Novel 1,2-Dilithiodisilanes Derived from Reduction of Stable Tetrakis(trialkylsilyl)disilenes with Lithium Metal

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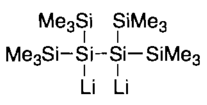
1,2-Dilithiotetrakis(trialkylsilyl)disilanes $[(R_3Si)_2SiLi]_2$ (R_3Si = *t*-$BuMe_2Si$ and *i*-Pr_2MeSi) were prepared as stable off-white powder by the reduction of the corresponding tetrakis(trialkylsilyl)disilenes with lithium in THF. The 1,2-dilithiodisilanes reacted with water, iodomethane, and chlorosilanes to give the corresponding disubstituted products in high yields.

Although dimetallooligosilanes are of growing interest because of their unique structures and potential applications to organic and organometallic synthesis as a new class of silyl anions,[1] rather limited studies of 1,2-dimetallodisilanes have been reported so far.[2] Gilman et al. first generated 1,2-dilithiotetrakis(trimethylsilyl)disilane (**1**) using the reaction of tris(trimethylsilyl)silyllithium with hexakis(trimethysilyl)disilane.[2a,3] 1,2-Dilithio-1,2-disilaacenaphthene **2**,[2b] 1,2-dimetallodisiloles **3**,[2c,2d] and 1,2-dimetallotetraaryldisilane **4a**[2e] were prepared in solution by the reduction of the corresponding 1,2-dihalodisilanes with metals and characterized by NMR spectroscopies as well as trapping experiments. Belzner et al. found that tetraaryl-1,2-dilithiodisilane **4b** was produced by the lithium reduction of the corresponding cyclotrisilane; **4b** was isolated and its structure in the solid state was determined by X-ray crystallography.[2f] Recently, West et al. reported that the reduction of a stable diaminosilylene with lithium afforded the corresponding 1,2-dilithio derivative of the silylene dimer (**5**).[2g]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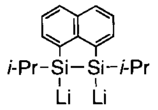
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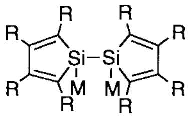
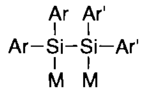
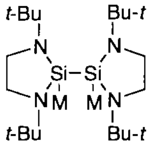
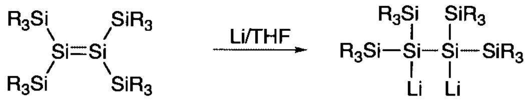

3, M = alkali metal
R = Me, Ph


4a, M = MgCl, Ar = mesityl,
Ar' = 2-(Me_2NCH_2)C_6H_4
4b, M = Li,
Ar = Ar' = 2-(Me_2NCH_2)C_6H_4

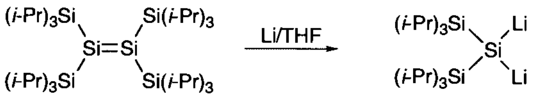

5, M = Na, K

We wish herein to report the preparation of novel 1,2-dilithiodisilanes based on the two-electron reduction of the corresponding disilenes. The reduction of tetrakis(trialkylsilyl)disilenes **6a** and **6b**[4] with lithium afforded the corresponding 1,2-dilithiodisilanes **7a** and **7b**, respectively, in quantitative yields, similarly to the reduction of tetrakis(trialkylsilyl)ethylenes with lithium giving the corresponding dilithioethanes (eq 1).[5] Interestingly, the reduction of highly congested disilene **6c** with lithium did not give the corresponding 1,2-dilithiodisilane but 1,1-dilithiobis(triisopropylsilyl)silane **8**[6,7] (eq 2).


