Communications to the Editor

Amine-Promoted Disproportionation and Redistribution of Trichlorosilane: Formation of Tetradecachlorocyclohexasilane Dianion[1]

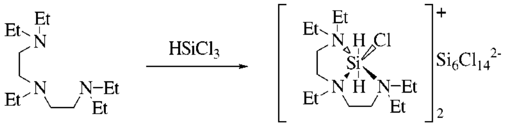
Seok-Bong Choi, Beon-Kyu Kim, Philip Boudjouk,* and Dean G. Grier

Center for Main Group Chemistry
Department of Chemistry
North Dakota State University
Fargo, North Dakota 58105

Received August 1, 2000

Amine-promoted redistributions and disproportionations of chlorosilanes have been known for several decades.[2] Typically, the product mixtures from such reactions are complex, defying unambiguous characterization. Recently, we demonstrated that aliphatic diamines and triamines, when reacted with trichlorosilane, produced neutral[3] and cationic[4] hexacoordinated complexes of silicon in high yields and with narrow product distributions. Here we report an unexpected and unique result: the amine-promoted oligomerization of trichlorosilane to form the novel inverse sandwich dianion, $Si_6Cl_{14}^{2-}$. Efficient catenation of silanes to form highly functionalized polysilanes is unprecedented.

We recently reported that the reaction of $HSiCl_3$ with pedeta in CH_2Cl_2 immediately followed by the addition of hexane gave $[pedeta{\cdot}H_2SiCl]^+Cl^-$ in high yield within 5 min.[4] Here we report that, if instead of adding hexane, we refluxed the solution of $HSiCl_3$ and pedeta in CH_2Cl_2 at 40−45 °C for 48 h we produce the novel complex $[pedeta{\cdot}H_2SiCl^+]_2[Si_6Cl_{14}^{2-}]$ (**1**) (eq 1).[5]



pedeta **1**

Analysis of the X-ray data for **1** shows two intermolecularly hexacoordinated cations in which the silicon atoms are at the center of slightly distorted octahedra and a dianion comprised of a planar cyclohexasilane ring bonded to 14 chlorine atoms forming an "inverse sandwich structure". To the best of our knowledge, this structural type is unique in group 14 chemistry (Figure 1). The chlorine atom in each cation is coplanar with the three nitrogen atoms of pedeta and the hydrogens occupy trans positions. All of the Si−N bond distances are in the range of typical ionic hexacoordinate silicon compounds (The average distance for Si−N in **1** is 2.069 Å).[4] The chlorine atoms are of

