Synthesis of a Series of 1,1-Difunctionalized Siloles

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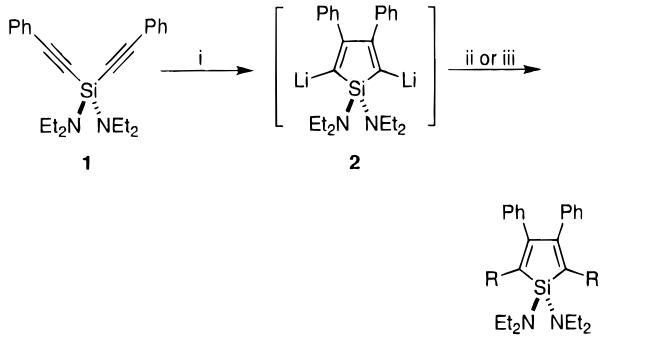
Summary: A series of 1,1-difunctionalized siloles have been synthesized from 1,1-diaminosiloles, which have been prepared via the intramolecular reductive cyclization of diaminobis(phenylethynyl)silane.

The chemistry of siloles (silacyclopentadienes) has continued to receive much attention with respect to their syntheses, reactivities, properties, coordination abilities to transition metals, and aromaticity of their anionic species.[1] Of special note are the recent and remarkable progresses in the silole anions[2] and in the silole-containing π-conjugated systems.[3−5] For these chemistries, functionalized siloles, especially 1,1-difunctionalized and 2,5-difunctionalized siloles, are an important class of compounds as starting materials. However, their synthetic methodologies have been rather limited.[6−10] 1-Functionalized and 1,1-difunctionalized siloles have been prepared by only three types of reactions, *i.e.*, the coupling reaction of 1,4-dilithiobutadiene derivatives with SiX_4,[6] the flash vacuum pyrolysis of 1-allylsilacyclopent-3-ene,[7] and the transmetalation from zirconacyclopentadienes,[8] followed by functional group transformation.[9] 2,5-Difunctionalized siloles are available generally by only one method, *i.e.*, intramolecular reductive cyclization of bis(phenylethynyl)silanes, which we have recently developed.[10,11] We now report a new route to a series of 1,1-difunctionalized siloles using 1,1-diaminosiloles as key compounds, which can be readily prepared by our methodology.[10]

Scheme 1[a]



[a] Reagents and Conditions: (i) LiNp (4 molar amount), THF, −78 °C, 1 h. (ii) Me_3SiCl (4 molar amount), −78 °C to room temperature, 8 h. (iii) $(MeO)_2SO_2$ (4 molar amount), −78 °C to room temperature, 10 h.

1,1-Diaminosiloles have been prepared by the intramolecular reductive cyclization[10] of diaminobis(phenylethynyl)silane, as shown in Scheme 1. Thus, bis(diethylamino)bis(phenylethynyl)silane (**1**)[12] was added dropwise into an excess amount of lithium naphthalenide (LiNp, 4 molar amount)[13] at −78 °C to cleanly form 2,5-dilithio-1,1-diaminosilole **2**.[14] The dilithiosilole **2**

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(1) Recent excellent reviews: (a) Dubac, J.; Laporterie, A.; Manuel, G. *Chem. Rev.* **1990**, *90*, 215. (b) Colomer, E.; Corriu, R, J. P.; Lheureux, M. *Chem. Rev.* **1990**, *90*, 265.

(2) (a) Gordon, M. S.; Boudjouk, P.; Anwari, F. *J. Am. Chem. Soc.* **1983**, *105*, 4972. (b) Damewood, J. R. *J. Org. Chem.* **1986**, *51*, 5028. (c) Joo, W.-C.; Hong, J.-H.; Choi, S.-B.; Son, H.-E.; Kim, C. H. *J. Organomet. Chem.* **1990**, *391*, 27. (d) Hong, J.-H.; Boudjouk, P. *J. Am. Chem. Soc.* **1993**, *115*, 5883. (e) Hong, J.-H.; Boudjouk, P.; Castellino, S. *Organometallics* **1994**, *13*, 3387. (f) Freeman, T. D.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 8428. (g) Goldfuss, B.; Schleyer, P. v. R. *Organometallics* **1995**, *14*, 1553. (h) West, R.; Sohn, H.; Bankwitz, U.; Calabrese, J.; Apeloig, Y.; Mueller, T. *J. Am. Chem. Soc.* **1995**, *117*, 11608. (i) Bankwitz, U.; Sohn, H.; Powell, D. R.; West, R. *J. Organomet. Chem.* **1995**, *499*, C7. (j) Goldfuss, B.; Schleyer, P. v. R.; Hampel, F. *Organometallics* **1996**, *15*, 1755. (k) Freeman, W. P.; Tilley, T. D.; Yap, G. A. P.; Rheingold, A. L. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 882. (l) Freeman, W. P.; Tilley, T. D.; Liable-Sands, L. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 10457.

