A Disilanyl Dianion and a Silyl Dianion from a Stable Silylene

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The stable silylene, *N*,*N*′-di-*t*-butyl-1,3-diaza-2-sila-2-ylidene, is reduced by Na/K or C_8K first to a disilanyl dianion and then to a silyl dianion. Both of these species can be derivatized by reaction with hydroxy compounds or with chlorotrimethylsilane.

The marginally-stable silylene **1**[1] is now readily available from the dissociation of its stable tetramer.[2] Many of the reactions of **1** resemble those of its better-known and much more robust analog, **2**.[3,4] It was therefore unexpected to find that **1** undergoes reduction to anionic species, whereas **2** does not.

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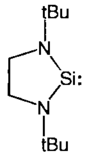

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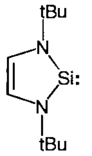

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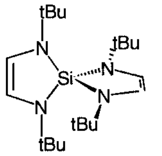
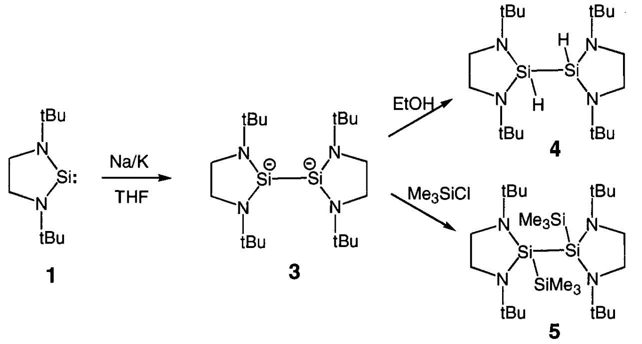
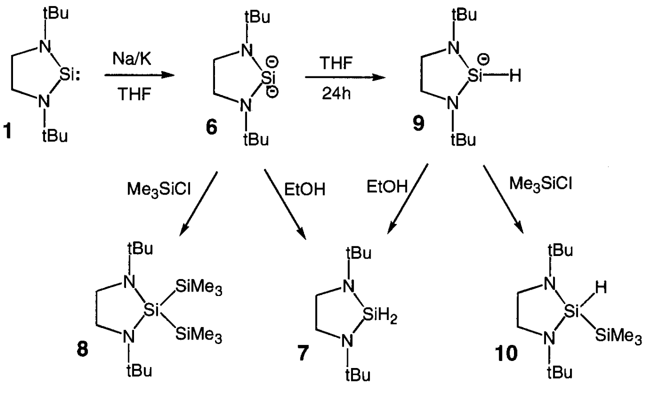


Reaction of **1** with one equiv of potassium, from Na/K or C_8K, leads to formation of the 1,2-disilanyl dianion **3**,[5] which can be trapped with alcohols or water to give the dihydride **4** and with Me_3SiCl to the tetrasilane **5** (Scheme 1). The structure of **4** was established by X-ray crystallography, and will be reported in a forthcoming publication.[6]



Scheme 1.

Similar reduction of **1** with 2 equiv of potassium provides the dianion **6**.[7] This species also reacts with water or alcohols to produce the known dihydride **7**[11] and with Me_3SiCl to give trisilane **8**, as shown in Scheme 2. Dianion **6** is stable in THF solution at –20 °C, but at 25 °C it slowly deprotonates THF ($t_{1/2}$ ~3h) to form the hydrosilyl monoanion, **9**.[8] The latter is indefinitely stable, and is once again trapped by electrophiles, as shown in the Scheme.



Scheme 2.

Reduction of **1** in two steps is consistent with cyclic voltammetric measurements, which indicate two irreversible reduction waves for the silylene, peaking at –1.75 V and –2.35 V vs Ag/AgCl (Figure 1). No such reduction waves were observed for the unsaturated silylene **2**.