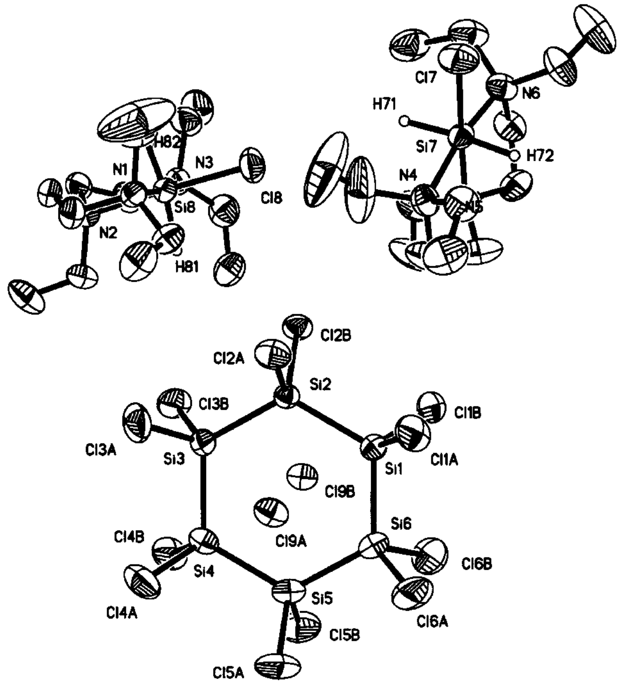


Figure 1. ORTEP diagram of **1** showing atom-labeling scheme. Some of hydrogens are omitted for clarity. Selected bond distances (Å) and angles (deg): Si(1)−Cl(1B), 2.070(3); Si(1)−Cl(1A), 2.087(3); Si(1)−Si(2), 2.314(2); Si(1)−Si(6), 2.318(3); Si(2)−Cl(2B), 2.073(2); Si(2)−Cl(2A), 2.083(2); Si(2)−Si(3), 2.323(2); Si(7)−N(5), 2.009(5); Si(7)−N(6), 2.082(6); Si(7)−N(4), 2.092(6); Si(7)−Cl(7), 2.216(2); Cl(1B)−Si(1)−Cl(1A), 101.72(12); Cl(1B)−Si(1)−Si(2), 108.73(10); Cl(1A)−Si(1)−Si(2), 107.07(11); Cl(1B)−Si(1)−Si(6), 109.07(12); Cl(1A)−Si(1)−Si(6), 109.27(12); Si(2)−Si(1)−Si(6), 119.51(10); N(5)−Si(7)−N(6), 85.3(2); N(5)−Si(7)−N(4), 85.3(2); N(6)−Si(7)−N(4), 169.7(2); N(5)−Si(7)−Cl(7), 178.1(2); N(6)−Si(7)−Cl(7), 93.03(16); N(4)−Si(7)−Cl(7), 96.26(17).

---

(1) Some preliminary results have been presented: (a) Kim, B.-K. Ph.D. Thesis, North Dakota State University, Fargo, North Dakota, 1998. (b) Boudjouk, P.; Choi, S.-B.; Kim, B.-K. Presented at the Organosilicon Symposium, Gunma, Japan, November 4−5, 1999. (c) Boudjouk, P.; Choi, S.-B.; Kim, B.-K. *Proceedings of the 32nd Great Lakes Regional Meeting of the American Chemical Society*, Fargo, North Dakota, June 4−6, 2000; Abstract 67. (d) Boudjouk, P.; Choi, S.-B.; Kim, B.-K. *Proceedings of the 33rd Organosilicon Symposium*, Saginaw, Michigan, April 6−8, 2000; Abstract No. A-1.

(2) (a) Fleischer, H.; Hensen, K.; Stumpt, T. *Chem. Ber.* **1996**, *129*, 765. (b) Benkeser, R.; Li, G. S.; Mozdezen, E. *J. Organomet. Chem.* **1971**, *178*, 21. (c) Urry, G. *J. Inorg. Nucl. Chem.* **1964**, *26*, 414. (d) Urry, G.; Nuss, J. W. *Angew. Chem., Int. Ed. Engl.* **1964**, *26*, 435. (e)Wiberg, E.; Neumaier, A. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 517. (f) Urry, G.; Kaczmarczyk, A.; Millard, M. *J. Inorg. Nucl. Chem.* **1961**, *17*, 186. (g) Urry, G.; Kaczmarczyk, A. *J. Am. Chem. Soc.* **1960**, *82*, 751.

(3) Boudjouk, P.; Kloos, S. D.; Kim, B.-K.; Page, M.; Thweatt, D. *J. Chem. Soc., Dalton Trans.* **1998**, 877.

(4) Kim, B.-K.; Choi, S.-B.; Kloos, S. D.; Boudjouk, P. *Inorg. Chem.* **2000**, *39*, 728.

(5) Trichlorosilane (34 g, 250 mmol) was added to a clear, colorless solution of pedeta (24 g, 100 mmol) in dry CH_2Cl_2 (150 mL). A slight warming of the reaction vessel contents occurred upon addition. After stirring for 48 h at 35−40 °C, white crystals precipitated. Filtration followed by washing with CH_2Cl_2 (50 mL × 3) gave 9 g of **1** as a white crystalline powder. Anal. Calcd for $[(H_2SiCl{\cdot}pedeta)_2\,Si_6Cl_{14}]$ (**1**): C, 26.22; H, 5.50; N, 6.55. Found: C, 26.25; H, 5.42; N, 6.45. X-ray structure determination of **1**: X-ray quality crystals of $C_{28}H_{70}C_{116}N_6Si_8$ (**1**) were grown from a concentrated CH_2Cl_2 solution at room temperature. A single crystal of **1** was mounted in a thin-walled glass capillary tube and sealed under argon. The space group is *Pbca*, orthorhombic, with unit-cell dimensions $a = 19.7106(18)$ Å, $b = 22.1508(19)$ Å, $c = 27.130(2)$ Å, $V = 11845.0\ (18)$ Å^3, $Z = 8$, fw = 1282.82, $d_{calc} = 1.439$ Mg/m^3, $F(000) = 5312$ and abs. coeff. = 0.941 mm^{-1}. Intensity data were collected at 295(2) K on a Siemens CCD SMART diffractometer with Mo Kα radiation and a graphite monochromator. A total 57160 unique reflections were measured, and 10437 [R(int) = 0.0570] having $I > 2\sigma(I)$ were independent. An absorption correction was applied using spherical harmonics with the program SADABS, a component of Bruker's SAINT package used for reduction of area detector data. The structure was solved by direct methods and refined by the full-matrix least-squares techniques on F^2 using the SHELXTL program (10437 data and 539 parameters). All hydrogen atoms except hydrogen H71, H72, H81, and H82 were treated as idealized contributions. All software sources of the scattering factors are contained in the SHELXTL v5.1 library (Siemens X-ray Diffraction, 1998, Madison, WI). Final $R = 0.0638$, $R_w = 0.1579$, and Goodness-of-fit on $F^2 = 1.045$ (for all reflections, $R = 0.1329$, $R_w = 0.1967$). Full details can be found in the Supporting Information.