(3) (a) Tamao, K.; Yamaguchi, S.; Shiozaki, M.; Nakagawa, Y.; Ito, Y. *J. Am. Chem. Soc.* **1992**, *114*, 5867. (b) Tamao, K.; Yamaguchi, S.; Ito, Y.; Matsuzaki, Y.; Yamabe, T.; Fukushima, M.; Mori, S. *Macromolecules* **1995**, *28*, 8668. (c) Yamaguchi, S.; Tamao, K. *Tetrahedron Lett.* **1996**, *37*, 2983. (d) Yamaguchi, S.; Tamao, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2327. (e) Tamao, K.; Ohno, S.; Yamaguchi, S. *J. Chem. Soc., Chem. Commun.* **1996**, 1873. (f) Tamao, K.; Yamaguchi, S. *Pure Appl. Chem.* **1996**, *68*, 139. (g) Tamao, K.; Uchida, M.; Izumizawa, T.; Furukawa, K.; Yamaguchi, S. *J. Am. Chem. Soc.* **1996**, *118*, 11974.

(4) (a) Corriu, R. J. P.; Douglas, W. E.; Yang, Z. -X.; Garnier, F.; Yassar, A. *J. Organomet. Chem.* **1991**, *417*, C50. (b) Bréfort, J. L.; Corriu, R. J. P.; Gerbier, P.; Guérin, C.; Henner, B. J. L.; Jean, A.; Kuhlmann, T. *Organometallics* **1992**, *11*, 2500. (c) Corriu, R. J. P.; Douglas, W. E.; Yang, Z. -X. *J. Organomet. Chem.* **1993**, *456*, 35.

(5) Toyoda, E.; Kunai, A.; Ishikawa, M. *Organometallics* **1995**, *14*, 1089.

(6) (a) Curtis, M. D. *J. Am. Chem. Soc.* **1967**, *89*, 4241. (b) Hagen, V.; Rühlmann, K. *Z. Chem.* **1968**, *8*, 114. (c) Müller, R. *Z. Chem.* **1968**, *8*, 262. (d) Curtis, M. D. *J. Am. Chem. Soc.* **1969**, *91*, 6011. (e) Jutzi, P.; Karl, A. *J. Organomet. Chem.* **1981**, *214*, 289. See also ref 2i.

(7) Béteille, J.-P.; Manuel, G.; Laporterie, A.; Iloughmane, H.; Dubac, J. *Organometallics* **1986**, *5*, 1742.

(8) (a) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310. (b) Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880. See also ref 2f.

(9) (a) Rühlmann, K.; Hagen, V.; Schiller, K. *Z. Chem.* **1967**, *7*, 353. (b) Ando, W.; Tanikawa, H.; Sekiguchi, A. *Tetrahedron Lett.* **1983**, *24*, 4245. (c) Sekiguchi, A.; Tanikawa, H.; Ando, W. *Organometallics* **1985**, *4*, 584. (d) Carré, F.; Colomer, E.; Corey, J. Y.; Corriu, R. J. P.; Guérin, C.; Henner, B. J. L.; Kolani, B.; Wong Chi Man, W. W. C. *Organometallics* **1986**, *5*, 910. (e) Béteille, J.-P.; Laporterie, A.; Dubac, J. *Organometallics* **1989**, *8*, 1799.

(10) 2,5-Difunctionalized siloles, see: Tamao, K.; Yamaguchi, S.; Shiro, M. *J. Am. Chem. Soc.* **1994**, *116*, 11715.

