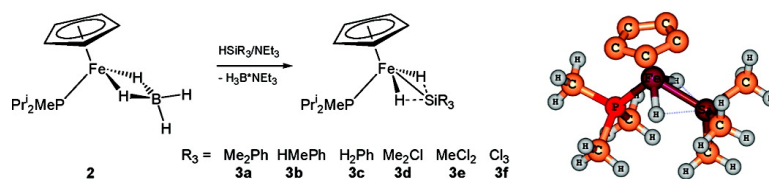


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Cp(*Pr*₂MeP)FeH₂SiR₃: Nonclassical Iron Silyl Dihydride

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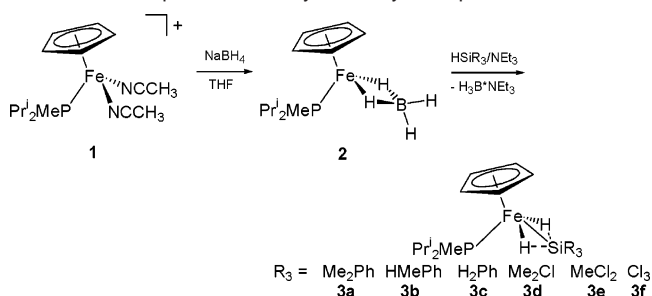
The skyrocketing price of precious metals and their recognized toxicity pose a question of finding cheaper and environmentally benign alternatives for applications in catalysis.^{1,2} The abundant and nontoxic iron is particularly attractive to serve as a “cheap metal for a noble task”,² such as hydrosilylation.³ Though Cp(OC)₂FeSiMe₃ was the first transition metal silyl complex⁴ and some iron hydrosilylation catalysts are available,^{1,3a,b} relatively little is known about iron hydrido silyl complexes.^{5–7} All Fe(II) derivatives appear to be classical silyl hydrides,^{5,6} whereas formally Fe(I),⁸ Fe(III),⁹ and many Fe(IV) complexes are in fact η²-HSiR₃^{10,11} or η³-H₂SiR₂ silane σ-complexes.^{1,12} Although X-ray study of formally Fe(IV) complexes (arene)FeH₂(SiX₃)₂ (X = F, Cl) suggested their classical structures,⁷ a recent DFT study of the isoelectronic rhodium derivative CpRhH₂(SiMe₃)₂ revealed the presence of significant Si–H interactions.¹³ The related half-sandwiches Cp(OC)FeH(SiX₃)₂,¹⁴ long believed to be classical Fe(IV) species,¹⁵ actually have highly delocalized Si···H···Si bonding.^{11d,16} Assuming that electron donating ligands could stabilize an Fe(IV) center, we targeted the preparation of the so far unknown class of dihydride silyl complexes Cp(R₃P)FeH₂(SiR₃). Their X-ray and DFT studies provide evidence for a novel H···SiR₃···H bonding and reveal an unusual mode of silane Si–H activation⁵ on the Cp(R₃P)FeH moiety.

The treatment of [Cp(*Pr*₂MeP)Fe(NCCH₃)₂]⁺[BF₄][–] (**1**) with NaBH₄ in THF affords a highly unstable complex Cp(*Pr*₂MeP)Fe(BH₄) (**2**), which is a rare example of an iron borohydride.^{17,18} Reactions of the *freshly* prepared **2** with silanes in the presence of NEt₃ afford the dihydride silyl derivatives **3a–f** unavailable previously (Scheme 1). Complex **1** catalyzes hydrosilylation of benzaldehyde by H₃SiPh (5% load, 3h, 22 °C), whereas catalysis by **3b** requires heating at 50 °C (H₂SiMePh, 5% load of **3b**, 12 h). In contrast, bulkier complex **3a** is inactive.

The compounds **3** were isolated in the form of yellow oils (**3b**, **c**) or crystals (**3a**, **d–f**) and studied by spectroscopic methods and X-ray analysis of **3e** and **3f**. In the ¹H NMR spectrum of **3f**, the equivalent hydrides give rise to a doublet at –13.93 ppm (*J*(P–H) = 25 Hz) flanked by ²⁹Si satellites. The ²⁹Si NMR displays a doublet of triplets at –13.8 ppm, (*J*(P–Si) = 14.5 Hz, *J*(H–Si) = 18.9 Hz), a pattern that does not change upon cooling to –80 °C. This can be consistent, in principle, both with a static structure and with a very fast degenerate exchange between two forms of a silane hydride complex: Cp(L)FeH^α(η²-H^βSiR₃) ⇌ Cp(L)Fe(η²-H^αSiR₃)-H^β. Such an exchange was originally postulated for related Rh¹⁹ and Ru²⁰ complexes but was later ruled out for the former on the basis of DFT calculations.¹³

