The First Synthesis and X-ray Structure of [1.1]Silaferrocenophane Containing Pentacoordinate Silicon Moieties

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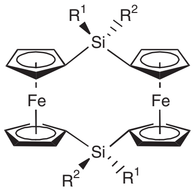
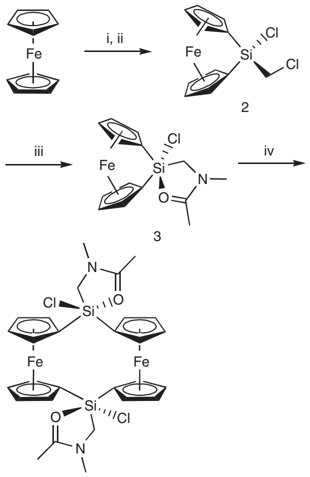
[1.1]Silaferrocenophane **4**, which contains pentacoordinate silicon moieties, was synthesized by the dimerization of **3** for the first time. The identity of **4** was established by multinuclear NMR spectroscopy, elemental analysis, and X-ray crystallography.

Compounds containing ferrocene units have attracted considerable attention because they exhibit interesting physical and chemical properties that are useful for various purposes.[1] Among them, the compounds that combine ferrocene and organosilane groups, including the silicon-bridged [1]silaferrocenophanes and their dimers and polymers, have been discussed in detail by Manners and co-workers.[2] [1.1]Silaferrocenophanes **1** containing tetracoordinate silicon moieties can be obtained by several methods. The ring-opening polymerization (ROP) of [1]silaferrocenophanes catalyzed by phosphine-free platinum or palladium complexes affords small amounts of **1** as by-products.[3] The dimerization of the [1]silaferrocenophane Fe(η-C_5H_4)$_2$SiMe$_2$ catalyzed by palladium–tricyclohexylphosphine complex provides **1a** in high yield along with small amounts of polymer.[4] The synthesis of **1a** via the intermediate, Fe[η-$C_5H_4SiMe_2(C_5H_5)]_2$ or $(C_5H_5)_2SiMe_2$, has also been reported to give the desired product in moderate yield along with higher cyclic oligo(ferrocenylsilanes)[5] or polymer.[6] Recently, we reported that the introduction of pentacoordinate silicon atoms into oligosilanes or pentasilanes leads to novel electronic and optical properties.[7] These interesting properties prompted us to continue our study of pentacoordinate silicon chemistry. In this paper, we report the first synthesis and X-ray structure of [1.1]silaferrocenophane **4**, which contains pentacoordinate silicon moieties.



1a: R^1 = R^2 = Me.
1b: R^1 = Me; R^2 = Cl.
1c: R^1 = Me; R^2 = CCPh.

Since the catalytic dimerization of [1]silaferrocenophane seemed to be a more convenient method for synthesis of [1.1]silaferrocenophane, we decided to prepare a pentacoordinate silicon-bridged [1]silaferrocenophane in advance and then dimerize it to form the desired product. [1]Silaferrocenophane **2**[8] was readily synthesized by the reaction of Cl_3SiCH_2Cl with 1,1′-dilithioferrocene-TMEDA derived from ferrocene. Compound **2** was then easily transformed into pentacoordinate silicon-bridged [1]silaferrocenophane **3**,[9] as illustrated in Scheme 1. Our first catalyst choice was PdCl$_2$(PCy$_3$)$_2$, which efficiently catalyzes the dimerization of Fe(η-C_5H_4)$_2$SiMe$_2$.[4] Compound **3** was insoluble in benzene at room temperature. Therefore a slurry of **3** in benzene was heated at 100 °C in an argon-purged, sealed tube in the presence of 5 mol % of PdCl$_2$(PCy$_3$)$_2$. The ^{1}H NMR spectrum of the reaction mixture showed decomposition of **3**, which indicats that it is not heat stable. When the reaction was carried out in dichloromethane, CH_2Cl_2, at room temperature for 48 h, none of the desired product was obtained, and starting material was recovered. PdCl$_2$ effectively catalyzes the ROP of Fe(η-C_5H_4)$_2$SiMe$_2$,[3a] so we tried PdCl$_2$ next. Surprisingly, when a solution of **3** in CH_2Cl_2 was stirred in the presence of 5 mol % of PdCl$_2$ at room temperature for 48 h, dimerization of **3** took place to afford **4**[10] as the sole product (Scheme 1). Recrystallization from CH_2Cl_2-hexane furnished highly pure **4** as a red crystalline solid in 62% yield. Attempts to use other phosphine-free palladium complexes such as Pd(cod)$_2$Cl$_2$ and Pd$_2$(dba)$_3$·CHCl$_3$ failed to provide pure product. The identities of **2**, **3**, and **4** were established by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy and elemental analysis; and an X-ray crystal structure of **4** was obtained. The single resonance in the ^{29}Si NMR spectrum of **4** exhibited an upfield chemical shift ($\delta -61.4$) [similar to that observed for the silicon atom of **3** ($\delta -69.6$)] relative to the corresponding resonance in the spectrum of **2** ($\delta -0.29$). This shift clearly demonstrated that the silicon atoms of **4** were pen-