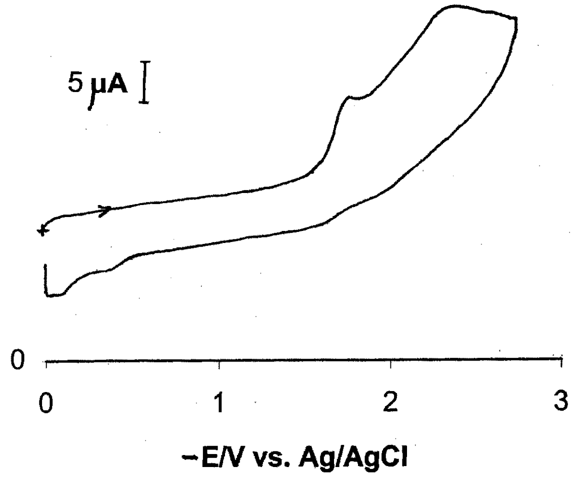


Figure 1. Cyclic Voltammogram for reduction of **1**, showing two irreversible reduction waves.

Theoretical calculations indicate that electron attachment to both **1** and **2** is endothermic, but when the potassium ion is included the (gas phase) reactions are slightly exothermic, by 11.3 kJ mol^{-1} for **1** and 12.1 kJ mol^{-1} for **2** (at UB3LYP/6-311+G**). The difference is small, and actually favors reduction of **2** over **1**. Why, then, are anions not obtained from **2**?

The reaction of **2** with excess alkali metal appears to break Si–N bonds, eventually liberating the diimine tBuN=CH-CH=NtBu, which then reacts with **2** to form the known spiro compound, **11**.[3] Evidently this type of side reaction does not take place readily with the saturated silylene **1**, perhaps because fragmentation cannot yield a neutral product like the diimine.

The ^{29}Si chemical shifts for the anionic silicons in **3**, **6**, and **9** are all positive, at 17.8, 54.0 and 7.8 ppm respectively, although silyl anions usually have strongly negative silicon resonances. Recent papers have shown, however, that nitrogen substitution on a silyl anion leads to deshielding, for example in **12** (27.9 ppm)[9] and **13** (60.1 ppm).[10] The deshielding can be attributed to electron-withdrawal by the nitrogen substituent.[9]

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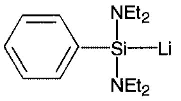

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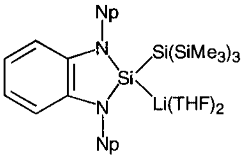

The new anionic species **3**, **6**, and **9** are expected to be valuable intermediates for forming derivatives of **1**, for instance transition metal complexes.[11–14]

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References and Notes

1 R. West and M. Denk, *Pure Appl. Chem.*, **68**, 785 (1996).

2 T. A. Schmedake, M. Haaf, Y. Apeloig, T. Mueller, S. Bukalov, and R. West, *J. Am. Chem. Soc.*, **121,** 2514 (1999).

3 M. Haaf, A. Schmeidl, T. A. Schmedake, D. R. Powell, A. J. Millevolte, M. Denk, and R. West, *J. Am. Chem. Soc.*, **120**, 12714 (1998).

4 For a review on stable silylenes and their chemistry, see M. Haaf, T. A. Schmedake, and R. West, *Acc. Chem. Res.*,**33**, 704 (2000).

