

## Effective Control of Two Elimination Processes from a Hydridobis(silyl)iron(IV) Complex

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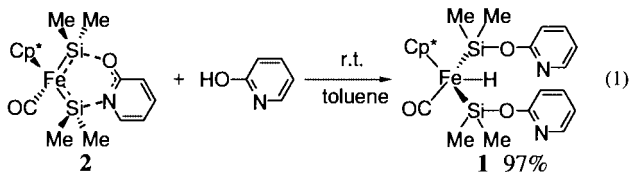
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A novel hydridobis(silyl)iron(IV) complex  $\text{Cp}^*(\text{CO})\text{Fe}(\text{H})\{\text{SiMe}_2\text{O}(2\text{-C}_5\text{H}_4\text{N})\}_2$  (**1**) ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) was synthesized in high yield. Two elimination processes from **1** were effectively controlled by the reaction conditions:  $\text{HSiMe}_2\text{O}(2\text{-C}_5\text{H}_4\text{N})$  is eliminated on heating or UV-irradiation, whereas  $\text{HO}(2\text{-C}_5\text{H}_4\text{N})$  is eliminated in the presence of  $\text{Et}_3\text{Al}$ . The latter reaction was applied to a "silylene introduction" toward a silyl complex producing a silyl(silylene) complex.

The reactivity of transition metal complexes containing metal–silicon bonds is attracting much attention. One of the reasons is that it could give grounds for the mechanisms of various transition-metal-mediated transformation of organosilicon compounds.<sup>1</sup> Among them, hydridobis(silyl) complex  $\text{L}_n\text{MH}(\text{SiR}_2\text{X})_2$  is considered as an important species because it is easily formed by the oxidative addition of hydrosilanes to a coordinatively unsaturated silyl complex, and is regarded as a key intermediate of the transition-metal-catalyzed polymerization of hydrosilanes.<sup>2</sup> Several different reaction patterns have been reported separately for this species, but, to our knowledge, there is no report on the attempt to control the reaction pathway by changing the reaction conditions. We report here a quantitative preparation of a stable hydridobis(2-pyridyloxysilyl)iron(IV) complex from a 2-pyridyloxy-bridged bis(silylene)iron complex,<sup>3</sup> and effective control of two elimination processes from this species, reductive elimination of hydrosilane and 1,2-elimination of 2-hydroxypyridine.

A hydridobis(2-pyridyloxysilyl)iron(IV) complex **1**<sup>4</sup> was prepared quantitatively by addition of 2-hydroxypyridine to an internal-base-stabilized bis(silylene)iron complex **2**<sup>3</sup> (eq 1).

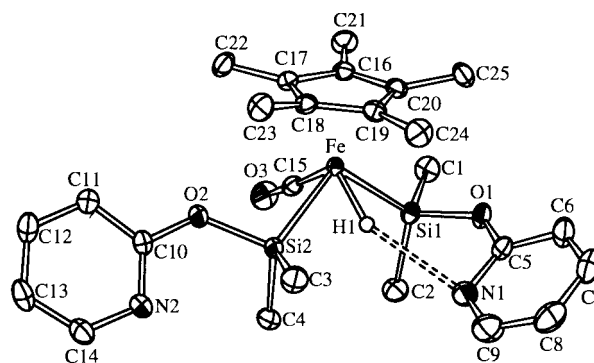


The addition appears to occur selectively to the Fe–Si bond on the N-side, although another route; i.e., addition to the Fe–Si bond on the O-side followed by 1,3-shift of Si from N to O, cannot be ruled out.

