Insertion of pyridine into an iron–silicon bond: structure of the product Cp*(CO)Fe{η³(*C,C,C*)-C₅H₅NSiMe₂NPh₂}†

Masatoshi Iwata, Masaaki Okazaki* and Hiromi Tobita*

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan.
E-mail: mokazaki@mail.tains.tohoku.ac.jp (MO). E-mail: tobita@mail.tains.tohoku.ac.jp (HT);
Fax: 81-22-217-6543; Tel: 81-22-217-6539

Heating a toluene solution of Cp*(CO)(C₅H₅N)FeSiMe₂NPh₂ led to insertion of pyridine into the iron–silicon bond to form Cp*(CO)Fe{η³(*C,C,C*)-C₅H₅NSiMe₂NPh₂}.

Hydrosilylation of alkenes, alkynes, and other organic substrates containing unsaturated bonds is a useful means of synthesizing various organosilicon compounds.[1] In the modified Chalk–Harrod mechanism, insertion of an alkene molecule into a metal–silicon bond is a crucial step in the catalytic hydrosilylation of alkene.[2] Thus, the reactivity of isolated silyl complexes toward the insertion of unsaturated molecules represents a challenging subject in transition metal–silicon chemistry. There are numerous examples of the insertion of alkenes, alkynes, nitriles, and organic carbonyl compounds into metal–silicon bonds.[3] What seems to be lacking, however, is an example of the insertion of aromatic compounds into metal–silicon bonds. The stoichiometric reaction of this type is expected to stimulate the development of the metal-catalyzed hydrosilylation of aromatic compounds. We report here for the first time the insertion of pyridine into a late transition metal–silicon bond through thermolysis of Cp*(CO)(C₅H₅N)FeSiMe₂NPh₂ to give the insertion product Cp*(CO)Fe{η³(*C,C,C*)-C₅H₅NSiMe₂NPh₂}. The structure of the product has been characterised by X-ray structure analysis.

Ultraviolet irradiation of Cp*(CO)₂FeSiMe₂NPh₂ (**1**)[4] and pyridine in toluene was performed in a Pyrex sealed tube (eqn. (1)). After 90 min, the solution turned from yellow to dark red in colour. Upon removal of volatiles, recrystallisation of the residue from toluene/hexane solution at −30 °C gave dark red crystals of **2** in 72% yield.‡ The molecular structure of **2** is depicted in Fig. 1.§ Complex **2** takes a typical three-legged piano-stool geometry in which one carbonyl ligand in **1** is replaced with pyridine. The Fe–Si bond distance (2.3330(4) Å) is shorter than that in **1** (2.3355(7) Å), while the Si–N1 bond distance (Si–N1 1.799(1) Å) is longer than that in **1** (1.787(2) Å).[4] These differences are attributable to enhanced back-

donation from the iron dπ orbital to the Si–N σ* orbital by coordination of the strongly electron-releasing pyridine.

(1)
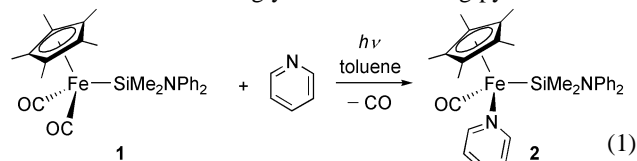
Substitution of CO by pyridine caused a large shift of ν(CO) to lower energies (**1**: 1973, 1917 cm⁻¹, **2**: 1867 cm⁻¹), reflecting the fact that the iron centre of **2** is more electron-rich than that of **1**. The ²⁹Si nuclear magnetic resonance (δ 53.5) is in the typical region for the silyl-iron complexes.