(11) For the synthesis of 2,5-distannyl-3-borylsiloles by other method, see: (a) Wrackmeyer, B. *J. Chem. Soc., Chem. Commun.* **1986**, 397. (b) Wrackmeyer, B. *J. Organomet. Chem.* **1986**, *310*, 151. (c) Köster, R.; Seidel, G.; Süss, J.; Wrackmeyer, B. *Chem. Ber.* **1993**, *126*, 1107. (d) Wrackmeyer, B.; Kehr, G.; Süss, J. *Chem. Ber.* **1993**, *126*, 2221.

(12) Compound **1** was prepared by the coupling reaction of PhC≡CLi with $(Et_2N)_2SiCl_2$. See the Supporting Information.

(13) Addition of **1** into the excess amount of lithium naphthalenide is essential for the present cyclization. See ref 10.

(14) In contrast to the reactions of di*alkyl*bis(phenylethynyl)silanes, which cleanly proceed at room temperature,[10] the low-temperature reactions were essential for the di*amino* analogs; a complex mixture resulted at room temperature.

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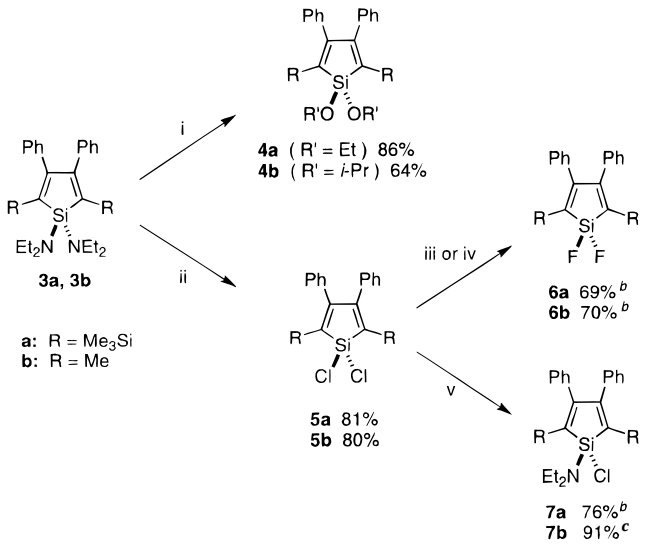
was successfully trapped with trimethylsilyl chloride and dimethyl sulfate to form 2,5-bis(trimethylsilyl)-1,1-diaminosilole, **3a**, and 2,5-dimethyl-1,1-diaminosilole, **3b**, respectively, in good yields.[15]

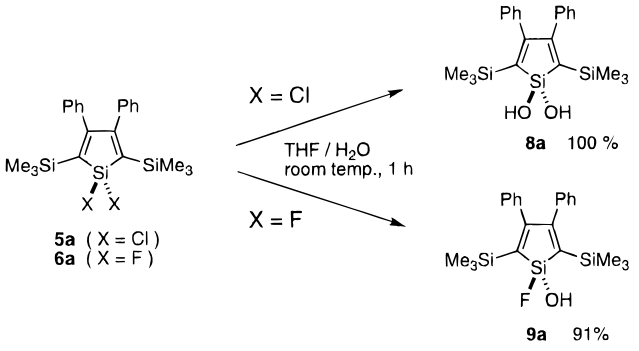
A series of 1,1-difunctionalized siloles having alkoxy, Cl, and F functionalities were prepared by transformation from 1,1-diaminosiloles as shown in Scheme 2.[16] Alcoholysis of diaminosiloles in the presence of $AlCl_3$ yielded 1,1-dialkoxysiloles **4**, which were isolated by column chromatography on silica gel. 1,1-Dichlorosiloles **5** were prepared in good yields by bubbling dry HCl gas through the ether solutions of diaminosiloles. 1,1-Difluorosiloles **6** were also obtained from diaminosiloles via dichlorosiloles, without isolation by subsequent treatment with $Py(HF)_x$ or ZnF_2. An attempt to prepare (monoamino)(monochloro)silole **7** by the direct mono-deaminochlorination of diaminosilole **3** using 1 molar amount of acetyl chloride failed, resulting in the formation of a mixture of dichlorosilole **5** and diaminosilole **3** due to the higher reactivity of aminochlorosilole **7** than diaminosilole **5**. However, **7** was obtainable by the highly selective monoamination of dichlorosiloles **5** using Et_2NH (1 molar amount)/Et_3N. While **7a** could be prepared coveniently from **3a** without isolation of **5a**, the preparation of **7b** required pure **5b** isolated by distillation. All of these 1-halogenated siloles, especially having 2,5-methyl groups, are unstable in the air and should be stored under an inert atmosphere.