The <sup>29</sup>Si NMR spectrum of **1** shows only one signal at  $\delta = 64.2$  ppm, which is consistent with the geometry in which two silyl groups are mutually *trans*. It was further confirmed by X-ray crystal structure analysis (Figure 1).<sup>5</sup>

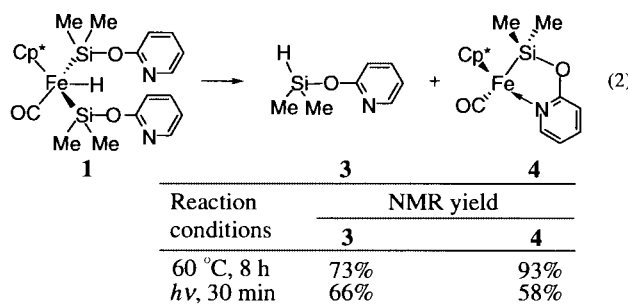
The lengths of two Fe–Si bonds are 2.3206(6) Å and 2.3178(6) Å, which are both in the range of normal single bonds (2.32–2.37 Å).<sup>1a</sup> The distance between a hydride attached to Fe and a nitrogen atom of one of pyridyloxy groups

was 2.58(3) Å, which is slightly shorter than the sum of the van der Waals radii of the two atoms, 2.70 Å.<sup>6</sup> There may be weak hydrogen bonding between a polarized  $\text{Fe}^{\delta-}\text{H}^{\delta+}$  bond and a negatively polarized nitrogen, though we could not find any examples of the hydrogen bonding of the type  $\text{M}-\text{H}\cdots\text{N}$  in the database of the Cambridge Crystallographic Data Centre.



**Figure 1.** Molecular structure of **1** with 50% thermal ellipsoids. Selected atomic distances (Å) and angles (°): Fe–H1 1.46(3), Fe–C15 1.721(2), C15–O3 1.162(3), Fe–Si1 2.3206(6), Fe–Si2 2.3178(6), Si1–O1 1.700(2), Si2–O2 1.711(2), O1–C5 1.344(3), O2–C10 1.350(3), C5–N1 1.326(3), C10–N2 1.327(3), N1–H1 2.58(3), Fe–C15–O3 176.7(2), Si1–Fe–C15 81.94(7), Si2–Fe–C15 81.37(8), Si1–Fe–H1 57(1), Si2–Fe–H1 61(1), Si1–Fe–Si2 107.41(2), Fe–H1–N1 154(1).

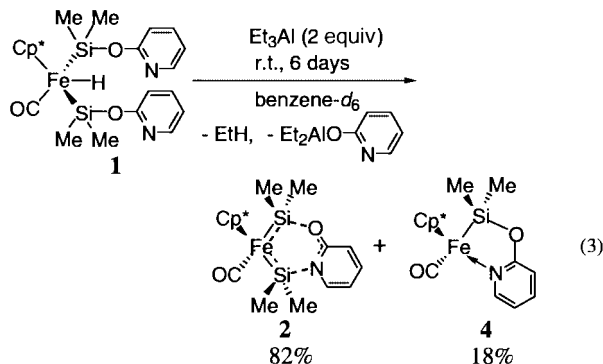
Complex **1** is stable at room temperature in hydrocarbon solvents, while it undergoes reductive elimination of hydrosilane  $\text{HSiMe}_2\text{O}(2\text{-C}_5\text{H}_4\text{N})$  (**3**)<sup>7</sup> on heating or UV-irradiation to afford a chelate complex **4** (eq 2).<sup>8</sup>



The reductive elimination in eq 2 proceeds irreversibly: **1** was not observed even when **4** was heated or irradiated in the presence of excess hydrosilane **3**. This means that the equilibrium of the reaction in eq 2 lies far to the right and the irreversibility is apparently due to the chelate effect. The detailed structure and reactivity of **4** will be reported elsewhere.

When **1** was treated with a small excess of  $\text{Et}_3\text{Al}$  (2 equiv) at room temperature, a bis(silylene) complex **2** was formed slowly as a main product by formal elimination of 2-hydroxy-

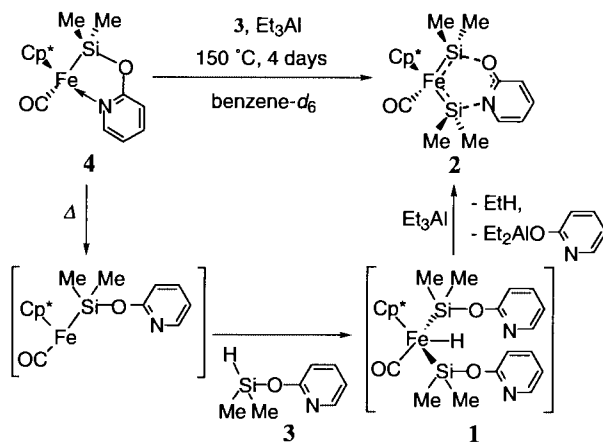
pyridine together with a small amount of reductive elimination product **4** (eq 3).