A toluene solution of **2** was heated at 60 °C for 2 days (eqn. (2)), after which volatiles were removed *in vacuo* and the residue extracted with pentane. Cooling of the concentrated pentane solution at −30 °C afforded orange crystals of **3** in 55% yield.‡

(2)
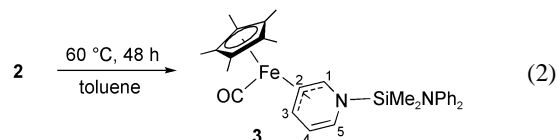
The structure of **3** was unequivocally determined by the X-ray diffraction study.§ An ORTEP drawing is depicted in Fig. 2. The iron(II) complex has one Cp* and one CO ligand and a π-allyl fragment formed through the insertion of pyridine into the iron–silicon bond, in which the aminosilyl group is bonded to the nitrogen atom of pyridine. The bonding parameters fall in the range expected for the π-allyl iron complexes:[5] the carbon–carbon bond distances in the allylic moiety are 1.413(4) Å
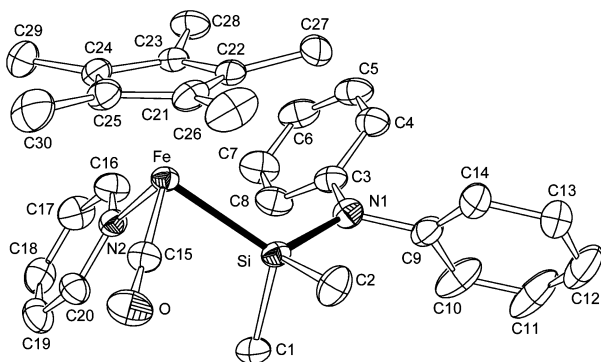
Fig. 1 Molecular structure of **2**. Selected bond distances (Å) and angles (°): Fe–Si 2.3330(4), Fe–N2 1.991(1), Fe–C15 1.716(2), Si–N1 1.799(1), O–C15 1.168(2), Si–Fe–N2 92.84(4), Si–Fe–C15 80.97(5), N2–Fe–C15 97.20(6), Fe–Si–N1 118.70(5).
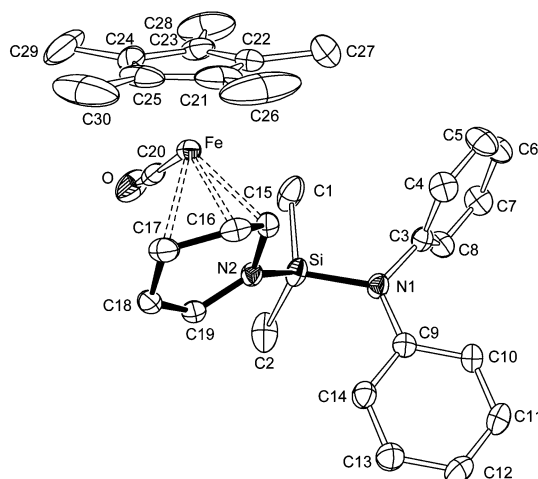
Fig. 2 Molecular structure of **3**. Selected bond distances (Å) and angles (°): Fe–C15 2.134(3), Fe–C16 1.995(3), Fe–C17 2.141(3), Fe–C20 1.730(3), C20–O 1.161(4), Si–N1 1.747(2), Si–N2 1.742(2), N2–C15 1.442(3), N2–C19 1.390(3), C15–C16 1.413(4), C16–C17 1.412(4), C17–C18 1.471(4), C18–C19 1.332(4), Si–N2–C15 118.0(2), Si–N2–C19 125.0(2), C15–N2–C19 116.3(2).

