dihydride. The same treatment of the PJT effect that successfully describes the g -values for the Fe(I) d^7 ion in trigonal symmetry predicts that the g -values for an Fe(III) d^5 ion must be less than $g_e = 2$, contrary to observation.¹²

Elimination of the Fe(III)-dihydride model for **3** is confirmed by analysis of the ^1H ENDOR results. The 2D ENDOR pattern for **3** can be compared with that predicted for this species based on a consensus geometry derived from NMR, neutron, and X-ray measurements of similar complexes ($d_{\text{H-H}} > 1.6 \text{ \AA}$; $d_{\text{Fe-H}} = 1.54 \text{ \AA}$; Figure 4A,B).¹³ The critical parameter in the ENDOR simulations is the value of the angle, β , made by the g_1 principal axis and the Fe-(H) vectors. In a Fe(III) dihydride complex, $\beta \geq 30^\circ$. Numerous attempts to generate acceptable ^1H ENDOR simulations using an angle $\beta \wedge 30^\circ$ (Figure 4B ($\beta = 30^\circ$); also see SI) show this to be incompatible with experiment, in contrast with the excellent fit for $\beta = 6^\circ$. Figure 4B illustrates this with simulations for a spectrum collected at a field where each component of the doublet observed at g_3 (and g_2) from Figure 3 splits into an intense peak and a less intense 'shoulder'. The calculated splitting increases as β increases from zero, and even with the best possible overall choices for the remainder of the hyperfine parameters, the splitting for $\beta \sim 30^\circ$ is far larger than seen in experiment. Thus, the EPR and ENDOR measurements combine to eliminate assignment of **3** as a dihydride.

Rejection of the assignment of **3** as an iron(I) monohydride or an iron(III)-dihydride, implies by elimination that **3** is an Fe(I)- H_2 adduct. The solution NMR data are qualitatively consistent with this formulation given the similar NMR pattern of **3** compared with **2**. The UV-vis data for **2** and **3** are also highly consistent with this notion (*vide supra*). The ENDOR simulations further show that even at 2 K, the H_2 of the Fe(I)- H_2 adduct is dynamically reorienting within the ligand-binding pocket of **3**. Taking a consensus geometry for the Fe(I)-H center ($d_{\text{H-H}} = 0.85 \text{ \AA}$; $d_{\text{Fe-H}} = 1.62 \text{ \AA}$),¹⁴ the H atoms would exhibit a geometrically determined angle, $\beta \sim 15^\circ$. As shown in Figure 4 (also see SI), the 2D ENDOR pattern of Figure 3 cannot be described by such a static structure. The electron-nuclear dipolar interaction for H_2 must therefore be modulated by rapid reorientation of H_2 about the Fe- H_2 bond axis..

The H_2 cannot be undergoing rotation that is only weakly hindered by the binding pocket environment, because then the ground state would correspond to the free-rotor ground rotational state ($m = 0$).¹⁵ As protons are fermions ($I = 1/2$), the wavefunction of a rotating $^1\text{H}_2$ must be antisymmetric to exchange of the two ^1H . For $^1\text{H}_2$ bound to the Fe(I) center of a statically distorted **3**, this wavefunction is the product of the $^1\text{H}_2$ rotational and spin functions. The ground rotor state is symmetric with respect to exchange of the two hydrogen nuclei ('para' state), and thus it must be associated with the antisymmetric $I = 0$ total nuclear spin state, which cannot exhibit a ^1H ENDOR signal.¹⁶ If **3** were instead undergoing a dynamic PJT distortion, the total H_2 wavefunction would have the vibronic electron-nuclear wavefunction as an additional factor. It can be shown that for **3** this factor is symmetric to exchange, so the conclusion remains.

