

(MeQn₂SiH)Fe[N(SiMe₃)₂]₂ (Qn = 8-quinolyl): an unusual δ -agostic iron complex containing an η^1 -SiH interaction†

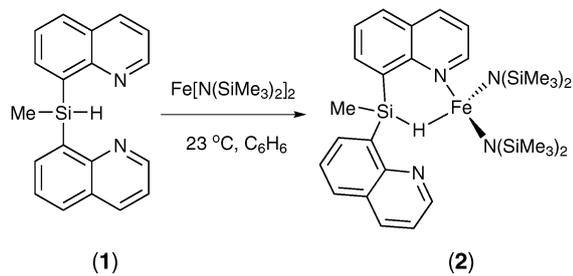
Jian Yang, Meg Fasulo and T. Don Tilley*

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Reaction of MeQn₂SiH (Qn = 8-quinolyl) (1) with Fe[N(SiMe₃)₂]₂ at room temperature afforded (MeQn₂SiH)Fe[N(SiMe₃)₂]₂ (2), which is an unusual example of a δ -agostic iron complex containing an η^1 -H-Si interaction. Treatment of 2 with excess 3-pentanone at 60 °C produced MeQn₂SiOCH₂Et₂ (3) in ca. 80% yield.

The chemistry of σ -silane complexes has attracted much interest because such species are highly relevant to Si-H bond activation and are frequently invoked as intermediates for catalytic silylation reactions.^{1,2} Understanding the coordination of the Si-H bond to first row metals is particularly interesting since it can provide insights into catalytic Si-H activation processes utilizing these inexpensive metals. Indeed, two notable examples of olefin hydrosilylation catalyzed by first row metals seem to involve σ -silane complexes as intermediates.³ Furthermore, most of the isolable σ -silane complexes exhibit η^2 -H-Si interactions with significant metal-silicon interaction.² In this contribution, we report the synthesis and structural characterization of an unusual δ -agostic iron complex incorporating an η^1 -H-Si interaction.^{4,5}



(1)

Reaction of bis(8-quinolyl)methylsilane⁶ (1) with Fe[N(SiMe₃)₂]₂⁷ at room temperature afforded a paramagnetic complex 2 in 86% isolated yield (eqn (1)). X-Ray quality crystals of 2 were obtained from a concentrated Hexanes solution at -30 °C. The ORTEP diagram is shown in Fig. 1.† The bis(8-quinolyl)methylsilane ligand is coordinated to the Fe(II) center in a chelate fashion *via* donation from a quinolyl group and from an agostic Si-H bond. The other quinolyl group is not bound to the iron center, presumably because of the steric crowding imposed by two bis(trimethylsilyl)amide ligands. The coordination geometry for the

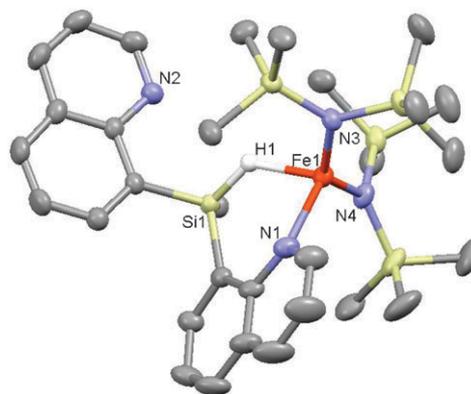


Fig. 1 Molecular structure of 2 with thermal ellipsoids drawn at the 50% probability level. Key bond distances (Å) and angles (°): Fe(1)-H(1) = 1.926(17), Si(1)-H(1) = 1.464(17), Si(1)···Fe(1) = 3.06(2), Fe(1)-N(1) = 2.1486(16), Fe(1)-N(3) = 1.9656(15), Fe(1)-N(4) = 1.9550(15), Fe(1)-H(1)-Si(1) = 128.6(7), N(4)-Fe(1)-N(3) = 136.46(7), N(4)-Fe(1)-N(1) = 115.72(7), N(3)-Fe(1)-N(1) = 101.46(6).

iron center is a highly distorted tetrahedron, as indicated by the nearly planar arrangement of donor nitrogen atoms [Σ (N-Fe-N) = 353.65°]. The most interesting feature of 2 is the coordinated Si-H bond. The Si-H bond length of 1.464(17) Å is normal; however, the Fe-H bond of 1.926(17) Å is rather long. The Fe···Si distance of 3.06(2) Å is well beyond the sum of covalent radii for Fe and Si (2.63 Å)⁸ and the Fe-H-Si angle is about 128.6(7)°, suggesting an η^1 -H-Si coordination mode with no appreciable Fe···Si interaction. A very similar bonding situation has been reported for [(POCOP)Ir(H)(Et₃SiH)]⁺[B(C₆F₅)₄]⁻ (POCOP = 2,6-[OP(*t*Bu)₂]₂C₆H₃),⁴ in which η^1 -coordination of Et₃SiH to the cationic Ir center has been investigated by structural, spectroscopic, and computational studies.