(C15–C16) and 1.412(4) Å (C16–C17). The distances between iron and allylic carbon atoms are 2.134(3) Å (Fe–C15), 1.995(3) Å (Fe–C16), and 2.141(3) Å (Fe–C17), and the C17–C18 and C18–C19 bond lengths are 1.471(4) Å and 1.332(4) Å, corresponding to a single and a double bond, respectively. The related molybdenum complex with a π-allyl ligand, $\eta^3(C,C,C)$-C_5H_4(4-OMe)N(COOMe), has been synthesised by Malinakova and Liebeskind.[6]

The migration of the aminosilyl ligand from the iron centre to the nitrogen atom is clearly reflected in the significant highfield shift of the ^{29}Si NMR signal (δ −2.3). The chemical shift indicates the absence of the iron–silicon bond and is typical of diamino-silanes. The ^{1}H and ^{13}C NMR signals of the inserted pyridine moiety were observed at $\delta(^1$H) 1.77 (2), 3.74 (3), 5.30 (4), 5.47 (5), and 5.73 (1) and $\delta(^{13}$C) 45.1 (2), 51.2 (3), 76.9 (1), 110.8 (4), and 121.1 (5), where the numbers in parentheses denote the positions (eqn. (2)). Assignments were established based on two-dimensional ^{1}H–^{1}H and ^{13}C–^{1}H COSY spectral data. The NMR parameters for the inserted pyridine ring are consistent with its π-allyl-type coordination in complex **3**. Furthermore, both X-ray and NMR data clearly indicate that the aromaticity of the pyridine moiety of **3** is disrupted.

A plausible formation mechanism for **3** is illustrated in Scheme 1. The first step is the transient formation of a $\eta^2(N,C)$- or $\eta^2(C,C)$-pyridine complex **A**. In complex **2**, coordination of electron-releasing Cp*, pyridine, and aminosilyl ligands make the iron centre extremely electron-rich. Isomerisation of **2** to **A** would be accelerated by such an electronic factor. Intermediate **A** undergoes the insertion of the N–C unsaturated bond to give an η^1-σ-allyl complex **B** with 16 valence electrons.[7] Finally, **B** isomerises to the η^3-π-allyl complex **3**.

We also attempted similar thermal reactions using Cp*(CO)(C_5H_5N)FeSiMe$_2$R (R = Cl (**2-Cl**), Me (**2-Me**) and OMe (**2-OMe**)). Under the same conditions as eqn. (2), however, no reaction took place. Thermolysis of **2-Cl** and **2-Me** under more forced conditions caused decomposition of **2-Cl** and **2-Me**, while the reaction of **2-OMe** at 90 °C for 24 h gave the pyridine-inserted product **3-OMe** in low yield (18%) together with Me$_2$Si(OMe)$_2$ (24%), unidentified products, and recovered **2-OMe** (9%). Purification of **3-OMe** is difficult and has not been achieved as yet.

The difference in reactivity toward the insertion of pyridine appears consistent with the proposed mechanism in Scheme 1. Based on the wave number of ν(CO), the electron density of the iron(II) centre can be estimated to fall into the following order: **2** (1867 cm^{-1}) > **2-OMe** ≈ **2-Me** (1873 cm^{-1}) > **2-Cl** (1882 cm^{-1}). As mentioned above, the electron-rich iron centre would facilitate the formation of the η^2-pyridine complexes leading to the insertion products.

Woo and Tilley demonstrated that insertion of pyridine into the Zr–Si bond proceeded readily at room temperature.[8] Interestingly, insertion of the N–C bond occurred in the opposite orientation to ours. Based on spectroscopic data, the product was characterised as CpCp*Zr[η^1(N)-NC$_5$H$_5$Si(Si-Me$_3$)$_3$]Me, in which the zirconium centre was bonded to the nitrogen, while the silyl group was bonded to the α-carbon of the inserted pyridine. The difference of the regiospecificity

Scheme 1 A plausible formation mechanism of **3**.

between Fe(II) and Zr(IV) seems to reflect the soft–soft and hard–hard preferences.

