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General Silaindene Synthesis Based on Intramolecular Reductive Cyclization toward New Fluorescent Silicon-Containing π-Electron Materials

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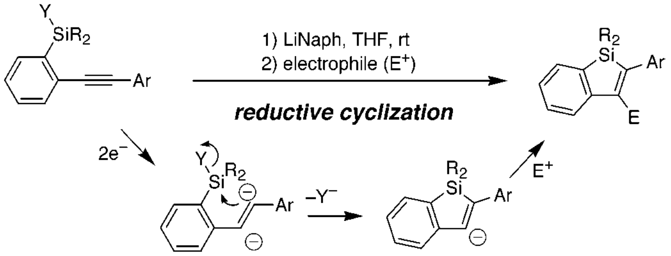
ABSTRACT



The reaction of (*o*-silylphenyl)acetylene derivatives with lithium naphthalenide undergoes intramolecular reductive cyclization to produce various silaindene derivatives. On the basis of this methodology, a series of silaindene-containing π-electron systems are synthesized that show intense blue to greenish-blue fluorescence.

Heteroindenes are fundamental and important skeletons in organic chemistry. A typical synthetic route to heteroindenes is the heteroannulation of arylacetylenes bearing nucleophilic element substituents such as −OH, −NHR, and −SR at the ortho position, as shown in Scheme 1a,[1−3] that proceeds through the metalation of the ortho substituents or through the activation of the acetylene moiety with electrophilic agents. This mode of cyclization is indeed useful for the synthesis of group 15 and 16 element-containing heteroindenes such as indoles,[1] benzofurans,[2] and benzothiophenes;[3] however, it is less effective for the synthesis of heteroindenes with other group elements such as group 14 silicon. Only a few examples related to this mode of cyclization have been reported for the synthesis of silaindenes,[4,5] which include the intramolecular hydrosilation of (*o*-silylphenyl)acetylenes catalyzed by a Pt complex[6] or a Lewis acid.[7] As a complement of this mode of cyclization, we now disclose a new intramolecular reductive cyclization of (*o*-silylphenyl)acetylene derivatives that produces various *functionalized* silain-

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(1) For recent indole preparations, see for instance: (a) Barluenga, J.; Trincado, M.; Rubio, E.; González, J. M. *Angew. Chem., Int. Ed.* **2003**, *42*, 2406−2409. (b) Kamijo, S.; Yamamoto, Y. *J. Org. Chem.* **2003**, *68*, 4764−4771. (c) Cacchi, S.; Fabrizi, G.; Parisi, L. M. *Org. Lett.* **2003**, *5*, 3843−3846. (d) Hiroya, K.; Itoh, S.; Ozawa, M.; Kanamori, Y.; Sakamoto, T. *Tetrahedron Lett.* **2002**, *43*, 1277−1280. (e) Koradin, C.; Dohle, W.; Rodriguez, A. L.; Schmid, B.; Knochel, P. *Tetrahedron* **2003**, *59*, 1571−1587. (f) Rodriguez, A. L.; Koradin, C.; Dohle, W.; Knochel, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 2488−2490 and references therein.

(2) For recent benzo[*b*]furan preparations, see for instance: (a) Anderson, S.; Taylor, P. N.; Verschoor, G. L. B. *Chem.—Eur. J.* **2004**, *10*, 518−527. (b) Dai, W.-M.; Lai, K. W. *Tetrahedron Lett.* **2002**, *43*, 9377−9380. (c) Hu, Y.; Zhang, Y.; Yang, Z.; Fathi, R. *J. Org. Chem.* **2002**, *67*, 2365−2368. (d) Bates, C. G.; Saejueng, P.; Murphy, J. M.; Venkataraman, D. *Org. Lett.* **2002**, *4*, 4727−4729. (e) Hiroya, K.; Suzuki, N.; Yasuhara, A.; Egawa, Y.; Kasano, A.; Sakamoto, T. *J. Chem. Soc., Perkin Trans. 1.* **2000**, 4339−4346. (f) Arcadi, A.; Cacchi, S.; Fabrizi, G.; Moro, L. *Eur. J. Org. Chem.* **1999**, 1137−1141 and references therein.

(3) For recent benzo[*b*]thiophene preparations, see for instance: (a) Hessian, K. O.; Flynn, B. L. *Org. Lett.* **2003**, *5*, 4377−4380. (b) Flynn, B. L.; Verdier-Pinard, P.; Hamel, E. *Org. Lett.* **2001**, *3*, 651−654. (c) Larock, R. C.; Yue, D. *Tetrahedron Lett.* **2001**, *42*, 6011−6013 and references therein. (d) Kitamura, T.; Takachi, T.; Miyaji, M.; Kawasato, H.; Taniguchi, H. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1907−1911.

