Synthesis and Structure of a Hypercoordinate Silicon-Bridged [1]Ferrocenophane

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Summary: The first hypercoordinate silicon-bridged [1]-ferrocenophane shows a pronounced Si−N interaction, a pseudo-trigonal-bipyramidal geometry at the bridging silicon atom, an elongated Si−Cp bond trans to the amino group, and an unusually long Fe−Si distance in comparison to the tetracoordinate analogues.

Hypercoordinate organosilicon compounds have been studied extensively in order to model the mechanism of nucleophilic substitution reactions at silicon and to elucidate stereoisomerization processes.[1] Significantly, pentacoordinate silicon species have been shown to display unusual reactivity; indeed, the enhanced reactivity detected in nucleophilic substitution reactions compared to their tetracoordinate counterparts suggests the possible presence of hexa- or even heptacoordinate intermediates.[1c] Furthermore, access to novel materials with unusual electronic properties may be anticipated by incorporation of hypercoordinate silanes into polymer structures. Very recently, the first examples of the attachment of intramolecularly donating groups to oligosilanes[2] and polycarbosilanes[3] have been reported.

We were particularly interested in higher coordinate silicon-bridged [1]ferrocenophanes because our recent studies on the thermal ring-opening polymerization (ROP)[4] of group 14 bridged [1]ferrocenophanes (**1**) revealed a process catalyzed by neutral nucleophilic species such as amines.[5] The proposed mechanism involves coordination of the nucleophile (Nu) to the bridging element (E), resulting in an elongated and weakened *ipso*-Cp−E bond trans to the incoming nucleophile (eq 1). Subsequent attack of the Cp carbon


$$\tag{1}$$
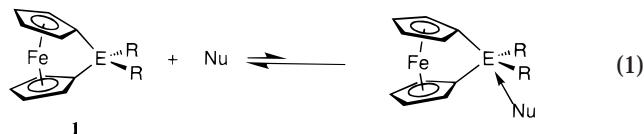
atom at the bridging element of another ferrocenophane monomer results in initiation of the polymerization

process.[5] However, our attempts to isolate such a penta-coordinate intermediate have not yet been successful. We anticipated that attachment of a weakly coordinating donor group at one of the substituents on silicon might provide a model compound in which the *ipso*-C−Si bond is weakened, but not cleaved, and could therefore allow insight into the effects of pentacoordination on the structure, properties, and reactivity of [1]ferro-cenophanes in detail.

Previously, we have shown that chlorosilyl-bridged [1]-ferrocenophanes (**1**; ER_x = $SiCl_2$, SiMeCl) undergo substitution reactions with alcohols and amines in the presence of a base under mild conditions and without cleavage of the *ipso*-C−Si bond.[6] Alkylated or arylated compounds, on the other hand, had not been accessible via this synthetic route. Addition of alkyl- or aryllithium reagents to dimethylsilyl-bridged ferrocenophane (**1**) is known to result in a living anionic polymerization at ambient temperature.[7] However, when chlorosilyl-bridged [1]ferrocenophanes such as fcSiMeCl (**1a**) were treated with alkyllithium species such as *t*BuLi at −78 °C selective substitution to afford fcSiMe*t*Bu (**1b**) and no polymerization of the [1]ferrocenophane was observed.[8] Accordingly, when **1a** was reacted with Li[2-$C_6H_4CH_2NMe_2$] at −78 °C in THF, [1]ferrocenophane **2**[9] formed selectively and was isolated as a red crystalline solid in 81% yield after recrystallization from hexanes (Scheme 1).

Scheme 1[a]
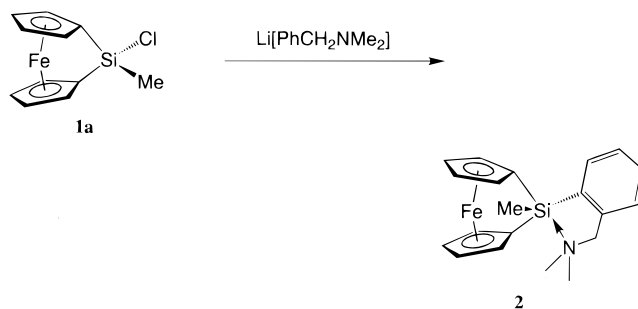
[a] Reagents and conditions: THF, −78 °C to room temperature.