Harrod and Samuel have reported the hydrosilylation and hydrogenation of pyridines as the first examples of the homogeneously catalysed hydrosilylation of an aromatic substrate.[9] A mixture of pyridine and PhMeSiH$_2$ was converted in the presence of titanocene to N-silyl-1,2,3-trihydropyridine. The present results could therefore be expected to provide a valuable insight into the mechanism of that catalytic reaction.
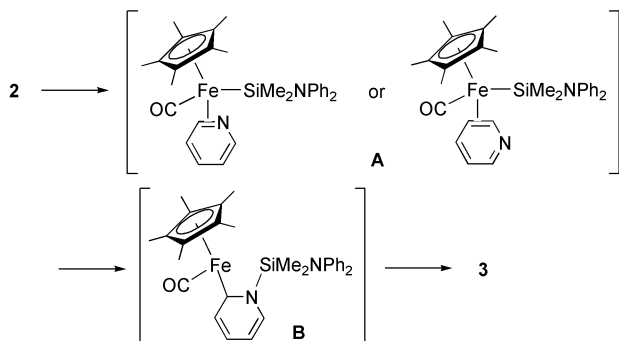
In conclusion, the structure of complex **3** formed through the insertion of an aromatic compound, pyridine, into the metal–silicon bond has been characterised by X-ray structure analysis for the first time. It was revealed that the electronic factor of substituents on the silyl silicon is crucial in control of the reactivity of transition-metal silyl complexes toward the insertion of unsaturated organic substrates. The amino substituent was also demonstrated to be an excellent tool for the insertion of pyridine. It should be noted that the introduction of an amino group onto silicon also has potential advantages with respect to further functionalisation of the product, because the amino group can readily be replaced with nucleophiles.

Notes and references

1 I. Ojima, Z. Li and J. Zhu, *The Chemistry of Organic Silicon Compounds*, ed. Z. Rappoport and Y. Apeloig, Wiley, New York, 1998, **vol. 2**, ch. 29, p. 1687.

2 M. A. Schroeder and M. S. Wrighton, *J. Organomet. Chem.*, 1977, **128**, 345; C. L. Reichel and M. S. Wrighton, *Inorg. Chem.*, 1980, **19**, 3858; C. L. Randolph and M. S. Wrighton, *J. Am. Chem. Soc.*, 1986, **108**, 3366.

3 M. S. Eisen, *The Chemistry of Organic Silicon Compounds*, ed. Z. Rappoport and Y. Apeloig, Wiley, New York, 1998, **vol. 2**, ch. 35, p. 2037; T. D. Tilley, *The Silicon-Heteroatom Bond*, ed. S. Patai and Z. Rappoport, Wiley, New York, 1991, ch. 9, 10, pp. 245, 309; P. Braunstein and M. Knorr, *J. Organomet. Chem.*, 1995, **500**, 21.

4 M. Okazaki, M. Iwata, H. Tobita and H. Ogino, *Dalton Trans.*, 2003, 1114.

5 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1989, S1.

6 H. C. Malinakova and L. S. Liebeskind, *Org. Lett.*, 2000, **2**, 3909; C. Shu, A. Alcudia, J. Yin and L. S. Liebeskind, *J. Am. Chem. Soc.*, 2001, **123**, 12477.

7 Insertion of the N–C triple bond of nitiles into the metal–silicon bonds with carbon–carbon bond activation has been reported by Bergman, Brookhart and Tilley: F. L. Taw, P. S. White, R. G. Bergman and M. Brookhart, *J. Am. Chem. Soc.*, 2002, **124**, 4192; S. R. Klei, T. D. Tilley and R. G. Bergman, *Organometallics*, 2002, **21**, 4648.

8 H.-G. Woo and T. D. Tilley, *J. Organomet. Chem.*, 1990, **393**, C6.

9 L. Hao, J. F. Harrod, A.-M. Lebuis, Y. Mu, R. Shu, E. Samuel and H.-G. Woo, *Angew. Chem., Int. Ed.*, 1998, **37**, 3126; J. F. Harrod, R. Shu, H.-G. Woo and E. Samuel, *Can. J. Chem.*, 2001, **79**, 1075.