Scheme 2[a]



[a] Reagents and Conditions: (i) R′OH, $AlCl_3$ (0.25 molar amount), room temperature, 20 h. (ii) dry HCl gas (ca. 10 molar amount), Et_2O, −78 °C. (iii) $Py(HF)_x$ (6 molar amount), −78 °C, 0.5 h. (iv) ZnF_2 (3 molar amount), room temperature, 2 h. (v) Et_2NH (1.2 molar amount), Et_3N (1.2 molar amount), room temperature, 20 h for R = TMS, and −78 °C, 4 h for R = Me. [b]Overall yields from **3**. [c]The yield was determined based on **5b**.

Scheme 3



Dichlorosilole and difluorosilole exhibited a different reaction mode toward hydrolysis, as shown in Scheme 3. While dichlorosilole **5a** reacted with H_2O to afford dihydroxysilole **8a** quantitatively, the hydrolysis of difluorosilole **6a** unexpectedly yielded fluorohydroxysilole **9a**.[16] However, the 2,5-dimethyl analogs **5b** and **6b** gave no characterizable products under the same conditions.

X-ray crystallography of dihydroxysilole, **8a**, and fluorohydroxysilole, **9a**, has revealed a network structure and a tetrameric structure through the intermolecular hydrogen bonding, respectively, as shown in Figure 1.[17,18] In both crystal structures, two crystallographically independent molecules are included. In fluorohydroxysilole, **9a**, the hydrogen bondings consist of only the hydroxy groups without participation of the fluorine atoms. Similar network and tetrameric structures have already been reported for $(t\text{-Bu})_2Si(OH)_2$[19a] and $(t\text{-Bu})_2SiF(OH)$,[19b] respectively.

(15) Preparation of **3a**: A THF (10 mL) solution of **1** (3.75 g, 10.0 mmol) was added dropwise at −78 °C to a THF (80 mL) solution of lithium naphthalenide, which was prepared from naphthalene (5.20 g, 40.6 mmol) and granular Li (0.28 g, 40.3 mmol). After the reaction mixture was stirred for 1 h, trimethylchlorosilane (5.60 mL, 44.0 mmol) was added. The mixture was allowed to warm to room temperature and concentrated under reduced pressure. Hexane was added to the mixture, and the resulting insoluble salt was filtered out. The filtrate was condensed under reduced pressure. After sublimation at 70 °C/1 mmHg to remove naphthalene, the residue was recrystallized from hexane to afford the titled compound (4.32 g, 8.30 mmol) in 83% yield as light yellow crystals: mp 92−94 °C. ^{1}H NMR ($CDCl_3$): δ −0.18 (s, 18H), 1.07 (t, J = 7.0 Hz, 12H), 2.99 (q, J = 7.0 Hz, 8H), 6.72−6.82 (m, 4H), 6.92−7.06 (m, 6H). ^{29}Si NMR (C_6D_6): δ −10.37, 3.01. Anal. Calcd for $C_{30}H_{48}N_2Si_3$: C, 69.16; H, 9.29; N, 5.38. Found: C, 69.09; H, 9.33; N, 5.41. The compound **3b** was also prepared in essentially the same manner and isolated after the sublimation of naphthalene by bulb-to-bulb distillation under reduced pressure (210−230 °C/0.5 mmHg) in 70% yield: mp 42−43 °C. ^{1}H NMR (C_6D_6): δ 1.15 (t, J = 7.0 Hz, 12H), 2.00 (s, 6H), 3.11 (q, J = 7.0 Hz, 8H), 6.90−7.12 (m, 10H). ^{29}Si NMR (C_6D_6): δ −8.77. Anal. Calcd for $C_{26}H_{36}N_2Si$: C, 77.17; H, 8.97; N, 6.92. Found: C, 77.09; H, 8.87; N, 6.74.