Scheme 1. (i) *n*-BuLi, TMEDA, hexane, rt, 20 h; (ii) Cl_3SiCH_2Cl, OEt$_2$, −78 °C, then rt 20 h; (iii) MeCON(Me)SiMe$_3$, hexane, rt, 2 h; (iv) PdCl$_2$ (5 mol%), CH_2Cl_2, rt, 48 h.

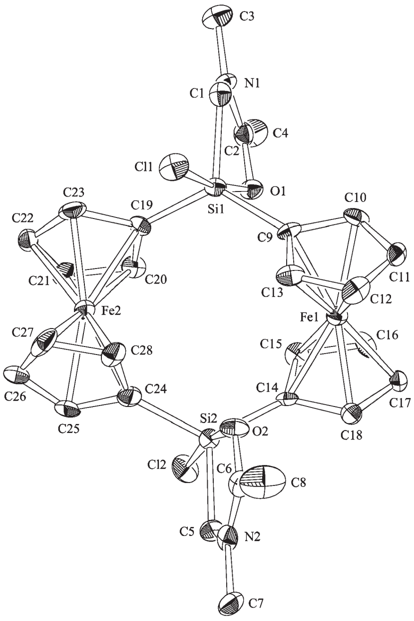


Figure 1. Molecular structure of **4**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Fe(1)–C(9), 2.046(7); Fe(1)–C(14), 2.062(7); Fe(2)–C(19), 2.085(7); Fe(2)–C(24), 2.092(7); Si(1)–Cl(1), 2.328(3); Si(1)–C(1), 1.902(8); Si(1)–C(9), 1.874(7); Si(1)–C(19), 1.846(7); Si(1)–O(1), 1.948(5); Si(2)–Cl(2), 2.294(3); Si(2)–C(5), 1.911(7); Si(2)–C(14), 1.861(7); Si(2)–C(24), 1.866(8); Si(2)–O(2), 1.934(5). C(9)–Fe(1)–C(14), 121.7(3); C(11)–Fe(1)–C(17), 105.3(3); C(19)–Fe(2)–C(24), 121.1(3); C(21)–Fe(2)–C(26), 113.3(3); Cl(1)–Si(1)–O(1), 171.4(2); Cl(1)–Si(1)–C(9), 92.2(2); C(1)–Si(1)–C(9), 118.8(3); C(1)–Si(1)–C(19), 114.4(3); C(9)–Si(1)–C(19), 126.4(3).

tacoordinate[11] (i.e., they were still strongly coordinated to O atom).

Figure 1 shows the molecular structure of compound **4** as established by X-ray crystallography.[12] Cyclic dimer **4**, like **1a**[5,6] and **1c**[2d], exists in an *anti*-conformation; however, the substituents on Si are in a *trans* orientation, which is just the opposite of the orientation observed for **1c**. The bond angles around the Si atoms revealed that the silicon moieties of **4** exist in an almost ideal trigonal bipyramidal (TBP) structure with the chlorine and oxygen atoms in the axial positions. The C_{ipso}–Si–C_{ipso} angles in **4** of 126.4(3)° and 126.3(3)° substantially more obtuse than the corresponding angles in **1a** (112.9(1)°),[6] whereas the distance between the Fe atoms in **4** of 5.163(2) Å is similar to the Fe–Fe distance found for **1a**.[6] As in **1c**, there is an unsymmetrical tilting of the Cp rings of **4** in the solid structure; the interplanar angle between the two Cp rings bonded to Fe(1) is 3.2°, and the other is 6.9°. The Fe(2)–C_{ipso} distances of 2.085(7) and 2.092(7) Å are longer than the Fe(1)–C_{ipso} distances of 2.046(7) and 2.062(7) Å, owing to the bigger interplanar angle of 6.9°.

In conclusion, we have synthesized and characterized the first pentacoordinate silicon-bridged [1.1]silaferrocenophane **4**. The reason that $PdCl_2$, a powerful catalyst for the ROP of [1]silaferrocenophane, promoted the dimerization of **3** effectively has not yet been clarified. Further studies, including measurement of the electronic properties of **3** and **4** and the cationic polymerization of **3**, are underway and will be reported in detail in the near future.