Instead, the measurements are probably best understood as a consequence of H_2 tunneling among localized states set up by a strong six-fold barrier associated with rotation of the 'dumbbell-shaped' H_2 within the three-fold molecular potential (Fig 5).⁵ In this limit, the ^1H ENDOR response is allowed, and tunneling would average the dipolar interaction so that the unique hyperfine axis lies along the axis of rotation. If the rotation axis were collinear with the g tensor tunneling would thus average the metrical angle, $\beta \approx 15^\circ$, to an *effective* angle, $\beta' = 0^\circ$, as compared to the measured value, $\beta = 6^\circ$. We attribute the non-zero β to tensor non-collinearity caused by the distortion from trigonal that is introduced by the PJT effect and observed in the X-ray structure (Table 1).

An H₂ that rapidly reorients at 2 K would be only more mobile at higher temperature, and thus provides an explanation for the absence of this ligand from the X-ray structure.

It is of interest to compare the stable (SiPⁱPr₃)Fe^I(H₂) complex described here to the presumed dihydrogen adduct, “[HIPTN₃N]Mo^{III}(H₂)” adduct.^{6b} In a recent report it was shown that the latter species undergoes facile heterolytic cleavage of H₂, delivering H[−] to Mo to afford [HIPTN₃N]Mo^{III}(H)][−] and H⁺, with the H⁺ presumably delivered to sacrificial [HIPTN₃N]^{3−} at reduced temperature.^{6c} By contrast, the Si atom of the (SiPⁱPr₃)Fe scaffold is insufficiently basic to accept H⁺ from the coordinated H₂, thus stabilizing the H₂-adduct complex **3** against heterolytic cleavage and allowing its thorough characterization. The stability of H₂ bound to the ‘(SiPⁱPr₃)Fe’ scaffold also extends to its corresponding cation, ‘(SiPⁱPr₃)Fe⁺’. Treating previously reported *S* = 1 {(SiPⁱPr₃)Fe(N₂)} {BAr₄^F}, **4**, with H₂ the reversibly generates what we assign as *S* = 1 complex {(SiPⁱPr₃)Fe(H₂)} {BAr₄^F}, **5** (Scheme 1). Complex **5** is EPR/ENDOR silent due to its integer-spin triplet state, thereby precluding unequivocal characterization of the hydrogenic ligand/s by the methods presented herein, but solution NMR and UV-vis data (See SI) provide circumstantial evidence for a species that is highly similar to the cationic N₂ adduct **4**. What is more, addition of an exogenous base (e.g., N_iPr Et) to **5** under N₂ cleanly effects heterolytic cleavage and affords the neutral iron(II) complex (SiPⁱPr₃ Fe(N₂)(H), **6** (Scheme 1).

In summary, we have exploited the capacity of the ‘(SiPⁱPr₃)Fe’ scaffold to accommodate an additional ligand in an axial site and have characterized the mononuclear, *S* = ½ Fe^I(H₂) adduct complex **3**. This complex provides a highly unusual example of a well-characterized, open-shell metal complex that binds dihydrogen as a ligand. Combined X-ray EPR and ENDOR data are consistent with a PJT-distorted d⁷ configuration and an H₂ ligand that at 2 K tunnels among the energetic minima created by the Fe-P bonds. The *S* = ½ title complex (SiPⁱPr₃)Fe(H₂) can be formally oxidized to its *S* = 1 cation, {(SiPⁱPr₃)Fe(H₂)}⁺, and the latter species also appears to bind H₂ as an intact ligand, but one that is subject to heterolytic cleavage upon addition of exogenous base.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

Funding Sources

We acknowledge the NIH (JCP, GM-070757; BMH HL 13531).

We acknowledge the NIH (JCP, GM-070757; BMH HL 13531). We thank Prof. Harden McConnell for characteristically insightful suggestions about low-temperature dynamics. Dr. Peter Müller provided assistance with XRD analyses. Professor George R. Rossman provided access to a near IR spectrometer at Caltech. Henry Fong is acknowledged for probing the deprotonation of **5**.