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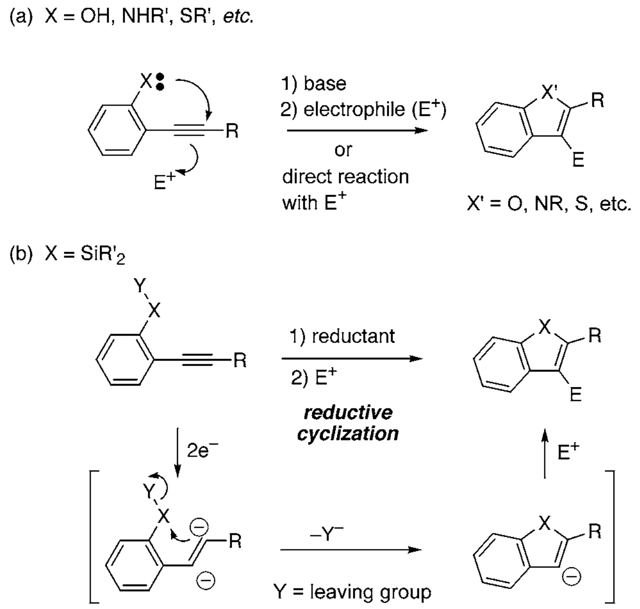
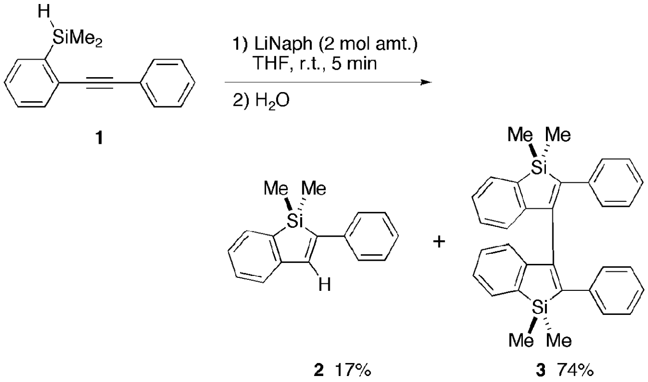
Scheme 1. Two Complementary Types of Cyclizations for the Heteroindene Synthesis



denes via a two-electron reduction of the acetylene moiety, as shown in Scheme 1b. The development of this methodology has led to the synthesis of a new family of highly fluorescent silicon-containing π-electron compounds, which are potential blue-emitting materials for organic light-emitting diodes (LEDs).[8,9] Here, we report the details of the cyclization as well as the fundamental photophysical properties of the produced π-electron compounds.

We have recently reported that the reaction of bis(*o*-silyl)-substituted diphenylacetylene with lithium naphthalenide (LiNaph) undergoes an intramolecular reductive cyclization to produce a disila-indeno[2,1-*a*]indene skeleton.[10] The postulated intermediate of this reaction is a dianion species produced by the two-electron reduction of the acetylene moiety. We envisioned that the idea of this reaction can be applied to the synthesis of the silaindene skeleton by replacing the starting material with mono(*o*-silyl)-substituted diphenylacetylene **1**. In fact, we found that when compound **1** having hydrogen as a leaving group on the silicon atom was treated with 2 mol amounts of LiNaph followed by quenching with water, the desired phenylsilaindene **2** was obtained in 17% yield, together with its dimeric product **3** in 74% yield (Scheme 2).[11] This result demonstrates that the present cyclization indeed proceeds even using the mono-(*o*-silyl)-substituted derivatives, while the formation of the latter dimeric product suggests that the two-electron reduction proceeds in a stepwise fashion.

Scheme 2. Cyclization of Mono(*o*-silyl)-diphenylacetylene



Notably, the present reductive cyclization more efficiently proceeds when π-extended starting materials are employed instead of the monoacetylenic compound, as shown in Scheme 3. Thus, the reaction of bis(phenylethynyl)benzene **4**, having two silyl groups at the terminal phenyl rings, with 4 mol amounts of LiNaph followed by quenching with water afforded bis(silaindenyl)benzene **5a** in 52% yield, while the use of compound **6**, which is analogous but has two silyl groups at the central benzene moiety, led to a totally new π-electron compound **7** consisting of a disila-*s*-indacene skeleton in 90% yield. In addition, the present cyclization also proceeds in the case of bis(*o*-silylphenyl)diacetylene **8** to give bis(silaindene) **9**, although the yield is moderate. Noteworthy is the fact that these are the first examples of the silaindene-based extended π-electron systems.