(1)

6a (R_3Si = *t*-$BuMe_2Si$)
6b (R_3Si = *i*-Pr_2MeSi)

7a (R_3Si = *t*-$BuMe_2Si$)
7b (R_3Si = *i*-Pr_2MeSi)


(2)

6c

8

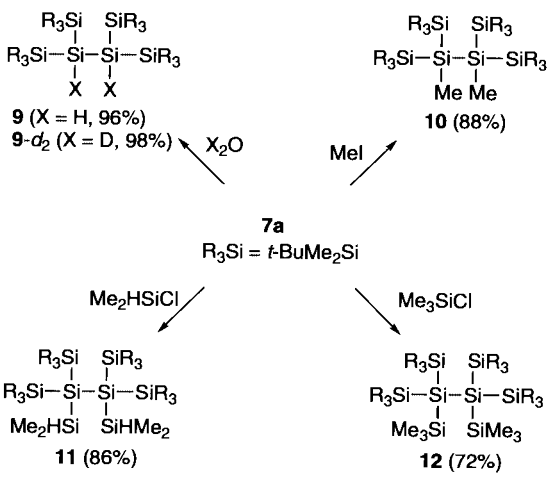
Treatment of tetrakis(*t*-butyldimethylsilyl)disilene **6a** (1.60 g, 3.1×10^{-3} mol) with an excess amount of lithium metal in THF (15 mL) at 0 °C for 12 h gave a dark red solution of the corresponding 1,2-dilithiodisilane **7a**; ^1H NMR spectra of the reaction mixture exhibited quantitative formation of **7a**. After removal of an excess amount of lithium by decantation, the solvent was distilled off in vacuo. Washing the resulting solid with hexane provided off-white powder of **7a**·6THF (1.9 g, 2.0×10^{-3} mol) in 65% yield.[8] The structure of **7a** was confirmed by NMR spectroscopies and several trapping experiments as shown below. Similarly, 1,2-dilithiodisilane **7b**[8] was prepared quantitatively by the reduction of **6b** with lithium.

The ^{29}Si NMR resonances due to the silicon nuclei bound to lithium appear at –185.9 ppm for **7a** and –190.9 ppm for **7b** in THF-d_8, which are similar to that reported for tris(trimethylsilyl)silyllithium (–189.4 ppm in THF).[9] The nature of the Si–Li bonds is still open.[10]

When the reduction of disilene **6c** was performed in the same conditions, 1,1-dilithiosilane **8** was obtained almost quantitatively (eq 2). The formation of **8** was confirmed by comparing the NMR data with those reported by Sekiguchi et al.[6] and by the hydrolysis of the reaction mixture giving the corresponding 1,1-dihydrosilane in quantitative yield.

It is interesting to note that the reduction modes of disilenes with alkali metals are remarkably dependent on the electronic and steric effects of the substituents. The lithium reduction of a tetraaryldisilene, $Tip_2Si{=}SiTip_2$ (Tip = 2,4,6-triisopropylphenyl), has been reported to cause Si–C bond cleavage giving the corresponding triaryldisilenyllithium $Tip_2Si{=}SiTipLi$ and TipLi.[11] Reactions of 1,2-dichlorodisilanes $[R_2ClSi]_2$ (R = *t*-Bu and 2,4,6-trimethylphenyl) with excess alkali metals afforded the corresponding disilene anion radicals probably via the corresponding disilene but no further reduction took place.[12] The relatively low second reduction potentials of tetrakis(trialkylsilyl)disilenes compared with those of tetraaryldisilenes,[13] would be responsible for the successful preparation of 1,2-dilithiodisilanes **7a** and **7b**, while **7c** formed from disilene **6c** is further reduced to give 1,1-dilithiosilane **8**.

Scheme 1.



1,2-Dilithiodisilane **7a** reacted with various electrophiles to provide the corresponding disubstituted products without formation of any undesired side products via electron-transfer reactions (Scheme 1). Hydrolysis and deuteriolysis of **7a** in ether provided the corresponding 1,2-dihydrodisilane **9** and 1,2-dideuteriodisilane **9**-d_2[14] in 96 and 98% yields, respectively. Methylation of **7a** with iodomethane occurred readily to afford 1,2-dimethyldisilane **10** (88%).[15] Interestingly, the reactions of **7a** with chlorodimethylsilane and chlorotrimethylsilane gave the corresponding 1,2-disilylated disilanes **11** and **12** in 86 and 72% yields, respectively.[16] These successful dialkylation and disilylation indicates that 1,2-dilithiodisilanes **7a** and **7b** are highly promising as useful bifunctional organosilicon reagents.