References

- (a) Tard C, Pickett CJ. Chem Rev. 2009; 109:2245–2274. [PubMed: 19438209] (b) Gloaguen F, Rauchfuss TB. Chem Soc Rev. 2009; 38:100–108. [PubMed: 19088969] (c) Vincent KA, Parkin A, Armstrong FA. Chem Rev. 2007; 107:4366–4413. [PubMed: 17845060] (d) Thomas CM, Liu TB, Hall MB, Darensbourg MY. Inorg Chem. 2008; 47:7009–7024. [PubMed: 18597449]
- (a) Smith JM, Lachiotte RJ, Pittard KA, Cundari TR, Rodgers KR, Lukat-Rodgers G, Lachiotte RJ, Flaschenriem CJ, Vela J, Holland PL. J Am Chem Soc. 2006; 123:756–769. [PubMed: 16417365] (b) Smith JM, Sadique AR, Cundari TR, Pittard KA, Lukat-Rodgers G, Rodgers KR, Holland PL. J

- Am Chem Soc. 2001; 123:9222–9223. [PubMed: 11552855] (c) Holland PL. Can Journal Chem. 2005; 83:296–301.
3. (a) Betley TA, Peters JC. J Am Chem Soc. 2004; 126:6252–6254. [PubMed: 15149221] (b) Hendrich MP, Gunderson W, Behan RK, Green MT, Mehn MP, Betley TA, Lu CC, Peters JC. Proc Natl Acad Sci. 2006; 103:17107–17112. [PubMed: 17090681] (c) Mankad NP, Whited MT, Peters JC. Angew Chem Int Ed. 2007; 46:5768–5771. (d) Brown SD, Betley TA, Peters JC. J Am Chem Soc. 2003; 125:322–323. [PubMed: 12517130]
4. (a) Betley TA, Peters JC. J Am Chem Soc. 2003; 125:10782–10783. [PubMed: 12952446] (b) Lee Y, Mankad NP, Peters JC. Nature Chemistry. 2010; 2:558–565. (c) Whited MT, Mankad NP, Lee Y, Oblad PF, Peters JC. Inorg Chem. 2009; 48:2507–2517. [PubMed: 19209938] (d) Brown SD, Mehn MP, Peters JC. J Am Chem Soc. 2005; 127:13146–13147. [PubMed: 16173733] (e) Lee Y, Peters JC. J Am Chem Soc. 2011; 133:4438–94446. [PubMed: 21375250]
5. Kubas GJ. Chem Rev. 2007; 107:4152–4205. [PubMed: 17927158]
6. For the few cases where H₂ has been suggested to be coordinated to an open-shell metal center, see: (a) Hetterscheid DGH, Hanna BS, Schrock RR. Inorg Chem. 2009; 48:8569–8577. [PubMed: 19639973] (b) Kinney RA, Hetterscheid DGH, Schrock RR, Hoffman BM. Inorg Chem. 2010; 49:704–713. [PubMed: 20000748] (c) Bart SC, Lobkovsky E, Chirik PJ. J Am Chem Soc. 2004; 126:13794. [PubMed: 15493939] (d) Baya M, Houghton J, Daran JC, Poli R, Male L, Albinati A, Gutman M. Chem Eur J. 2007; 13:5347.
7. (a) Heinekey DM, Lledós A, Lluch J. Chem Soc Rev. 2004; 33:175–182. [PubMed: 15026822] (b) Jessop PG, Morris RH. Coord Chem Rev. 1992; 121:155–284. (c) Morris RH. Coord Chem Rev. 2008; 252:2381–2394.
8. (a) Bersuker, IB. The Jahn-Teller Effect. 1. Cambridge University Press; Cambridge: 2006. (b) McNaughton RL, Roemelt M, Chin JM, Schrock RR, Neese F, Hoffman BM. J Am Chem Soc. 2010; 132:8645. [PubMed: 20429559]
9. Doan PE. J Mag Res. 2011; 208:76–86.
10. As expected, DFT calculations show that an isomer with one H-atom on Si and on H-atom on iron, (HSiPⁱPr₃)Fe(H), is energetically inaccessible relative to either (SiPⁱPr₃)Fe(H₂) or (SiPⁱPr₃)Fe(H)₂ isomers.
11. Gurbiel RJ, Bolin JT, Ronco AE, Mortenson L, Hoffman BM. J Mag Res. 1991; 91:227–240.
12. Ammeter JH. J Mag Res. 1978; 30:299–325.
13. Cambridge Structural Data Base (CSD).
14. Bruno IJ, Cole JC, Edgington PR, Kessler M, Macrae CF, McCabe P, Pearson J, Taylor R. Acta Cryst. 2002; B58:389–397.
15. McConnell HM. J Chem Phys. 1958; 29:1422.
16. Eckert J, Kubas GJ. J Phys Chem. 1993; 97:2378–2384.