Compared with the conventional synthesis of silaindenes,[4,5] the present cyclization has a great advantage in terms of facile functionalization. Thus, the present reductive cyclization produces the anionic intermediates that can be easily transformed into various functionalized derivatives by treatment with the appropriate electrophiles. For instance, in the reaction of **4** with 4 mol amounts of LiNaph followed by treatments with

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(4) Conventional silaindene synthesis based on the reaction of dilithiostyrenes with halosilanes: (a) Korneev, S. M.; Kaufmann, D. E. *Synthesis* **2002**, 491−496. (b) Ura, Y.; Li, Y.; Tsai, F.-Y.; Nakajima, K.; Kotora, M.; Takahashi, T. *Heterocycles* **2000**, *52*, 1171−1189. (c) Xi, C.; Huo, S.; Afifi, T. H.; Hara, R.; Takahashi, T. *Tetrahedron Lett.* **1997**, *38*, 4099−4102. (d) Choi, S.-B.; Boudjouk, P.; Wei, P. *J. Am. Chem. Soc.* **1998**, *120*, 5814−5815. (e) Rausch, M. D.; Klemann, L. P. *J. Am. Chem. Soc.* **1967**, *89*, 5732−5733. For other silaindene synthesis, see: (f) Kunai, A.; Yuzuriha, Y.; Naka, A.; Ishikawa, M. *J. Organomet. Chem.* **1993**, *455*, 77−81. (g) Barton, T. J.; Groh, B. L. *Organometallics* **1985**, *4*, 575−580.

(5) Versatile synthesis of heteroindenes by the reaction of dilithiostyrenes with metal halides: Kurita, J.; Ishii, M.; Yasuike, S.; Tsuchiya, T. *J. Chem. Soc., Chem. Commun.* **1993**, 1309−1310.

(6) Märkl, G.; Berr, K.-P. *Tetrahedron Lett.* **1992**, *33*, 1601−1604.

(7) Sudo, T.; Asao, N.; Yamamoto, Y. *J. Org. Chem.* **2000**, *65*, 8919−8923.

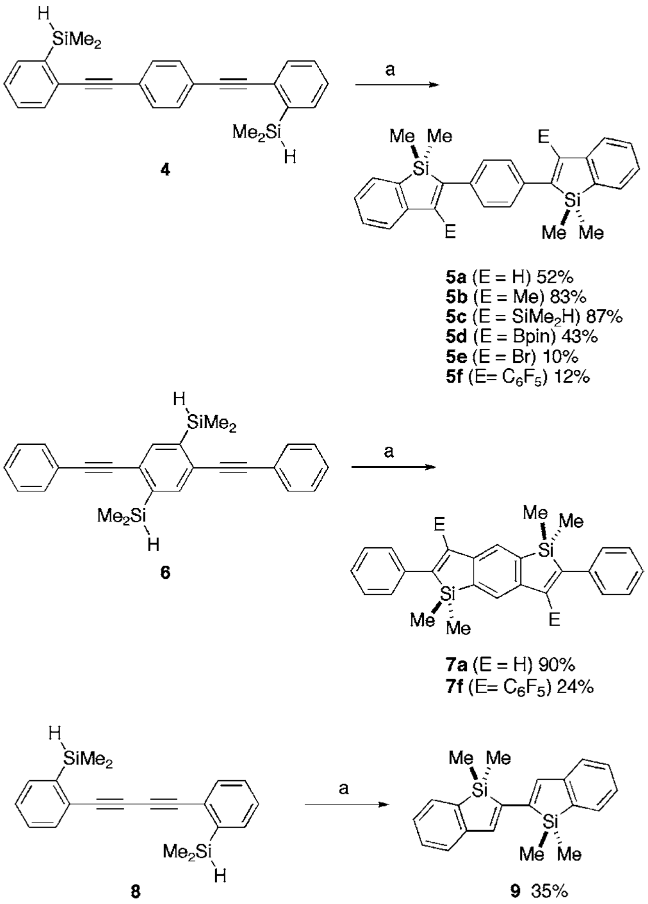
(8) For silicon-containing π-electron compounds applicable to organic LEDs, see for instance: (a) Yamaguchi, S.; Tamao, K. *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons: Chichester, 2001; pp 641−694 and references therein. (b) Tamao, K.; Uchida, M.; Izumizawa, T.; Furukawa, K.; Yamaguchi, S. *J. Am. Chem. Soc.* **1996**, *118*, 11974−11975. (c) Murata, H.; Kafafi, Z. H.; Uchida, M. *Appl. Phys. Lett.* **2002**, *80*, 189−191. (d) Ohshita, J.; Kai, H.; Sumida, T.; Kunai, A.; Adachi, A.; Sakamaki, K.; Okita, K. *J. Organomet. Chem.* **2002**, *642*, 137. (e) Luo, J.; Xie, Z.; Lam, J. W. Y.; Cheng, L.; Chen, H.; Qiu, C.; Kwok, H. S.; Zhan, X.; Liu, Y.; Zhu, D.; Tang, B. Z. *Chem. Commun.* **2001**, 1740−1741.