NMR spectroscopy is a very powerful tool, allowing us to probe the coordination state of the silicon atom of

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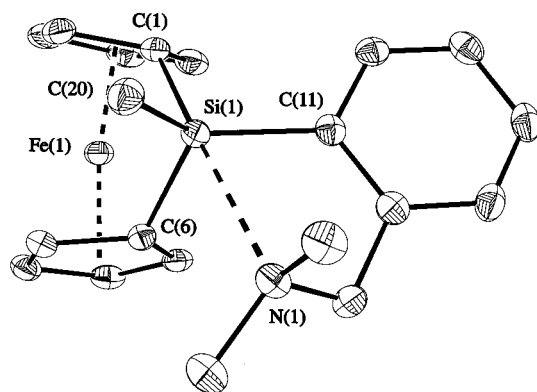
(5) Jäkle, F.; Rulkens, R.; Zech, G.; Massey, J. A.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 4231.

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2 in solution. Particularly useful is a comparison with the unsubstituted analogue **1c** (ER_2 = SiMePh),[10] which is structurally typical of the sila[1]ferrocenophanes reported to date,[11,12] and the model compound 2-($SiMe_3$)-$C_6H_4CH_2NMe_2$ (**3**).[13] The most interesting feature of the proton NMR spectrum of **2** is that the signal for the phenyl proton in a position ortho to the Si substituent is strongly downfield shifted in comparison to both **1c** and **3** (δ 8.29 (**2**), 7.89 (**1c**), 7.59 (**3**)), which is typical for hypercoordinate silanes containing aryl substituents.[1a] Furthermore, the methylene resonance of the ligand is found at slightly lower field in comparison to **3** (δ 3.50 (**2**), 3.39 (**3**)). The *ipso*-C(Cp) resonance in **2** is strongly downfield shifted in comparison to **1c** (δ 37.4 (**2**), 32.1 (**1c**)), which is indeed at lower field than for any silicon-bridged [1]ferrocenophane investigated to date.[11] Importantly, a significant high-field shift is observed for the ^{29}Si NMR signal of **2** compared to **1c** (δ −13.9 (**2**), −10.9 (**1c**)) in benzene. In comparison, the chemical shift difference between $PhSiMe_3$ and the corresponding amino-functionalized $ArSiMe_3$ derivative **3** was previously determined to be less than 1 ppm, indicating the absence of any Si−N interaction in solution.[13]

A single-crystal X-ray structure of **2** was obtained.[14] This confirmed the attachment of the 2-$C_6H_4CH_2NMe_2$ substituent without cleavage of the *ipso*-C−Si bonds and revealed an unprecedented strained ferrocenophane structure (Figure 1). The Si−N distance of 2.776(2) Å is the shortest reported for a tetraorganosilane.[15] This is at the upper limit of Si−N interactions described as donor−acceptor complexes and at the lower limit of

(8) Selective alkylation and arylation of chlorosilyl-bridged [1]-ferrocenophanes was found to be a general synthetic route, and no polymer formation was found when the reaction was performed at low temperature. These observations may be attributed to the fact that a chloride ion is a much better leaving group than a ferrocenyl substituent and at low temperature the kinetic product is expected to form.