(16) Selected data for **4**−**9**. **4a**: mp 39−40 °C. ^{1}H NMR ($CDCl_3$): δ −0.13 (s, 18H), 1.31 (t, J = 7.0 Hz, 6H), 3.88 (q, J = 7.0 Hz, 4H), 6.76−6.84 (m, 4H), 6.96−7.08 (m, 6H). ^{29}Si NMR ($CDCl_3$): δ −9.92, −8.87. Anal. Calcd for $C_{26}H_{38}O_2Si_3$: C, 66.89; H, 8.20. Found C, 66.85; H, 8.29. **4b**: mp 49−50 °C. ^{1}H NMR ($CDCl_3$): δ 1.28 (d, J = 6.2 Hz, 12H), 1.76 (s, 6H), 4.25 (sept, J = 6.2 Hz, 2H), 6.75−6.86 (m, 4H), 6.99−7.16 (m, 6H). ^{29}Si NMR ($CDCl_3$): δ −21.49. Anal. Calcd for $C_{24}H_{30}O_2Si$: C, 76.14; H, 7.99. Found C, 75.84; H, 7.95. **5a**: mp 79−81 °C. ^{1}H NMR (C_6D_6): δ 0.17 (s, 18H), 6.72−6.91 (m, 10H). ^{29}Si NMR (C_6D_6): δ −7.56, 19.61. Anal. Calcd for $C_{22}H_{28}Cl_2Si_3$: C, 59.03; H, 6.30. Found: C, 59.43; H, 6.43. **5b**: mp 94−96 °C. ^{1}H NMR (C_6D_6): δ 1.87 (s, 6H), 6.66−6.78 (m, 4H), 6.82−6.98 (m, 6H). ^{29}Si NMR (C_6D_6): δ 10.29. Anal. Calcd for $C_{18}H_{16}Cl_2Si$: C, 65.25; H, 4.87. Found: C, 65.45; H, 4.85. **6a**: mp 93−95 °C. ^{1}H NMR (C_6D_6): δ 0.09 (s, 18H), 6.72−6.92 (m, 10H). ^{29}Si NMR (C_6D_6): δ −9.54 (t, J_{SiF} = 327.9Hz), −8.37. Anal. Calcd for $C_{22}H_{28}F_2Si_3$: C, 63.72; H, 6.81. Found C, 63.53; H, 6.96. **6b**: ^{1}H NMR ($CDCl_3$) δ 1.77 (s, 6H), 6.75−6.85 (m, 4H), 7.02−7.18 (m, 6H). ^{29}Si NMR ($CDCl_3$): δ −21.09 (t, J_{SiF} = 319.2Hz). HRMS (EI): calcd for $C_{18}H_{16}F_2Si$ 298.0990, found: 298.0971. Satisfactory results for the elemental analysis were not obtained due to its low stability. **7a**: mp 107−108 °C. ^{1}H NMR (C_6D_6): δ 0.16 (s, 18H), 1.15 (t, J = 7.0 Hz, 6H), 3.12 (q, J = 7.0 Hz, 4H), 6.78−6.97 (m, 10H). ^{29}Si NMR (C_6D_6): δ −8.92, 6.72. Anal. Calcd for $C_{26}H_{38}NClSi_3$: C, 64.48; H, 7.91; N, 2.89. Found C, 64.42; H, 8.08; N, 2.76. **7b**: mp 39−40 °C. ^{1}H NMR ($CDCl_3$) δ 1.12 (t, J = 7.0 Hz, 6H), 1.81 (s, 6H), 3.05 (q, J = 7.0 Hz, 4H), 6.73−6.88 (m, 4H), 6.98−7.17 (m, 6H). ^{29}Si NMR (C_6D_6) δ −2.23. Anal. Calcd for $C_{22}H_{26}ClNSi$: C, 71.81; H, 7.12; N, 3.81. Found C, 71.38; H, 6.96; N, 3.80. **8a**: mp 205−206 °C. ^{1}H NMR ($CDCl_3$): δ −0.12 (s, 18H), 2.52 (s, 2H), 6.75−6.86 (m, 4H), 6.98−7.07 (m, 6H). ^{29}Si NMR ($CDCl_3$): δ −9.44, −4.11. Anal. Calcd for $C_{22}H_{30}O_2Si_3$: C, 64.33; H, 7.36. Found C, 64.20; H, 7.34. **9a**: mp 101−103 °C. ^{1}H NMR ($CDCl_3$): δ −0.10 (s, 18H), 2.92 (s, 1H), 6.77−6.88 (m, 4H), 6.98−7.09 (m, 6H). ^{29}Si NMR (C_6D_6): δ −8.89, −6.77 (d, J_{SiF} = 311.1Hz). Anal. Calcd for $C_{22}H_{29}FOSi_3$: C, 64.02; H, 7.08. Found C, 63.65; H, 7.29.