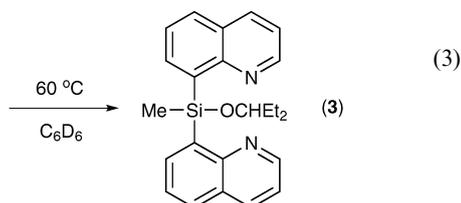
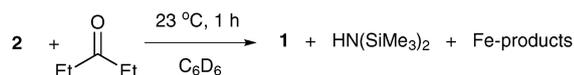
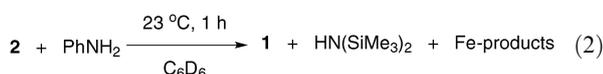
In most transition-metal η^2 -silane complexes, the metal-silicon distances remain relatively short and the silicon-hydrogen bond is substantially elongated.² For example, Sabo-Etienne *et al.* have recently described the agostic Ru complex Ru{ η^2 -H-SiMe₂CH(*o*-C₆H₄)PPh₂}₂ with Ru-Si (ca. 2.45 Å) and Si-H (ca. 1.71 Å) bond distances that are typical for η^2 -H-Si interactions.⁹ Also for comparison, Chirik's iron σ -silane complex (ⁱPrPDI)Fe(η^2 -PhSiH₃)₂ (ⁱPrPDI = (2,6-CHMe₂)₂C₆H₃N=CMe₂C₃H₃N), in which two η^2 -H-Si bonds are coordinated to iron, exhibits a short Fe-Si bond [2.3266(8) Å] and a long Si-H bond [1.82(3) Å], while the other coordinated silane is less activated and associated with a longer Fe-Si bond [2.4733(7) Å] and a shorter Si-H

Department of Chemistry, University of California, Berkeley, California 94720, USA. E-mail: dttilley@berkeley.edu

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bond [1.59(2) Å].^{3b} Note that complex **2**, characterized by a much longer Fe...Si distance, a normal Si–H bond, a long Fe–H bond, and a large Fe–H–Si angle, may model a very early stage of oxidative addition of a Si–H bond to a transition-metal center.^{2d}

The reactivity of **2** toward a few organic molecules has been briefly explored. While no reaction was observed between **2** and 1-hexene at 23 °C over 1 d in benzene-*d*₆, addition of aniline to **2** resulted in rapid formation of HN(SiMe₃)₂ and release of free **1**, as observed by ¹H and ¹³C NMR spectroscopy (eqn (2)). Similarly, treatment of a benzene-*d*₆ solution of **2** with 3-pentanone (4.15 equiv.) at 23 °C resulted in formation of **1** and HN(SiMe₃)₂. Heating this reaction mixture to 60 °C for 6 d afforded the corresponding hydrosilylation product Qn₂MeSiOCHEt₂ (**3**) in ca. 80% yield§ (eqn (3)).¹⁰ The paramagnetic iron-containing products for these reactions have yet to be identified.



In summary, we report here an unusual example of a δ-agostic iron complex containing an η¹-H–Si interaction. The structural data suggest that it may model the early stage of oxidative addition of an Si–H bond to an unsaturated metal fragment. Further studies are ongoing to explore stoichiometric and catalytic reactions involving such species.

Experimental

(MeQn₂SiH)Fe[N(SiMe₃)₂]₂ (**2**)

A benzene (3 mL) solution of **1**⁶ (0.086 g, 0.286 mmol) was added to a solution of Fe[N(SiMe₃)₂]₂⁷ (0.108 g, 0.287 mmol) in benzene (3 mL). The light green solution immediately turned dark red. After stirring at room temperature for 2 h, all volatiles were removed *in vacuo*. The red-violet solid was washed with cold pentane (1 mL × 2) and dried *in vacuo* to yield **2** (0.166 g, 0.245 mmol, 86%). ¹H NMR (C₆D₆, 600.13 MHz): δ 28.1, 18.4, 8.2, –4.6. Anal. calcd (%) for C₃₁H₅₂N₄Si₃Fe (677.04): C, 54.99, H, 7.74, N, 8.28. Found: C, 55.27, H, 7.66, N, 8.02%. Magnetic susceptibility: μ_{eff} = 5.13 μ_B (C₆D₆). Crystals suitable

for X-ray analysis were grown from a concentrated hexanes solution of **2** at –30 °C.

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Notes and references

‡ Crystal data for **2**: C₃₁H₅₂FeN₄Si₃, *M* = 677.07, triclinic, space group *P* $\bar{1}$, *a* = 11.3439(8), *b* = 11.7230(8), *c* = 14.6618(0) Å, α = 86.7540(10)°, β = 85.8280(10)°, γ = 83.0680(10)°, *V* = 1928.2(2) Å³, *Z* = 2, *T* = 138(2) K, 49 035 reflections collected, 7057 unique (*R*_{int} = 0.0397), *R*₁ = 0.0329, *wR*₂ = 0.0912, *R* indices based on 7057 reflections with *I* > 2σ(*I*) (refinement on *F*²).

§ Determined by ¹H NMR relative to Me₄Si as an internal standard. Characterization data of **3**: δ_H (600 MHz; C₆D₆) 8.58 (2H, dd, *J* 4 and 2), 8.30 (2H, dd, *J* 7 and 2), 7.53 (2H, dd, *J* 8 and 2), 7.45 (2H, dd, *J* 8 and 2), 7.25 (2H, dd, *J* 8 and 7), 6.70 (2H, dd, *J* 8 and 4) (aryl hydrogens, total 12H), 4.39 (1H, quintet, *J* 6), 1.73–1.62 (4H, m), 1.60 (3H, s, SiCH₃), 0.93 (6H, t, *J* 8). δ_C (151 MHz; C₆D₆): 153.6, 149.5, 141.1, 138.9, 136.3, 129.7, 126.9, 120.9 (aryl carbons, one resonance is obscured by C₆D₆), 76.2, 30.2, 10.5, 2.79 (Si–CH₃). δ_{Si} (119 MHz; C₆D₆): –4.5. GC-MS *m/z* 386 (*M*⁺), 371, 315, 299, 283, 272, 256, 242, 228, 215, 207, 188.

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- A control experiment shows that there is no appreciable reactivity of **1** towards 3-pentanone at 60 °C over 2 d with or without the presence of HN(SiMe₃)₂.