(9) Selected spectroscopic data are as follows. For **2**: ^1H NMR (400 MHz, C_6D_6, 20 °C) δ 8.29 (m, 1 H, Ph H6), 7.22−7.10 (m, 3 H, Ph H3−5), 4.45, 4.38, 4.15, 3.89 (4 × m, 4 × 2 H, Cp H), 3.50 (s, 2 H, CH_2), 1.97 (s, 6 H, NCH_3), 0.70 (s, 3 H, $SiCH_3$); $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6, 20 °C) δ 147.5 (*ipso*-Ph), 137.0 (Ph), 135.1 (*ipso*-Ph), 129.9 (Ph), 128.5 (Ph), 127.0 (Ph), 77.1, 77.0, 76.1, 75.5 (Cp), 64.3 (CH_2), 44.5 (NCH_3), 37.4 (*ipso*-Cp), −2.1 ($SiCH_3$); ^{29}Si NMR (79.3 MHz, C_6D_6, 20 °C) δ −13.9; solid state ^{29}Si CP-MAS NMR (79.5 MHz, 20 °C) δ −12.8; MS (EI, 70 eV) *m/z* (%) 361 (42) [M^+], 346 (100) [M^+ − Me], 317 (27) [M^+ − NMe_2]; UV−vis (10^{-3} M in CH_2Cl_2) λ_{max} 482 nm, ϵ = 276; For **4**·CH_2Cl_2: ^1H NMR (300 MHz, C_6D_6, 20 °C) δ 7.93, 7.84 (d, d, 1 H, 1 H, *J* = 7.5 Hz, *J* = 7.7 Hz, Ph H3, 6), 7.32, 7.18 (ps t, ps t, 1 H, 1 H, Ph H4, 5), 4.91 (s, 2 H, CH_2N), 4.36 (s, 2 H, Cp H) 4.29 (m, 4 H, Cp H, CH_2Cl_2), 4.01, 3.47 (2 × s, 2 × 2 H, Cp H), 2.83 (s, 9 H, NCH_3), 0.43 (s, 3 H, $SiCH_3$); $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 20 °C) δ 138.5 (*ipso*-Ph), 136.6 (Ph), 135.2 (Ph), 134.0 (*ipso*-Ph), 130.9 (Ph), 130.0 (Ph), 122.1 (q, *J* = 321 Hz, CF_3), 78.6, 78.5, 76.5, 76.1 (Cp), 68.3 (CH_2), 52.5 (NCH_3), 31.9 (*ipso*-Cp), −2.5 ($SiCH_3$); ^{19}F NMR (282.3 MHz, C_6D_6, 20 °C) δ −78.1; ^{29}Si NMR (79.3 MHz, C_6D_6, 20 °C) δ −9.2; UV−vis (10^{-3} M in CH_2Cl_2) λ_{max} 487 nm, ϵ = 305. For detailed spectroscopic data and synthetic procedures, see the Supporting Information.

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(12) For X-ray crystal structures of sila[1]ferrocenophanes see, for example: (a) Stoeckli-Evans, H.; Osborne, A. G.; Whiteley, R. H. *Helv. Chim. Acta* **1976**, *59*, 2402. (b) Butler, I. R.; Cullen, W. R.; Rettig, S. J. *Can. J. Chem.* **1987**, *65*, 1452. (c) Finckh, W.; Tang, B.-Z.; Foucher, D. A.; Zamble, D. B.; Ziembinski, R.; Lough, A.; Manners, I. *Organometallics* **1993**, *12*, 823. (d) Pudelski, J. K.; Foucher, D. A.; Honeyman, C. H.; Lough, A. J.; Manners, I.; Barlow, S.; O'Hare, D. *Organometallics* **1995**, *14*, 2470. (e) Pannell, K. H.; Dementiev, V. V.; Li, H.; Cervantes-Lee, F.; Nguyen, M. T.; Diaz, A. F. *Organometallics* **1994**, *13*, 3644.