Generation of a significant amount of ethane was observed by  $^1\text{H}$  NMR during the reaction. Therefore, the actual counterparts of the elimination reaction giving **2** in eq 3 are probably ethane and  $\text{Et}_2\text{AlO}(2\text{-C}_5\text{H}_4\text{N})$ , although the latter has not been identified yet.

There are at least two possible roles conceivable for  $\text{Et}_3\text{Al}$ . The one is to enhance the ability of the 2-pyridyloxy group as a leaving group by coordination to either N or O. This may accelerate the 1,2-elimination of 2-hydroxypyridine. The other is to change the elimination product 2-hydroxypyridine, which has been already demonstrated to be very reactive toward **2** to give **1** as shown in eq 1, to inactive  $\text{Et}_2\text{AlO}(2\text{-C}_5\text{H}_4\text{N})$  and ethane. This makes the 1,2-elimination irreversible. The 1,2-elimination reaction also proceeds more slowly by treatment of **1** with  $\text{Ph}_3\text{B}$  (2 equiv) instead of  $\text{Et}_3\text{Al}$  to give **2** in 82% on conversion of 89% of **1** after 2 weeks at room temperature. Formation of a reasonable amount of benzene was observed in this reaction.

When **4** was combined with **3** (3 equiv) and  $\text{Et}_3\text{Al}$  (1 equiv), and heated up to  $120\text{ }^\circ\text{C}$ , slow formation of **2** was observed. After heating at  $150\text{ }^\circ\text{C}$  for 4 days, **4** mostly disappeared and **2** was obtained in 45% yield. A possible mechanism of this "silylene introduction" reaction is illustrated in Scheme 1. First, from **4** the unsaturated metal center is thermally generated above  $120\text{ }^\circ\text{C}$  by the cleavage of the Fe–N coordinate bond. Second, hydrosilane **3** undergoes oxidative addition to the unsaturated Fe center to give **1**. Finally, 1,2-



Scheme 1.

elimination of 2-hydroxypyridine from **1** occurs in the presence of  $\text{Et}_3\text{Al}$  to afford **2**. This sequence is a novel route to introduce a silylene fragment to a metal center by means of a hydro(alkoxy)silane, although Roper et al. reported a similar reaction with use of aminohydrosilanes.<sup>9</sup> This "oxidative addition–1,2-elimination" sequence utilizing alkoxy-functionalized hydrosilane could be applied to the preparation of a wide variety of alkoxy-stabilized silylene complexes.