The X-ray structures of **3e** and **3f** (Figure 1) suggest the presence of double Si···H interactions. Complex **3f** has a remarkably short Fe–Si bond of 2.168(1) Å, which is much shorter than the Fe–Si distances in the closely related compounds (η⁶-C₆H₅Me)FeH₂-

Scheme 1. Preparation of Dihydrido Silyl Complexes **3a–f**



(SiCl₃)₂^{7b} (2.220(2) Å) and Cp(OC)FeH(SiCl₃)₂^{14b} (2.252(3) Å) and is comparable to the Fe=Si double bond in the silylene derivative Cp*(OC)Fe(=SiMe₂)(SiMe₃) (2.154(1) Å).²¹ A similar situation has been previously observed for the η³-silane complex [PhB(CH₂Pr₂)₃]FeH(η³-H₂SiMePh),¹² in which a short Fe–Si bond of 2.1280(7) Å is an inevitable consequence of two Si–H bonds being simultaneously coordinated to the iron center.²²

Additional evidence for the occurrence of two interligand Si···H interactions in **3f** comes from the observation of two sets of Si–Cl bonds: those two lying *trans* to the hydrides (the H–Si–Cl bond angle of 153.2°) are noticeably longer than the unique *cis* Si–Cl bond (2.1125(9) vs 2.0835(14) Å, Δ = 0.0290(17) Å).²³ In contrast, in related complexes Cp(OC)FeH(SiCl₃)₂ and (η⁶-C₆H₆)FeH₂(SiCl₃)₂ both Si–Cl bonds are short and almost identical (2.048–2.061(4) Å and 2.072–2.079(2) Å). Finally, two hydrides, strongly tilted toward the silyl group to make a H–Si distance of 1.88(3) Å, were observed. Compared with the accurate ND values for terminal Fe–H bonds (1.526(12)–1.609(2) Å),²⁴ the Fe–H distance of 1.35(3) Å is obviously subject to a systematic foreshortening, pertinent to the X-ray diffraction method.²⁵ However, estimation shows that elongation of the Fe–H bond to 1.6 Å would result in an increase of the Si–H distance only to 1.93 Å.

DFT calculations revealed unusual features of silane H³–SiMe₃ addition to Cp(Me₃P)FeH.² Activation proceeds without barrier and starts at an Fe–Si separation of about 3.0 Å by the formation of an η¹-silane σ-complex characterized by the Fe–H³ bond of 1.692 Å (Mayer index (MI) of 0.37) and the Si–H³ bond of 1.641 Å (*J*(H³–Si) = –115.9 Hz, MI = 0.52). At an Fe–Si distance of 2.65 Å, the Si–H³ bond is significantly weakened (1.930 Å, *J*(H³–Si) = –51.7 Hz, MI = 0.39) but the Si···H² interaction starts to build up. At about this point, the sign of *J*(H²–Si) turns negative²⁶ (–0.7 Hz) and a significant value of the MI is achieved (0.11). The equilibrium structure **4** shows the presence of *two simultaneous and equivalent Si···H interactions* characterized by the Si–H distances of 2 Å and increased MIs of 0.18 (Table 1).

Double Si–H bonding has precedents in the SISHA^{11e} interactions between a hydride and η²-silane ligands, in which two Si–H interactions are not equivalent. The most remarkable new feature of the *equivalent Si–H interactions* in complexes **3** is that the extent

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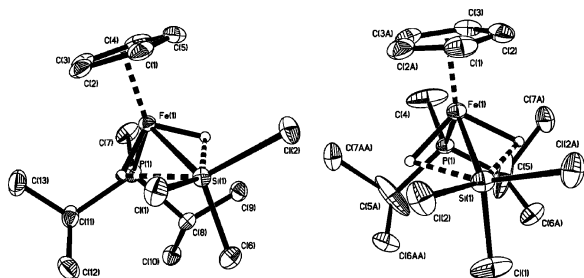


Figure 1. Molecular structures (bond lengths in Å) of compounds **3e** and **3f** (local C_s symmetry; only one rotamer of the disordered Pr^f group is shown). Hydrogen atoms apart from hydrides are omitted. **3e**: Fe–Si 2.1948(6), Fe1–P1 2.2089(6), Fe1–H1 1.37(2), Fe1–H2 1.43(2), Si1–H1 1.90(2), Si1–H2 1.91(2), Si1–Cl1 2.1355(7), Si1–Cl2 2.1378(7). **3f**: Fe–Si 2.168(1), Fe1–P1 2.2165(9), Fe–H 1.35(3), Si1–H1 1.88(3), Si1–Cl1 2.0835(14), Si1–Cl2 2.1125(9).