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Figure 1. Molecular structure (ORTEP drawing) of **2**. Selected bond lengths (Å), interatomic distances (Å), and angles (deg): Fe(1)···Si(1) = 2.7584(6), Si(1)···N(1) = 2.776-(2), Si(1)−C(1) = 1.919(2), Si(1)−C(6) = 1.891(2), Si(1)−C(11) = 1.883(2), Si(1)−C(20) = 1.865(2); C(1)−Si−C(6) = 93.68(8), C(1)−Si(1)−C(11) = 103.76(9), C(6)−Si(1)−C(11) = 113.36(9), C(1)−Si(1)−C(20) = 106.58(9), C(6)−Si(1)−C(20) = 112.90(9), C(11)−Si(1)−C(20) = 121.74(9), N(1)−Si(1)−C(1) = 174.63(7) C(6)−Si(1)−N(1) = 83.88(7), C(11)−Si(1)−N(1) = 73.00(7), C(20)−Si(1)−N(1) = 78.78(7); C(1−5)//C(6−10) = 21.27(1), C(1−5)//Si(1)C(11)C(20) = 21.09(1), C(6−10)//Si(1)C(11)C(20) = 0.94(2).

Coulomb-dominated donor−acceptor bonding.[16] The relatively short distance may be attributed to the fact that the silicon atom is incorporated into a strained cyclic system with a small endocyclic C(1)−Si−C(6) angle and large exocyclic C−Si−R angles,[17] although the unusual electronic structure of strained ferrocenophanes is also likely to be important.[18] The Fe···Si distance of 2.7584-(6) Å is significantly longer than in **1c** (2.692(1) Å).[19] In trigonal-bipyramidal structures with silicon as the central atom, axial bonds are typically longer than those in the equatorial position. Significantly, in **2** the *ipso*-C(1)−Si bond trans to the amino group is found to be slightly longer than the corresponding C(6)−Si bond (**2**: C(1)−Si = 1.919(2) Å, C(6)−Si = 1.891(2) Å). Both Si−C bonds are longer than those usually found in silicon-bridged [1]ferrocenophanes (**1c**: C(1)−Si =

(14) Crystallographic data for $C_{20}H_{23}FeNSi$: M_r = 361.3, monoclinic, space group $P2_1/n$, a = 7.5146(2) Å, b = 12.8744(4) Å, c = 18.0268(5) Å, β = 97.01(2)°, U = 1730.98(9) Å^3, Z = 4, D_c = 1.378 g cm^{-3}, μ = 0.939 mm^{-1}, 3964 observed reflections (I > $2\sigma(I)$), R1 = 0.0352; wR2 = 0.0827, GOF = 0.986. Data were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) at 100.0(1) K. A combination of 1° ψ and ω (with κ offsets) scans were used to collect sufficient data. The data frames were integrated and scaled using the Denzo-SMN package.[22] The structure was solved and refined using the SHELXTL\PC V5.1 package.[23] Refinement was done by full-matrix least squares based on F^2 using all data (negative intensities included). Hydrogen atoms were included in calculated positions.

(15) For related X-ray structures see, for example: (a) Belzner, J.; Ihmels, H.; Kneisel, B. O.; Gould, R. O.; Herbst-Irmer, R. *Organometallics* **1995**, *14*, 305. (b) Steenwinkel, P.; Jastrzebski, J. T. B. H.; Deelman, B.-J.; Grove, D. M.; Kooijman, H.; Veldman, N.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1997**, *16*, 5486 and references 2 and 3.

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(17) For other examples of hypercoordinate tetraorganosilanes incorporated into ring systems, see, for example: (a) Tamao, K.; Asahara, M.; Kawachi, A. *J. Organomet. Chem.* **1996**, *521*, 325. (b) Spiniello, M.; White, J. M. *Organometallics* **2000**, *19*, 1350 and reference 15.

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1.879(4) Å, C(6)−Si = 1.880(4) Å). From the angles around silicon in **2**, an intermediate geometry between a trigonal bipyramid and a capped-tetrahedral structure can be deduced. The angle N(1)−Si(1)−C(1) of 174.63-(7)° approaches the theoretical value of 180°. Furthermore, the angle between the methyl and phenyl substituents on silicon of 121.74(9)° is very close to the expected 120° angle in a bipyramidal structure and significantly larger than in other silicon-bridged [1]-ferrocenophanes (**1c**: 112.4(2)°). The angle C(1)−Si−C(6) of 93.68(8)° is smaller than in other strained silicon-bridged [1]ferrocenophanes (**1c**: 96.2(2)°) and approaches 90°, as expected for a bipyramidal geometry around silicon. The sum of equatorial angles around silicon is 347.96°, corresponding to a value of 38% of pentacoordination character TBP$_e$.[20] The tilt angle α between the Cp planes is 21.27(1)°, and the average β angle between the Cp plane and the Si−C bond is 35.9°. In comparison to other silicon-bridged [1]ferrocenophanes, β is slightly smaller and α larger.[12]