References and Notes

1 O. Kadkin, C. Näther, and W. Friedrichsen, *J. Organomet. Chem.*, **649**, 161 (2002), and references therein.

2 a) R. D. Archer, "Inorganic and Organometallic polymers," Wiley-VCH, New York (2001), p 71. b) K. Temple, F. Jäkle, J. B. Sheridan, and I. Manners, *J. Am. Chem. Soc.*, **123**, 1355 (2001). c) K. Temple, S. Dziadek, and I. Manners, *Organometallics*, **21**, 4377 (2002). d) A. Berenbaum, A. J. Lough, and I. Manners, *Organometallics*, **21**, 4415 (2002). e) J. Raez, Y. Zhang, L. Cao, S. Petrov, K. Erlacher, U. Wiesner, I. Manners, and M. A. Winnik, *J. Am. Chem. Soc.*, **125**, 6010 (2003).

3 a) Y. Ni, R. Rulkens, J. K. Pudelski, and I. Manners, *Macromol. Rapid Commun.*, **16**, 637 (1995). b) D. L. Zechel, K. C. Hultzsch, R. Rulkens, D. Balaishis, Y. Ni, J. K. Pudelski, A. J. Lough, and I. Manners, *Organometallics*, **15**, 1972 (1996). c) See Ref. 2d).

4 N. P. Reddy, N. Choi, S. Shimada, and M. Tanaka, *Chem. Lett.*, **1996**, 649.

5 D. L. Zechel, D. A. Foucher, J. K. Pudelski, G. P. A. Yap, A. L. Rheingold, and I. Manners, *J. Chem. Soc., Dalton Trans.*, **1995**, 1893.

6 J. Park, Y. Seo, S. Cho, D. Whang, K. Kim, and T. Chang, *J. Organomet. Chem.*, **489**, 23 (1995).

7 a) I. El-Sayed, Y. Hatanaka, C. Muguruma, S. Shimada, M. Tanaka, N. Koga, and M. Mikami, *J. Am. Chem. Soc.*, **121**, 5095 (1999). b) I. El-Sayed, Y. Hatanaka, S. Onozawa, and M. Tanaka, *J. Am. Chem. Soc.*, **123**, 3597 (2001).

8 Compound **2**: ^1H NMR (500 MHz, CD_2Cl_2) δ 4.67 (br, 2H), 4.66 (br, 2H), 4.30 (br, 2H), 4.28 (br, 2H), 3.39 (s, 2H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 79.5, 79.4, 76.0, 74.5, 31.3, 28.6; ^{29}Si NMR (60 MHz, CD_2Cl_2) $\delta -0.29$; Anal. Calcd for $C_{11}H_{10}Cl_2FeSi$: C, 44.48; H, 3.39. Found: C, 44.56; H, 3.44%.

9 Compound **3**: ^1H NMR (500 MHz, CD_2Cl_2) δ 4.52–4.25 (m, 8H), 3.21 (s, 3H), 3.19 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 174.8, 81.8, 79.7, 77.5, 77.1, 47.5, 44.0, 37.1, 17.3; ^{29}Si NMR (60 MHz, CD_2Cl_2) $\delta -69.6$; Anal. Calcd for $C_{14}H_{16}ClFeNOSi$: C, 50.39; H, 4.83; N, 4.20. Found: C, 50.15; H, 5.19; N, 4.17%.

10 Compound **4**: ^1H NMR (500 MHz, CD_2Cl_2) δ 4.83 (m, 4H), 4.34 (m, 12H), 3.03 (s, 6H), 2.75 (s, 4H), 2.16 (s, 6H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 173.2, 78.8, 76.8, 76.4, 70.5, 70.4, 46.0, 37.4, 17.4; ^{29}Si NMR (60 MHz, CD_2Cl_2) $\delta -61.4$; Anal. Calcd for $C_{28}H_{32}Cl_2Fe_2N_2O_2Si_2$: C, 50.39; H, 4.83; N, 4.20. Found: C, 49.94; H, 5.26; N, 3.84%.

11 The ^{29}Si NMR chemical shifts for pentacoordinate Si usually exhibit an upfield chemical shift relative to the shifts for tetracoordinate Si. See Ref. 7a.

12 Crystal data for **4**: $C_{28}H_{32}Cl_2Fe_2N_2O_2Si_2$, $M_r = 667.34$, Monoclinic, space group $P2_1/c$, $a = 9.547(2)$, $b = 15.610(3)$, $c = 19.520(2)$ Å, $\beta = 103.65(1)°$, $V = 2826.9(8)$ Å^3, $T = 173.0$ K, $Z = 4$, $D_{calcd} = 1.568\,g\,cm^{-3}$, $\mu = 13.29\,cm^{-1}$ for Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å, goodness of fit = 0.96, $R1$ $[I > 2\sigma(I)] = 0.051$, $wR_2 = 0.163$ (all data). Atomic coordinates, additional bond lengths and angles, and other important parameters have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication, CCDC No. 232427. Copies of this information can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44(1233)336033 or e-mail: deposit@ccdc.cam.ac.uk).

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