Table 1. Calculated Bond Lengths (in Å)/Mayer Bond Indices and Si–H Coupling Constants (in Hz) for the Most Stable Isomers of **4–7**

bond	4 ^a	5 ^b	6 ^c	7 ^a
Fe–Si	2.320/0.74	2.262/0.79	2.222/0.81	2.194/0.89
Fe–H ²	1.513/0.70	1.507/0.70	1.508/0.69	1.512/0.70
Fe–H ³	1.511/0.70	1.507/0.70	1.514/0.70	1.512/0.70
Si–H ²	2.000/0.18	2.007/0.16	1.994/0.18	1.995/0.17
Si–H ³	1.984/0.18	2.007/0.16	1.991/0.17	1.995/0.17
Si–Cl(t)	-	-	2.152/0.84	2.122/0.87
Si–Cl(c)	-	2.171/0.82	2.146/0.83	2.126/0.85
$J(\text{Si–H}^2)$	–23.5	–22.9	–42.4	–10.1
$J(\text{Si–H}^3)$	–24.3	–22.9	+1.3	–10.1
J_{ave}^d	–23.9 (21.6)	–20.3 (21.9)	–17.3(19.2)	–10.1(18.9)

^a C_s structure. ^b C_s structure with the Cl group *cis* to hydrides; ^c Cl(c) is *cis* to hydrides, Cl(t) is *trans* to H³. ^d Weighted according to the Boltzmann population of three rotamers at 298 K, experimental data in parentheses.

of bonding does not depend on the substitution at Si (Table 1) and the orientation of the silyl group.²⁷ In the related silane σ -complexes^{5,11} and complexes with interligand hypervalent interactions (IHI),^{11d} electron-withdrawing groups on Si tend to weaken the Si–H bonding, which is not the case for model complexes Cp(Me₃P)FeH₂(SiMe_{3–n}Cl_n) ($n = 0–4$, **4–7**). The IHI additionally requires the presence of an accepting group *trans* to the hydride, but the data of Table 1 show that such a stereochemical condition does not hold for **4–7**. And in fact rotamers **5a,b**²⁷ have the longest Si–H bond to the hydride that is *trans* to the Cl substituent.

Calculation of significant attractive values of Mayer diatomic energies²⁸ (range from –40.4 to –44.6 kcal·mol^{–1}) unambiguously proves the existence of Si \cdots H interactions in **4–7**. A large proportion of this energy results from the interatomic exchange, indicating that this Si \cdots H attraction has a substantial covalent character.

Another unusual feature of the multicentral bonding in **3–7** is that substitution at silicon does not affect the value of $J(\text{Si–H})$. The experimental coupling constants are close to 20 Hz and decrease only slightly in magnitude from **3a** to **3f** (Table 1), as do averaged calculated values. The $J(\text{H–Si})$ for individual Si–H pairs vary largely in the range 0–40 Hz and are negative, suggesting a direct Si–H bonding.²⁶ The largest magnitude of $J(\text{H–Si})$ is observed for the hydride located *cis* to the chloride group on silicon.²⁹ Tentatively, we describe these unique^{30,31} multicentral Si \cdots H interactions in terms of adduct formation between the hypervalent anion [H₂SiR₃][–] and [Cp(L)Fe]⁺, i.e., as Cp(L)Fe(η^3 -H₂SiR₃).¹⁶

In conclusion, silane Si–H activation on Cp(Pr^{*i*}₂MeP)FeH proceeds differently from the conventionally postulated Si–H oxidative addition or silane σ -complexation. It starts primarily from the Si–H \rightarrow Fe donation, but at a later stage it also involves significant interaction between the silyl and metal-bound hydride, resulting in a structure with novel H \cdots SiR₃ \cdots H bonding.

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Supporting Information Available: Experimental and computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>

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