The possibility of dynamic behavior for **2** in solution was examined by variable-temperature NMR spectroscopy. The ^{29}Si NMR shift of **2** in solution (toluene) was found to be slightly temperature dependent. The signal was increasingly high field shifted as the temperature decreased (+80 °C, −13.4 ppm; +25 °C, −13.8 ppm; −80 °C, −15.6 ppm). This may suggest the existence of an equilibrium between coordinated and uncoordinated species.[13] In comparison, the solid-state ^{29}Si NMR spectrum shows a signal at −12.8 ppm at 25 °C, which is similar to the value in solution. A fluxional structure of **2** in solution at room temperature is evident from the presence of only one set of signals for the ((dimethyl-amino)methyl)phenyl substituent and of four sharp Cp signals in the ^{1}H NMR spectrum. However, at −80 °C the ^{1}H NMR spectrum of **2** shows two broad signals for the methylene protons and broadening of the Cp and dimethylamino resonances. The free energy of the exchange process was estimated from the coalescence temperature of the methylene protons at T_c = −58 °C and the chemical shift difference of 706 Hz at −80 °C to be $\Delta G^{\ddagger}$ = 39 kJ mol^{-1}.[21] This dynamic behavior may either be attributed to a fast equilibrium between coordinated and uncoordinated species[13] or to a pseudorotation process.[17b] As a result of the Si−N interaction, the absorption maximum for the d−d transition in **2** is blue-shifted and exhibits a slightly smaller absorption coefficient ϵ in comparison to **1c** (**2**, λ_{max} = 482 nm, ϵ = 276; **1c**, λ_{max} = 487 nm, ϵ = 308; 10^{-3} M in CH$_2$Cl$_2$).

Pentacoordination in **2** can be suppressed by complexation of the nitrogen functionality with electrophiles. Selective alkylation of **2** with MeOTf takes place at 0 °C in benzene to give the ammonium salt **4**.[9]
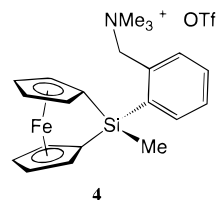
Quarternization of the nitrogen can be monitored by a pronounced downfield shift of the methylene and the methyl groups in the ^{1}H NMR spectrum of **4** (δ 4.91, 2.83) in comparison to **2** (δ 3.50, 1.97). As expected, the *ipso*-C(Cp) resonance at δ 31.9 and the ^{29}Si NMR shift at δ −9.2 are close to those found for **1c** but different from the chemical shifts of the pentacoordinate [1]-ferrocenophane **2**.

In summary, our findings show that pentacoordination at the bridging silicon atom leads to dramatic structural changes for sila[1]ferrocenophanes in the solid state. The tetrahedral silicon environment is substantially distorted toward a trigonal-bipyramidal configuration, and **2** may therefore indeed serve as a structural model for the proposed intermediate in the nucleophically assisted ring-opening polymerization of [1]ferrocenophanes.[5] The NMR spectroscopic data for **2** suggest that a pentacoordinate silicon bridge is also present in solution. Dynamic behavior is apparent from a variable-temperature NMR study. This may either be attributed to a fast equilibrium between coordinated and uncoordinated species or to a pseudorotation process. Currently, we are exploring the polymerization behavior of species such as **2** in order to prepare poly(ferrocenes) with pentacoordinate silicon centers in the polymer backbone.

Supporting Information Available: Synthetic procedures for **1b** and **2**−**4** and tables giving details on the X-ray crystal structure analysis of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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