Figure 1.
 ^1H -NMR spectra of A) $(\text{SiP}^i\text{Pr}_3)\text{Fe}(\text{N}_2)$ (**2**) B), $(\text{SiP}^i\text{Pr}_3)\text{Fe}(\text{H}_2)$ (**3**), C) **3** under full vacuum and D) a mixture of **2** and **3** measured in C_6D_6 at room temperature.

Figure 2.

(A) Displacement ellipsoid (50%) representation of (SiPⁱPr₃)Fe(H₂) (**3**) obtained from a crystal grown under an H₂ atmosphere. Hydrogen atoms have been removed from SiPⁱPr₃ for clarity. (B) Overlay of the closely related core structures of **2** (blue) and **3** (red).

Figure 3.

Q-band stochastic 2D field-frequency CW ENDOR pattern for **3** (black) with simulations of the exogenous ' H_2 ' ^1H ENDOR response (red, see text for details). The corresponding ^2H ENDOR spectrum collected from **3'** at $g_3 = 2.015$ (blue) is scaled by the ratio of the ^1H and ^2H nuclear g values. The star at selected fields corresponds to an ENDOR response from the phosphorous nuclei in the $[\text{SiPiPr}_3]^-$ ligand.

Figure 4.

Simulations of ¹H ENDOR spectra for models of **3**, for the spectrum at $g = 2.146$. The simulations are based on the hyper-fine tensor determined through a fit to the 2D field frequency plot of Figure 3 ($\mathbf{A} = [2.3, -40.6, -37.8]$ MHz), but with the dipolar interaction rotated by the angle (β) between the hydrogen nuclei and the g_1 axis, which is taken to lie along the Fe-Si bond (g_1).

Figure 5.
A schematic representation of H₂ hopping/tunneling on the potential energy surface for PJT-distorted **3**.

Scheme 1.

Table 1

Select data for complexes discussed in the text.

Complex	d _{FeSi} (Å)	d _{FeP} (Å)	∠PFeP	μ _{eff} ^c
Fe(N ₂) 2	2.2713(6)	2.2657(5)	111.82(2)	1.90
		2.2841(7)	113.59(2)	
		2.3244(6)	128.64(2)	
Fe(CO)	2.2942(4)	2.2620(4)	114.88(2)	1.86
		2.2752(4)	117.63(2)	
		2.2909(4)	120.91(2)	
Fe(H ₂) 3^a	2.254(1)	2.2442(9)	113.31(3)	1.88
		2.260(1)	118.07(3)	
		2.2631(9)	122.36(4)	
Fe(H ₂) 3^b	2.2478(3)	2.2418(3)	113.157(9)	
		2.2577(3)	117.63(1)	
		2.2613(2)	123.16(1)	

^aData was obtained from a crystal grown under vacuum.^bData was obtained from a crystal grown under H₂ atmosphere.^cMagnetic moments obtained in C₆D₆ by the method of Evans at 22 °C.