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8 **7a**: mp 151–153 ˚C (dec); ^{1}H NMR (THF-d_8, 293 K, δ) 0.13 (s, 24 H, SiMe), 0.93 (s, 36H, *t*-Bu); ^{13}C NMR (THF-d_8, 293 K, δ) 2.8 (SiMe), 20.2 ($\underline{C}(CH_3)_3$), 30.1 ($C(\underline{C}H_3)_3$); ^{29}Si (THF-d_8, 293 K, δ) –185.9 (SiLi), 6.7 (*t*-BuMe$_2$Si); ^{7}Li (THF-d_8, δ) 0.26 (brs, $\nu_{1/2}$ = 29 Hz); ^{1}H NMR (toluene-d_8, 293 K, δ) 0.50 (s, 24H, Me), 1.21 (s, 36H, *t*-Bu), 1.35–1.40 (m, 24H, THF), 3.45–3.49 (m, 24H, THF); ^{13}C NMR (toluene-d_8, 293 K, δ) 2.7 ($Si\underline{C}H_3$), 20.2 ($\underline{C}(CH_3)_3$), 25.7 (THF), 30.0 ($C(\underline{C}H_3)_3$), 69.0 (THF); ^{29}Si NMR (toluene-d_8, 293 K, δ) –182.6 ($\underline{Si}Li$), 7.3 (*t*-BuMe$_2\underline{Si}$); ^{7}Li NMR (toluene-d_8, 293 K, δ) 1.54 (brs, $\nu_{1/2}$ = 43.6 Hz). **7b**: mp 136–138 ˚C (dec); ^{1}H NMR (THF-d_8, 293 K, δ) 0.06 (s, 12H), 0.94–1.02 (m, 8H), 1.02–1.11 (m, 48 H); ^{13}C NMR (THF-d_8, 293 K, δ) –1.70 ($SiCH_3$), 17.8 ($\underline{C}H(CH_3)_2$), 21.4, 22.0 ($CH(\underline{C}H_3)_2$); ^{29}Si NMR (THF-d_8, 293 K, δ) –190.9 (SiLi), 8.3 (*i*-Pr$_2$MeSi); ^{7}Li (THF-d_8, δ) 0.62 (s, $\nu_{1/2}$ = 22 Hz).

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13 M. Kira, T. Ishima, T. Iwamoto, and M. Ichinohe, *J. Am. Chem. Soc.*, **123**, 1676 (2001). Tetrakis(trialkylsilyl)disilenes **6a** and **6c** show two reduction peaks in THF; typically, $E_{p,Red}$ = –1.82 and –2.41 V for $[(i\text{-}Pr)_2MeSi]_2Si{=}Si[SiMe(i\text{-}Pr)_2]_2$, while tetraaryldisilenes exhibit only one reduction peak ($E_{p,Red}$ = –2.66 V for $Tip_2Si{=}SiTip_2$).

14 **9**: a colorless oil; ^{1}H NMR (C_6D_6, δ) 0.28 (s, 24H, SiMe), 1.06 (s, 36H, *t*-Bu), 3.18 (s, 2H, SiH); ^{13}C NMR (C_6D_6, δ) –1.8 (SiMe), 19.1 ($\underline{C}(CH_3)_3$), 27.6 ($C(\underline{C}H_3)_3$); ^{29}Si NMR (C_6D_6, δ) –124.1 (SiH), 1.1 (*t*-BuMe$_2$Si); MS (EI, 70 eV) *m*/*z*(%) 518 (0.6, M$^+$), 461 (1.5), 288(8.2), 73 (100); HRMS (EI, 70 eV) found: *m*/*z* 518.3475. Calcd for $C_{24}H_{62}Si_6$: M$^+$, 518.3467. **9**-d_2: a colorless oil; ^{1}H NMR (C_6D_6, δ) 0.28 (s, 24H, SiMe), 1.06 (s, 36H, *t*-Bu); ^{13}C NMR (C_6D_6, δ) –1.8 (SiMe), 19.1 ($\underline{C}(CH_3)_3$), 27.6 ($C(\underline{C}H_3)_3$); ^{29}Si NMR (C_6D_6, δ) –124.2 (t, *J*(Si-D) = 23 Hz, SiD), 1.1 (*t*-BuMe$_2$Si); MS (EI, 70 eV) *m*/*z*(%) 520 (0.5, M$^+$), 463 (1.2), 290 (6.8), 73 (100). HRMS (EI, 70 eV) found: *m*/*z* 520.3598. Calcd for $C_{24}H_{60}D_2Si_6$: M$^+$ 520.3591.

