Reaction of Hydrosilanes with Lithium. Formation of Silole Anions from 1-Methylsilole via Carbodianion

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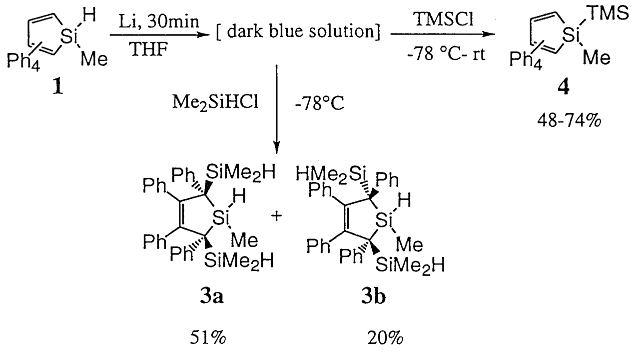
Three different types of silacyclopentadienyl anions have been obtained in the reduction of 1-methylsilole **1** with excess lithium. Treatment of lithiated solution with dimethylchlorosilane gave 2,5-bis(dimethylsilyl)silole derivatives **3a** and **3b**, and with trimethylchlorosilane gave 1-trimethylsilyl-1-methylsilole derivative **4** at an early stage, and 1,1-bis(triemthylsilyl)silole derivative **8** at a late stage. Silole 1,1-dianion **7** has been formed via silole 2,5-dianion **2** and silole 1-anion **5**.

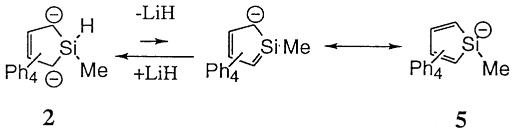
The chemistry of silyllithiums has continued to receive much attention with respect to their polysilane synthesis and to their silylating reagents in organic synthesis.[1] However, their synthetic methodologies have been rather limited in reductions of chlorosilanes, disilanes, and metal-lithium exchange reaction. The reduction of hydrosilanes have not been studied so far since high reduction potential of Si-H bond. Gilman reported the disilane formation by reduction of Ph_3SiH with lithium.[2] Recently we have reported the interesting formation of disilaanthracene dimer in the reduction of 9,10-dihydro-9,10-disilaanthrcenes with excess lithium.[3] In contrast, the hydrosilanes in which no aromatic nuclei are attached to central silicon atom, such as triethylsilane, do not react with lithium metal. Electron accepting groups on the silicon center may be required for silyllithium formation. 2,3,4,5-Tetraphenylsiloles are known as good electron acceptors. The one of the reasons for the low-lying LUMO of these compounds is thought to be the existence of the σ^*-π^* conjugation.[4] There are a few reports that silole reacts with lithium or potassium to give the corresponding dianions or tetraanion.[5] There is also considerable interest in the structure and bonding in silole anions.[6-10] We herein report the reduction of 1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (**1**) with lithium and the formation of silyl anions via carbanions.

Sonication of **1** with excess lithium (ca. 30 eq.) in THF for 30 min at 0 ℃ produced a dark blue solution. After removing unreacted lithium, addition of an excess of dimethylchlorosilane to this solution at -78 ℃ afforded 2,5-bis(dimethylsilyl)-1-methyl-2,3,4,5-tetraphenyl-1-silacyclo-3-pentenes (**3a** and **3b**)[11] in 71% yield. The formation of **3a** and **3b** clearly reveals that silole **1** is readily reduced with lithium to afford 2,5-dilithio-1-methyl-2,3,4,5-tetraphenyl-1-silacyclo-3-pentene(**2**). (Scheme 1)



Scheme 1.

Interestingly, treatment of this solution with trimethylchlorosilane gave 1-trimethylsilyl-1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (**4**) in 48-74% yields. When trimethylchlorosilane was added at -78 ℃, the color of the solution did not change until the mixture was warmed up to room temperature over 1 h. These results would be ascribed to the presence of the equilibrium between carbanion **2** and silyl anion **5**, as shown in Scheme 2.[6,12-13]



Scheme 2.

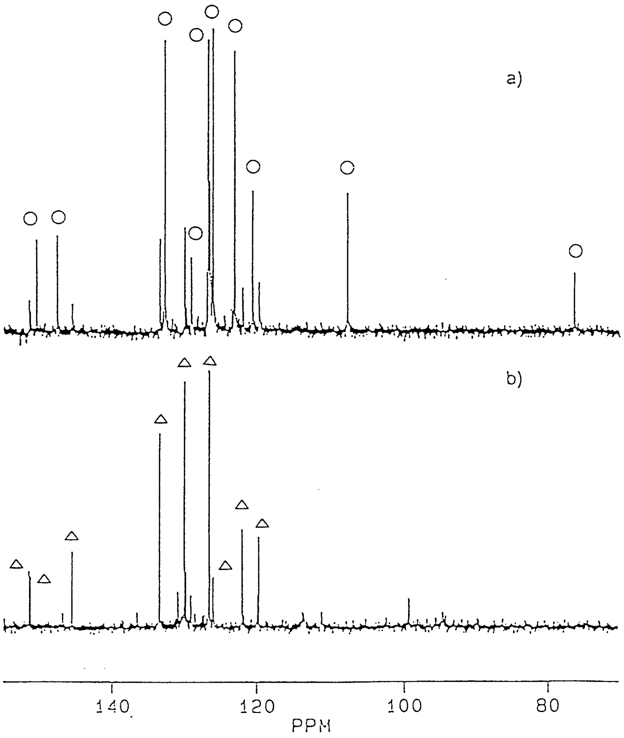
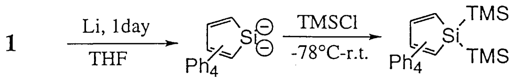


Figure 1. ^{13}C-NMR spectra of the reaction mixture of **1** with excess lithium, a) after 1 h, b) after 4 h. (○=**2**, △=**8**)

In order to shed light on this reaction, NMR measurements were carried out. The ^{13}C NMR spectrum of the major product in this solution was assigned for the carbanion **2**.[14] The NMR data of **2** are very similar to the dianion of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (**6**), [5b] which was futher reduced to tetraanion **7**.