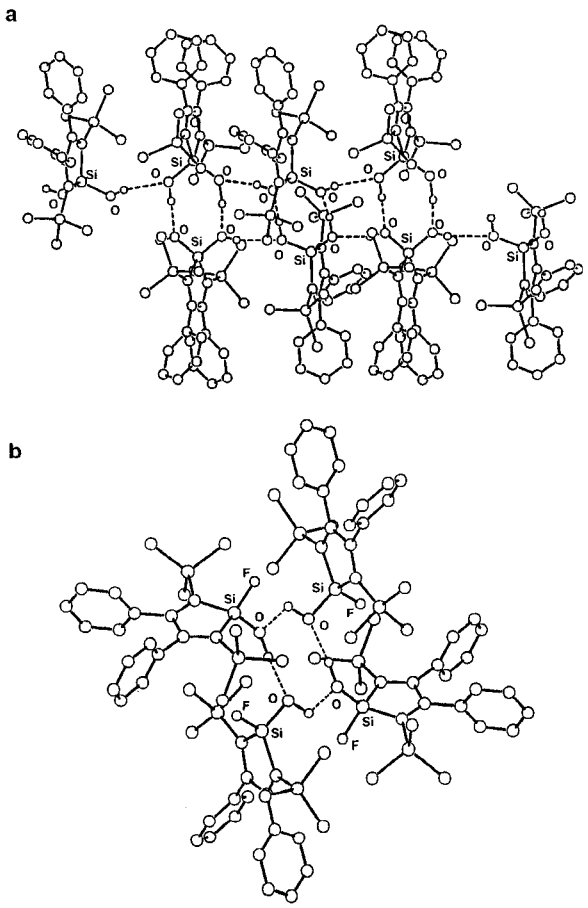
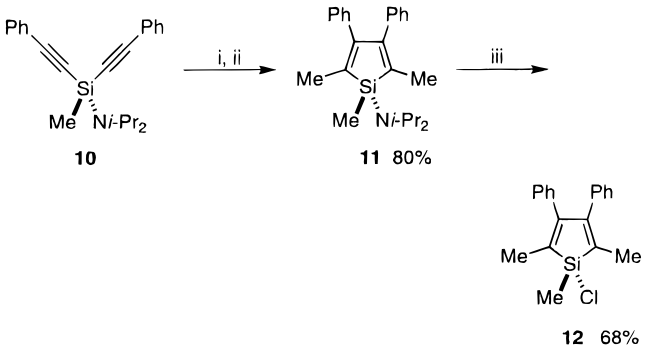


Figure 1. Crystal structure of (a) dihydroxysilole **8a** and (b) fluorohydroxysilole **9a**.

The present methodology is also applicable to the synthesis of 1-monofunctionalized siloles. Thus, as a representative example, 1-chloro-1-methyl-2,5-dimethylsilole **12** has been prepared from the corresponding aminomethylbis(phenylethynyl)silane, **10**,[12] via 1-amino-1-methyl-2,5-dimethylsilole **11**, as shown in Scheme 4.[20]

The reactivities and stabilities of these 1,1-difunctionalized siloles largely depend on the bulkiness of the 2,5-substituents, as noted by the very different reactivities between the 2,5-bis(trimethylsilyl) and 2,5-dimethyl derivatives. These results demonstrate the importance of the appropriate choice of 2,5-substituents for preparation and handling of the siloles having functionalities on silicon. Remarkably, the present methodology has a decisive merit in this respect that a variety of substituents can be introduced onto the 2,5-positions of the silole rings, although the 3,4-substituents are restricted only to the phenyl groups.[10]

Scheme 4[a]



10 **11** 80% **12** 68%

[a] Reagents and Conditions: (i) LiNp (4 molar amount), THF, −78 °C, 2 h. (ii) $(MeO)_2SO_2$ (4 molar amount), −78 to 0 °C, 0.5 h. (iii) dry HCl gas (ca. 5 molar amount), Et_2O, −78 °C.