15 **10**: colorless crystals; mp 165–167 °C; ^{1}H NMR (C_6D_6, δ) 0.30 (s, 24H, SiMe), 0.64 (s, 6H, SiMe), 1.04 (s, 36 H, *t*-Bu); ^{13}C NMR (C_6D_6, δ) –2.3 (SiMe), –0.6 (SiMe), –0.1 (SiMe), 20.6 ($\underline{C}(CH_3)_3$), 28.9 ($C(\underline{C}H_3)_3$); ^{29}Si NMR (C_6D_6, δ) –67.7 ((*t*-BuMe$_2$Si)$_2\underline{Si}$Me), –1.0 (*t*-BuMe$_2$Si); MS (EI, 70 eV) *m*/*z* (%) 546 (3.4, M$^+$), 431 (21.9), 258 (100), 115 (7.3), 73 (48.5); Anal. Calcd for $C_{26}H_{66}Si_6$: C, 57.06; H, 12.15%. Found: C, 57.26; H, 11.95%.

16 **11**: colorless crystals; mp 170–171 °C; ^{1}H NMR (C_6D_6, δ) 0.44 (s, 24H, SiMe), 0.52 (d, *J* = 4.3 Hz, 12H, SiMe$_2$H), 1.10 (s, 36H, *t*-Bu), 4.61 (sept, *J* = 4.3 Hz, 2H); ^{13}C NMR (C_6D_6, δ) 1.9 (SiMe), 2.7 (SiMe), 3.3 (SiMe), 21.6 ($\underline{C}(CH_3)_3$), 29.6 ($C(\underline{C}H_3)_3$); ^{29}Si NMR (C_6D_6, δ) –107.9 ((*t*-BuMe$_2$Si)$_2\underline{Si}$), –27.5 ($\underline{Si}Me_2H$), 5.6 (*t*-BuMe$_2$Si); MS (EI, 70 eV) *m*/*z* (%) 634 (8.6, M$^+$) 577 (12.1), 519 (33.8), 402 (32.8), 317 (100); Anal. Calcd for $C_{28}H_{74}Si_8$: C, 52.91; H, 11.74%. Found: C, 53.12; H, 11.65%. **12**: colorless crystals; mp 176–178 °C; ^{1}H NMR (C_6D_6, δ) 0.12 (s , 18 H, SiMe), 0.38 (s, 12H, SiMe), 0.39 (s, 12H, SiMe), 1.11 (s, 36H, *t*-Bu); ^{13}C NMR (C_6D_6, δ) –0.2 (SiMe), 1.4 (SiMe), 1.5 (SiMe), 21.0 ($\underline{C}(CH_3)_3$), 29.2 ($C(\underline{C}H_3)_3$); ^{29}Si NMR (C_6D_6, δ) –124.2 ((*t*-BuMe$_2$Si)$_2\underline{Si}$), –0.4 (SiMe$_3$), 15.9 (*t*-BuMe$_2$Si); MS (EI, 70 eV) *m*/*z* (%) 662 (7.2, M$^+$), 605 (11.2), 547 (35.2), 474 (20.6), 331 (100); Anal. Calcd for $C_{30}H_{78}Si_8$: C, 54.30; H, 11.85%. Found: C, 54.52; H, 11.92%.