The 11 resonance peaks due to **2** disappear over a period of approximately 4 h at room temperature and are replaced by 9 new resonances[7b] assigned a new speies **8** (Figure 1). This reaction occurs only in the presence of excess lithium metal.

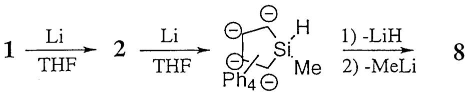
Derivatization of **8** with trimethylchlorosilane gives 1,1-bis(trimethylsilyl)silole **9** (Scheme 3). Stirring **1** with an excess of lithium in THF at room temperature for 1 day afforded to a dark orange solution. After removal of unreacted lithium, addition of an excess trimethylchlorosilane to the reaction mixture gave 1,1-bis(trimethylsilyl)- 2,3,4,5-tetraphenyl-1-silacyclopentadiene (**9**)[6b] in 73% yield, which was derived from 1,1-dilithio-1-silacyclopentadiene (**8**). [7b,7d,15]



8 **9** 73 %

Scheme 3.

One of the possible reaction mechanisms for the formation of silyl dianion **8** is shown in Scheme 4. O'Brien and Breeden have reported the formation tetraanion **7** by the further reduction of dianion **6**.[5b] Under the reactions, it would be considered to form tetraanion **10**, which undergoes elimination of LiH and MeLi to give silyl dianion **8**.



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Scheme 4.

To conclude, from the chemical trapping reactions and NMR spectroscopic measurements, hydrosilane **1** was firstly converted to the carbanion **2** and/or silole monoanion **5**. Further reduction of **2** or **5** produced the silyl dianion **8**.

References and Notes

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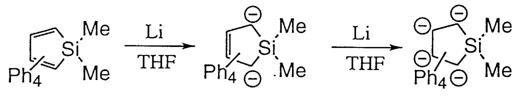

6 **7**

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11 Compound **3a**: colorless crystals mp 123-125 ℃, ; ^{1}H NMR(C_6D_6) δ -0.18 (d,3H, J=3.5Hz), 0.27(d, 6H, J=3.8Hz), 0.29(d, 6H, J=3.8Hz), 4.75(m, 2H), 4.88(m,1H), 6.75-7.56(m, 20H); ^{13}C NMR(C_6D_6) δ -6.14(q), -3.50(q), -2.55(q), 38.23(s), 124.42(d), 126.91(d), 127.58(d), 128.30(d), 128.89(d), 131.60(d), 142.10(s), 143.97(s), 147.51(s); ^{29}Si NMR(C_6D_6) δ -9.54, 7.27; MS(M^+, relative abundance) 518(M^+, 4), 458(M^+-60, 35), 135(M^+-383, 100); Anal. Found: C, 76.22; H, 7.34%. Calcd for $C_{33}H_{38}Si_3$: C, 76.38; H, 7.38%. Compound **3b**: colorless crystals mp 172-173 ℃ ^{1}H NMR($CDCl_3$) δ -0.25 (d,3H, J=3.6Hz), -0.10(d, 3H, J=3.6Hz), -0.04(d, 6H, J=3.7Hz), -0.01(d, 3H, J=3.8Hz), 0.01(d, 3H, J=3.6Hz), 4.15(m, 1H), 4.31(m,1H), 4.41 (m,1H), 6.96-7.69(m, 20H); ^{13}C NMR($CDCl_3$) δ -5.00 (q), -4.54 (q), -3.49(q), -3.32(q), 38.20(s), 38.88(s), 123.98(d), 124.07(d), 126.85(d), 126.96 (d), 127.26(d), 127.31(d), 127.90(d), 128,14(d), 128.35(d), 128.58(d), 131.35(d), 131.51(d), 142.00(s), 142.17(s), 145.49(s), 146.25(s), 146.62(s), 149.49(s); ^{29}Si NMR($CDCl_3$) δ -14.01, -11.53, 25.18; MS(M^+, relative abundance) 518(M^+, 4), 458(M^+-60, 35), 135(M^+-383, 100); HRMS; m/e 518.2311 (calcd for $C_{33}H_{38}Si_3$; 518.2281). Anal. Found: C, 76.29; H, 7.42%. Calcd for $C_{33}H_{38}Si_3$: C, 76.38; H, 7.38%.

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14 Compound **2**: ^{13}C NMR(THF-d8) δ 2.58(q), 76.42(s), 107.65(d), 120.53(d), 123.05(d), 125.98(d), 126.62(d), 128.82(s), 132.47(d), 147.82(s), 150.33(s); ^{29}Si NMR(THF-d8) δ -34.14

15 The ^{29}Si NMR spectrum for **8** was observed at 67.6 ppm in THF-d8.