10.1021/ja002831a CCC: $20.00

two kinds: a set of 12 bonded in pairs to each of the six silicon atoms (average bond distance = 2.078 Å) and a set of two located on the six-fold axis of the ring. The average bond distance between silicon and axial chlorines (3.000 Å) is significantly shorter than a typical Si−Cl van der Waals bond (r_{vdw}(Si−Cl) = 3.90 Å) but longer than the sum of the covalent radii (r_{cov} (Si−Cl) = 2.17 Å).[6] The average Si−Si bond distance (2.319 Å) is slightly shorter than those in neutral cyclopolysilanes (2.34 Å).[7] The average Si−Si−Si bond angle is 119.9(5)°, resulting in a sum of internal angles of 719.5°, close to the ideal 720° for a planar structure. The rms deviation of the six silicon atoms was 0.0378 Å, with the maximum deviation from planarity among the Si atoms being 0.0609(14) Å.

We have not studied the nature of the bonding in this unusual dianion, but it seems clear that terminal chlorine atoms are playing a dominant role. We have observed that Si_6Me_{12} does not form adducts with halide ions to give complexes such as **1**; thus, the chlorine atoms are likely generating strong Lewis acid sites above and below the ring. Repulsive forces between the chloride ion and the ring chlorines may exist; however, the distances between the axial chlorides and the ring chlorines average 3.635 Å, very close to the sum of the van der Waals radii for chlorine (3.60 Å) and only slightly longer than the sum of the ionic radius of chloride and the van der Waals radius of chloride (3.50 Å), suggesting that interactions of any kind are minimal.

In pursuit of a plausible mechanism for eq 1, we detected the anion $SiCl_3^-$ (^{29}Si δ = 29.9 ppm, ref Me_4Si) from the NMR study of the reaction of $HSiCl_3$ with pedeta in CD_2Cl_2.[8] However, we did not observe the products expected from silylene insertion, $Et_3SiSiCl_2H$ or 1,1-dichlorosilacyclopentene, when we ran the reaction in the presence of Et_3SiH and 1,3-butadiene, respectively, two well-known silylene trapping agents. We also found that the addition of $SiCl_4$ to a solution of [pedeta•$H_2SiCl]^+Cl^-$ in CH_2Cl_2 produced **1**. Similarly, [pedeta•$H_2SiCl]^+Cl^-$ and $SiBr_4$ led to the precipitation of [pedeta•$H_2SiBr^+]_2[Si_6Br_{14}{}^{2-}]$ (**2**). Elemental analysis and X-ray analysis confirmed the formula of **2** (eq 2).[9]

$$[\text{pedeta}\cdot\text{H}_2\text{SiCl}]^+\text{Cl}^- \;+\; \text{SiCl}_4 \xrightarrow{\text{CH}_2\text{Cl}_2} \mathbf{1}$$

$$[\text{pedeta}\cdot\text{H}_2\text{SiCl}]^+\text{Cl}^- \;+\; \text{SiBr}_4 \xrightarrow{\text{CH}_2\text{Cl}_2} \underset{\mathbf{2}}{[\text{Si}_6\text{Br}_{14}]^{2-}\cdot 2[\text{pedeta}\cdot\text{H}_2\text{SiBr}]^+}$$

The reaction of [pedeta•$H_2SiCl]^+Cl^-$ with $SiCl_4$ was monitored by ^{1}H- and ^{29}Si NMR. The addition of $SiCl_4$ to [pedeta•$H_2SiCl]^+Cl^-$ in a 1:1 mole ratio caused the reduction of the two Si−H peaks (4.38 and 4.79 ppm) in the salt[4] and the generation of a new peak at 6.12 ppm ($HSiCl_3$). $HSiCl_3$ was also detected by ^{29}Si NMR (−9.6 ppm)[8(b)]. These observations suggest equilibria involving the redistribution of pedeta•H_2SiCl_2 and $SiCl_4$ to form $HSiCl_3$.

Details of the mechanism for formation of **1** from $HSiCl_3$ are not yet available. However, it seems clear that deprotonation of $HSiCl_3$ by pedeta and formation of [pedeta•$H_2SiCl]^+Cl^-$ are important steps in the formation of **1**.