5 Under Schlenk conditions, 2.00 g of **1** in 150 mL of THF was added to Na/K alloy (0.085 g Na, 0.280 g K) and stirred at 10 °C. The reaction was monitored by taking aliquots of the reaction mixture, trapping with chlorotrimethylsilane, and determining the ^{1}H NMR of the resulting mixture. Yield of **3** (NMR): 90%. Tetrasilane **5**: Colorless solid, recrystallized from THF. ^{1}H NMR (C_6D_6, δ): 0.399 (s, 18H), 1.300 (s, 36H), 2.9 (m, 8H). ^{13}C NMR (C_6D_6, δ): 4.06, 30.55, 45.27, 51.26. ^{29}Si NMR (C_6D_6, δ): –17.85, –8.64. Disilanyl dihydride **4**: 5.0 mmol of **3** in 100 mL THF was cooled to –78 °C and treated with 1 equiv of ethanol to produce **4** in 95% yield (by NMR). Crystals suitable for X-ray analysis were grown from THF. ^{1}H NMR (C_6D_6, δ): 1.293 (s, 36H), 2.965 (s, 8H), 5.739 (s, 2H). ^{13}C NMR (C_6D_6, δ): 29.71, 44.78, 50.73. ^{29}Si NMR (C_6D_6, δ): –23.9. Identical results were obtained when water or phenol were used as the trapping agents.

6 a) T. A. Schmedake, M. Haaf, B. J. Paradise, D. R. Powell, and R. West, *Can. J. Chem.*, **78**, 1526 (2000). This communication will correct the information given in 6a, in which reduction of **1** is reported to lead only to **3**. b) T. A. Schmedake, Ph. D. Thesis, University of Wisconsin, Madison, WI, U. S. A., 2000.

7 2.00 g of **1** in 150 mL of THF was stirred with Na/K alloy (0.170 g Na, 0.579 g K) under anaerobic conditions at 10 °C. The reaction was monitored by the ^{1}H NMR of the trimethylsilyl derivative **8**, as in the synthesis of **3**. Yield of **6** (NMR) 85%, ^{29}Si NMR (THF, δ) 54.0. Trisilane **8**: A solution of 10.1 mmol **6** in 150 mL THF was cooled to –78 °C and 30 mmol of Me_3SiCl was added. Workup yielded **8** as a colorless liquid**,** purified by fractional distillation (bp 80 °C, 0.1 Torr). Yield, 90%. Crystals were grown from hexane at –20 °C and kept below this temperature during X-ray determination. ^{1}H NMR (C_6D_6, δ): 0.289 (s, 18H), 1.199 (s, 18H), 2.85 (s, 4H). ^{13}C NMR (C_6D_6, δ): 1.45, 30.57, 45.94, 50.81. Dihydride **7**: Addition of 2 equiv of EtOH to a THF solution of **6** at 0 °C and workup gave colorless crystals of the known dihydride **7**,[11] purified by sublimation (60 °C, 0.1 Torr). Yield 65%; ^{1}H NMR (C_6D_6, δ): 1.15 (s, 18H), 2.86 (s, 4H), 5.13 (s, 2H.

8 Hydrosilyl monoanion **9**: A solution of 2.0 g (10.1 mmol) of **6** in 150 mL THF was stirred under a low Ar flow at room temperature. After 24 h the solution had turned to a clear orange-yellow indicating complete conversion of the dianion. ^{1}H NMR (C_6D_6, δ): 1.319 (s, 18H), 3.029 (s, 4H), 5.531 (s, 1H). ^{29}Si NMR (THF/C_6D_6 capillary, δ) 7.81 (calc. = 0.3 ppm). Yield (NMR): 85%. A solution of 5.0 mmol **9** in 100 mL THF was treated with 1 equiv of ethanol at 0 °C. The solution was warmed to room temperature and the ^{1}H NMR of the solution indicated formation of the previously characterized[11] dihydride **7**. Yield (NMR) 85%.

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10 B. Gehrhus, P. B. Hitchcock, M. F. Lappert, and J. C. Slootweg, *Chem. Commun.*, **2000**, 1427.

11 M. Denk, Ph. D. dissertation, Technische Universität München, Garching, Germany, 1992.

12 M. Denk, R. Hayashi, and R. West, *J. Chem. Soc., Chem. Commun.*, **1994**, 33.

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14 B. Gehrhus, P. B. Hitchcock, M. F. Lappert, and H. Maciejewski, *Organometallics*, **17**, 5599 (1998).