A series of siloles having functionalities, such as NR_2, OR, Cl, F, and OH, on the ring-silicon have been prepared by functional group transformations from 1,1-diaminosiloles. The 1,1-difunctionalized siloles prepared herein would be useful precursors for interesting but still veiled silole derivatives, such as functionalized silole anions, silole-containing polysiloxanes, and poly(1,1-silole)s. Further studies along this line are now in progress in our laboratory. Among them, preliminary results for the synthesis of oligosiloles catenated through silicon atoms as models of poly(1,1-silole)s will be presented in due course.

Acknowledgment. We thank the Ministry of Education, Science, Sports, and Culture, Japan, for the Grant-in-Aid (Grant No. 07555280).

Supporting Information Available: Text of the experimental procedures for all of the compounds and ORTEP diagrams and tables of atomic coordinates, anisotropic displacement parameters, bond lengths, bond angles, and nonbonded contacts for **8a** and **9a** (35 pages). Ordering information is given on any current masthead page.

OM970091H

(17) Crystal data for **8a** (instrument; Rigaku RAXIS IV): $C_{23.50}H_{31.50}O_2Si_3$, 0.20 × 0.15 × 0.10 mm, monoclinic, $P2_1/a$ (No. 14); a = 11.149(2) Å, b = 36.691(5) Å, c = 12.395(7) Å, β = 91.18(3)°, V = 5069.3501 Å^3, Z = 8, D_c = 1.127 g cm^{-3}, μ (Mo Kα) = 2.03 cm^{-1}, temperature 25 °C, R = 0.045, R_w = 0.064, and goodness of fit indicator = 1.16; number of unique reflections = 7844. Crystal structure of **8a** includes benzene in the ratio of **8a**:benezene = 2:0.5 in the unit cell.

(18) Crystal data for **9a** (instrument; Rigaku RAXIS II): $C_{22}H_{29}FOSi_3$, 0.30 × 0.25 × 0.10 mm, triclinic, $P\bar{1}$ (No. 2); a = 14.181(1) Å, b = 14.926(1) Å, c = 12.057(1) Å, α = 98.996(4)°, β = 108.136(4)°, γ = 80.849(4)°, V = 2364.9 Å^3, Z = 4, D_c = 1.159 g cm^{-3}, μ (Mo Kα) = 2.17 cm^{-1}, temperature 25 °C, R = 0.052, R_w = 0.086, and goodness of fit indicator = 1.48; number of unique reflections = 6811.

(19) (a) Buttrus, N. H.; Eaborn, C.; Hitchcock, P. B.; Saxena, A. K. *J. Organomet. Chem.* **1985**, *284*, 291. (b) Buttrus, N. H.; Eaborn, C.; Hitchcock, P. B.; Saxena, A. K. *J. Organomet. Chem.* **1985**, *287*, 157.

(20) Selected data for **11**−**12**. **11**: mp 73−75 °C. ^{1}H NMR ($CDCl_3$): δ 0.38 (s, 3H), 1.15 (d, J = 6.8 Hz, 12H), 1.77 (s, 6H), 3.26 (sept, J = 6.8 Hz, 2H), 6.75−6.84 (m, 4H), 6.98−7.14 (m, 6H). ^{29}Si NMR ($CDCl_3$): δ −0.60. Anal. Calcd for $C_{25}H_{33}NSi$: C, 79.94; H, 8.85; N, 3.73. Found C, 79.56; H, 9.02; N, 3.65. **12**: mp 70−71 °C. ^{1}H NMR ($CDCl_3$): δ 0.67 (s, 3H), 1.83 (s, 6H), 6.74−6.88 (m, 4H), 7.02−7.17 (m, 6H). ^{29}Si NMR (C_6D_6): δ 19.69. Anal. Calcd for $C_{19}H_{19}ClSi$: C, 73.40; H, 6.16. Found C, 73.65; H, 6.22.