#### References and Notes

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- H. Tobita, T. Sato, M. Okazaki, and H. Ogino, *J. Organomet. Chem.*, **611**, 314 (2000).
- 1**: pale yellow crystals. mp  $88\text{ }^\circ\text{C}$ . Anal. Found: C, 56.87; H, 6.78; N, 5.35%. Calcd for  $\text{C}_{25}\text{H}_{36}\text{FeN}_2\text{O}_3\text{Si}_2$ : C, 57.24; H, 6.92; N, 5.34%.  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  –11.15 (s, 1H, FeH), 1.11 (s, 6H, SiMe), 1.15 (s, 6H, SiMe), 1.56 (s, 15H, Cp\*), 6.40–6.44, 6.64–6.67, 7.05–7.09, 8.11–8.13 (m, aromatic protons).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  9.8 ( $\text{C}_5\text{Me}_5$ ), 10.3 (SiMe), 10.5 (SiMe), 95.3 ( $\text{C}_5\text{Me}_5$ ), 113.4, 116.3, 138.6, 147.9, 163.9 (pyridine ring), 214.7 (FeCO).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (59.6 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  64.2. IR (hexane solution)  $1977$  (w, sh,  $\nu_{\text{FeH}}$ ),  $1934$  (vs,  $\nu_{\text{CO}}$ )  $\text{cm}^{-1}$ . UV (hexane solution)  $\lambda_{\text{max}}$  266 (14000), 311 nm (sh,  $2000\text{ mol}^{-1}\text{ dm}^3\text{ cm}^{-1}$ ). MS (EI, 70 eV)  $m/z$  523 ( $\text{M}^+ - \text{H}$ , 0.2).
- Crystal data for **1**:  $\text{C}_{25}\text{H}_{36}\text{FeN}_2\text{O}_3\text{Si}_2$ ;  $M_r = 524.59$ , monoclinic,  $a = 11.5362(3)$ ,  $b = 13.7135(2)$ ,  $c = 17.1380(3)$  Å,  $\beta = 104.132(1)^\circ$ ,  $V = 2629.2(1)$  Å<sup>3</sup>,  $T = 150(1)$  K, space group  $P2_1/c$  (No.14),  $Z = 4$ ,  $\mu(\text{Mo K}\alpha) = 6.93\text{ cm}^{-1}$ ,  $D_{\text{calc}} = 1.325\text{ g cm}^{-3}$ , GOF = 1.19,  $R_1 = 0.038$  for unique 5306 reflections with  $I > 2\sigma(I)$ .
- A. J. Gordon and R. A. Ford, "The Chemist's Companion: A Handbook of Practical Data, Techniques, and References," Wiley, New York (1972).
- 3**: colorless liquid. bp  $90\text{ }^\circ\text{C}/24$  Torr. Anal. Found: C, 54.62; H, 7.33; N, 9.10%. Calcd for  $\text{C}_7\text{H}_{11}\text{NOSi}$ : C, 54.86; H, 7.23; N, 9.14%.  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.39 (d, 6H, SiMe,  $^3J_{\text{HH}} = 2.8$  Hz), 5.34 (septet, 1H, SiH,  $^3J_{\text{HH}} = 2.8$  Hz), 6.36–6.41, 6.56–6.60, 6.97–7.03, 7.97–8.00 (m, aromatic protons).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  –1.2 (SiMe), 112.5, 117.1, 139.1, 147.5, 163.1 (pyridine ring).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (59.6 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  3.6. IR (neat, NaCl plate)  $2156$  ( $\nu_{\text{SiH}}$ )  $\text{cm}^{-1}$ . MS (EI, 70 eV)  $m/z$  153 ( $\text{M}^+$ , 40).
- 4**: red crystals. mp  $112\text{ }^\circ\text{C}$  (dec.). Anal. Found: C, 57.78; H, 6.77; N, 3.73%. Calcd for  $\text{C}_{18}\text{H}_{25}\text{FeNO}_2\text{Si}$ : C, 58.22; H, 6.79; N, 3.77%.  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.94 (s, 3H, SiMe), 1.04 (s, 3H, SiMe), 1.54 (s, 15H, Cp\*), 5.86–5.91, 6.36–6.39, 6.57–6.62, 7.76–7.78 (m, aromatic protons).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.3 (SiMe), 9.9 (SiMe), 10.5 ( $\text{C}_5\text{Me}_5$ ), 89.8 ( $\text{C}_5\text{Me}_5$ ), 110.5, 114.6, 137.6, 154.5, 170.6 (pyridine ring), 224.4 (FeCO).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (59.6 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  114.4. IR (KBr pellet)  $1886$  ( $\nu_{\text{CO}}$ )  $\text{cm}^{-1}$ . UV (hexane solution)  $\lambda_{\text{max}}$  246 (6000), 323 (2000), 405 nm ( $800\text{ mol}^{-1}\text{ dm}^3\text{ cm}^{-1}$ ). MS (EI, 70 eV)  $m/z$  371 ( $\text{M}^+$ , 12).
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