Complex **1** is a useful synthetic agent. For example, the synthesis of dodecahydrocyclohexasilane, Si_6H_{12}, normally requires the isolation of dodecaphenylcyclohexasilane, Si_6Ph_{12}, from a mixture of catenated silanes produced from Wurtz-type coupling reactions of diphenyldichlorosilane, followed by chlorodephenylation and reduction with hydride. The overall yield from this tedious and time-consuming process is <1%.[10] However, we were able to prepare Si_6H_{12} in 95% yield by the reduction of **1** with $LiAlH_4$.[11] Similarly, treatment of **1** with MeMgBr led to Si_6Me_{12}[12] in 85% yield.

Acknowledgment. Financial support from the National Science Foundation through Grant No. 9874802 is gratefully acknowledged.

Supporting Information Available: Details of the crystallographic analyses of **1** (PDF). An X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

JA002831A

---

[6] Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry*, 4th ed.; Harper Collins College Publishers: New York 1993; p 292.

[7] (a) Kaftory, M.; Kapon, M.; Botoshansky, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons Ltd: New York, 1998; Vol. 2, pp 198 and 202 and references therein. (b) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons Ltd: New York, 1989; pp 249 and 251 and references therein.

[8] (a) Oehme, E.; Weiss, H. *J. Organomet. Chem.* **1987**, *319*, C16−18. (b) Boudjouk, P. *Proceedings of the XIth International Symposium on Organosilicon Chemistry*, Montpellier, France, September 1−6, 1996; Abstract No. LC8.

[9] A solution of [pedeta•$H_2SiCl]^+Cl^-$ (1.0 g, 2.9 mmol) in dry CH_2Cl_2 (10 mL) was added to a solution of $SiBr_4$ (1.0 g, 2.9 mmol) in CH_2Cl_2 (4 mL). After 2 days, this solution produced white crystals of [pedeta•$H_2SiBr^+]_2$ $[Si_6Br_{14}{}^{2-}](CH_2Cl_2)$(0.4 g); mp = 250 °C (dec), IR 2268 cm^{-1} (ν(SiH)). Anal. Calcd for $C_{29}H_{72}N_6Si_8Cl_2Br_{16}$; C,16.75; H, 3.49; N, 4.04; Br, 61.49; Si, 10.80; Cl, 3.41, Found: C, 16.75; H, 3.80; N, 4.43; Br, 61.15; Si, 9.87; Cl, 2.53. X-ray analysis confirms a structure similar to that of **1**.

[10] (a) Kovar, D.; Utvary, K.; Hengge, E. *Monatsh. Chem.* **1979**, *110*, 1295. (b) Hengge, E.; Kovar, D. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 403.

[11] Synthesis of Si_6H_{12}. **1** (30.0 g, 23.4 mmol) and $LiAlH_4$ pellets (3.6 g, 94 mmol) were placed in a dry, nitrogen-filled two-necked flask followed by the addition of ether (300 mL) and stirring for 10 h at room temperature. During the course of the reaction, SiH_4 evolved and was hydrolyzed in a KOH (aq) trap. At the end of the 10 h period, the solids were removed by filtration under nitrogen and washed with hexane. Combining of the liquids followed by vacuum evaporation left **1** as a clear colorless oil (3.7 g, yield 95%). Selected data for $Si_6H_{12:}$ ^{1}H NMR ($CDCl_3$, ref; $CDCl_3$ = 7.25 ppm): 3.40 (s). ^{29}Si NMR (CDCL$_3$, ref: ext. TMS = 0.00): −106.50 (J_{SiH} = 198 Hz).[11]

[12] Synthesis of Si_6Me_{12}. Tetrahydrofuran (15 mL) and **1** (1.0 g, 0.8 mmol) were placed in dry, nitrogen-filled three-necked flask. To this was slowly added methylmagnesium bromide (13 mmol). After stirring for 24 h at room temperature, the reaction mixture was hydrolyzed and extracted with hexane and ether. Dodecamethylcyclohexasilane was isolated (yield 0.2 g, 85%). Selected data for Si6Me$_{12}$: ^{1}H NMR: δ 0.22; ^{13}C NMR: δ −6.2; ^{29}Si NMR: δ −41.73. (a) West, R.; Brough, L. F.; Wojnowski, W. *Inorg. Synth.* **1979**, *19*, 265. (b) Oakley, R. T.; Stanislaski, D. A.; West, R. *J. Organomet. Chem.* **1978**, *157*, 389. (c) Gilman, H.; Tomasi, R. A. *J. Org. Chem.* **1963**, *28*, 1651. (d) Stolberg, U. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 150.