$(MeQn_2SiH)Fe[N(SiMe_3)_2]_2$ (Qn = 8-quinolyl): an unusual δ-agostic iron complex containing an η^1-SiH interaction†

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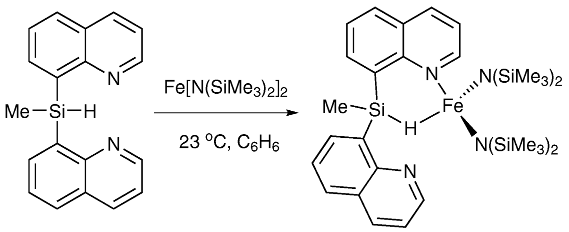
Reaction of $MeQn_2SiH$ (Qn = 8-quinolyl) (1) with $Fe[N(SiMe_3)_2]_2$ at room temperature afforded $(MeQn_2SiH)Fe[N(SiMe_3)_2]_2$ (2), which is an unusual δ-agostic iron complex containing an η^1-H–Si interaction. Treatment of 2 with excess 3-pentanone at 60 °C produced $MeQn_2SiOCHEt_2$ (3) in *ca.* 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) **(2)**

(1)

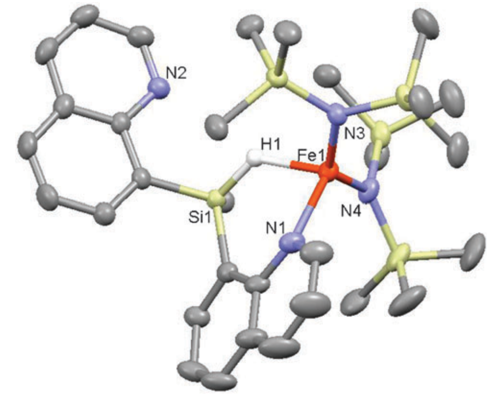


Fig. 1 Molecular structure of **2** with thermal ellipsoids drawn at the 50% probability level. Key bond distances (Å) and angles (°): Fe(1)–H(1) = 1.926(17), Si(1)–H(1) = 1.464(17), Si(1)···Fe(1) = 3.06(2), Fe(1)–N(1) = 2.1486(16), Fe(1)–N(3) = 1.9656(15), Fe(1)–N(4) = 1.9550(15), Fe(1)–H(1)–Si(1) =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

Reaction of bis(8-quinolyl)methylsilane[6] **(1)** with $Fe[N(SiMe_3)_2]_2$[7] 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 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 $[(POCOP)Ir(H)(Et_3SiH)]^+[B(C_6F_5)_4]^-$ (POCOP = 2,6-$[OP(tBu)_2]_2C_6H_3$),[4] in which η^1-coordination of Et_3SiH 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 $Ru\{\eta^2\text{-H–SiMe}_2CH(o\text{-}C_6H_4)PPh_2\}_2$ 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 $(^{iPr}PDI)Fe(\eta^2\text{-}PhSiH_3)_2$ (^{iPr}PDI = $(2,6\text{-}CHMe_2)_2C_6H_3N{=}CMe)_2C_5H_3N$), 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

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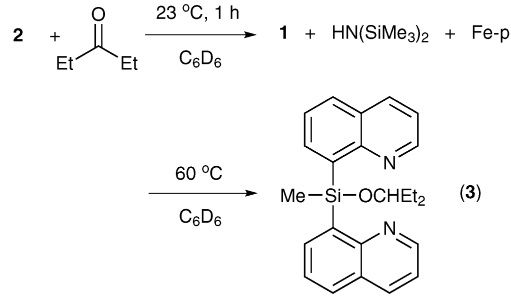
bond [1.59(2) Å].[3b] Note that complex **2**, characterized by a much longer Fe···Si distance, a normal Si–H bond, a long Fe–H bond, and a large Fe–H–Si angle, may model a very early stage of oxidative addition of a Si–H bond to a transition-metal center.[2d]

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 $HN(SiMe_3)_2$ and release of free **1**, as observed by ^1H and ^{13}C 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 $HN(SiMe_3)_2$. Heating this reaction mixture to 60 °C for 6 d afforded the corresponding hydrosilylation product $Qn_2MeSiOCHEt_2$ (**3**) in *ca.* 80% yield§ (eqn (3)).[10] The paramagnetic iron-containing products for these reactions have yet to be identified.

$$\mathbf{2} + \mathrm{PhNH_2} \xrightarrow[\mathrm{C_6D_6}]{23\ ^\circ\mathrm{C},\ 1\ \mathrm{h}} \mathbf{1} + \mathrm{HN(SiMe_3)_2} + \text{Fe-products} \quad (2)$$



(3)

In summary, we report here an unusual example of a δ-agostic iron complex containing an η^1-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

$(MeQn_2SiH)Fe[N(SiMe_3)_2]_2$ (2)

A benzene (3 mL) solution of **1**[6] (0.086 g, 0.286 mmol) was added to a solution of $Fe[N(SiMe_3)_2]_2$[7] (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 (C_6D_6, 600.13 MHz): δ 28.1, 18.4, 8.2, −4.6. Anal. calcd (%) for $C_{31}H_{52}N_4Si_5Fe$ (677.04): C, 54.99, H, 7.74, N, 8.28. Found: C, 55.27, H, 7.66, N, 8.02%. Magnetic susceptibility: $\mu_{eff} = 5.13\ \mu_B$ (C_6D_6). 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**: $C_{31}H_{52}FeN_4Si_5$, $M = 677.07$, triclinic, space group $P\bar{1}$, $a = 11.3439(8)$, $b = 11.7230(8)$, $c = 14.6618(0)$ Å, $\alpha = 86.7540(10)^\circ$, $\beta = 85.8280(10)^\circ$, $\gamma = 83.0680(10)^\circ$, $V = 1928.2(2)$ Å^3, $Z = 2$, $T = 138(2)$ K, 49 035 reflections collected, 7057 unique ($R_{int} = 0.0397$), $R_1 = 0.0329$, w$R_2 = 0.0912$, R indices based on 7057 reflections with $I > 2\sigma(I)$ (refinement on F^2).

§ Determined by ^1H NMR relative to Me_4Si as an internal standard. Characterization data of **3**: δ_H (600 MHz; C_6D_6) 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, SiCH_3), 0.93 (6H, t, *J* 8). δ_C (151 MHz; C_6D_6): 153.6, 149.5, 141.1, 138.9, 136.3, 129.7, 126.9, 120.9 (aryl carbons, one resonance is obscured by C_6D_6), 76.2, 30.2, 10.5, 2.79 (Si–CH_3). δ_{Si} (119 MHz; C_6D_6): −4.5. GC-MS *m*/*z* 386 (M^+), 371, 315, 299, 283, 272, 256, 242, 228, 215, 207, 188.

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10 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 $HN(SiMe_3)_2$.