(9) Use of silaindene-based materials for organic LEDs has been reported in a patent; see: Kohama, T.; Tominaga, T.; Murase, S. JP2002198176.

(10) Yamaguchi, S.; Xu, C.; Tamao, K. *J. Am. Chem. Soc.* **2003**, *125*, 13662−13663.

(11) Besides the diphenylacetylene derivative **1**, we found that (trimethylsilyl)(*o*-dimethylsilylphenyl)acetylene also underwent the present reductive cyclization to give the corresponding cyclized product in a good yield.

Scheme 3. Synthesis of a Series of Silaindene-Containing π-Electron Systems



[a] Reagents and conditions: (1) LiNaph (4 mol amt.), THF, rt, 5 min; (2) electrophiles such as H_2O, $(MeO)_2SO_2$, HMe_2SiCl, *i*-PrOBpin, Br_2, or C_6F_6. pin = pinacolato.

various electrophiles, a series of the substituted bis(silaindenyl)benzenes **5b**−**f** having Me, $SiMe_2H$, B(pin), Br, and C_6F_5 groups were obtained, as shown in Scheme 3, although the yields of **5e** and **5f** were rather low due to undesirable side-reactions such as protonation. Similarly, 3,7-C_6F_5-substituted disilaindacene **7f** was also synthesized. Among these groups, B(pin) and Br functionalities may be particularly useful for further transformation through the well-established cross-coupling methodologies. These results demonstrate the great utility of the present cyclization as the first general synthetic route to the functionalized silaindene-based π-electron systems.

Among the produced new π-electron systems, the structures of compounds **5a** and **7a** have been determined by X-ray crystallography, as shown in Figure 1.[12] Notably, both compounds have highly coplanar π-conjugated frameworks. The dihedral angles between the central benzene plane and the outer benzene planes are 26.8 and 27.9° for **5a** and 6.60° for **7a**, respectively. These results suggest that both the silaindene and disila-*s*-indacene skeletons are effective building units for the π-electron systems with well-extended π-conjugation.

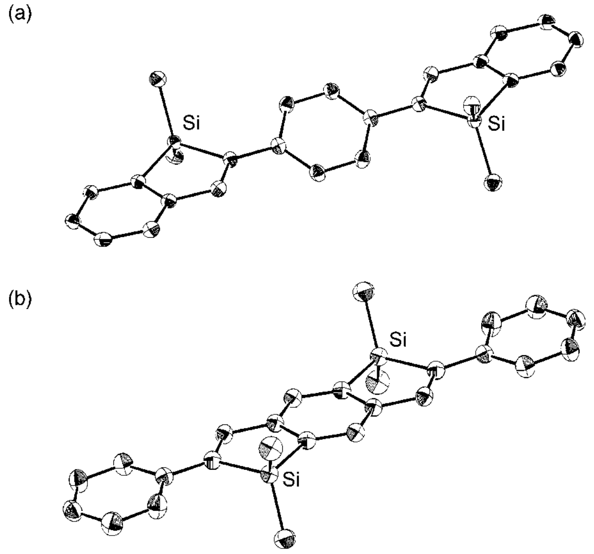


Figure 1. ORTEP drawings of compounds (a) **5a** and (b) **7a** (50% probability for thermal ellipsoids).

All the produced silaindene-based π-electron compounds show intense blue to greenish-blue photoluminescence. In Table 1, the UV−visible absorption and fluorescence spectral data for the selected compounds, **5a**, **7a**, and **9**, are summarized, together with those of the previously reported

Table 1. Photophysical Properties of Silaindene Derivatives and Related Compounds.

	UV−vis absorption[a]		fluorescence[a]		
cmpd	λ_{max} (nm)[b]	log ϵ	λ_{max} (nm)[c]	Φ_F[d]	τ_S (ns)[e]
5a	376	4.59	413, 437	0.86	1.9
7a	398	4.51	445, 467	0.73	2.6
9	364	4.52	396, 417	0.49	1.7
10[f]	424	4.43	473, 499	0.50	3.5

[a] In THF. [b] Only the absorption maxima with the highest intensity are listed. [c] Emission maxima upon excitation at the absorption maximum wavelengths. [d] Determined with 9,10-diphenylanthracene for **5a**, anthracene for **9**, and perylene for **7a** and **10** as a standard, respectively. The Φ_F is the average of values of repeated measurements within ±5% error. [e] Fluorescence lifetimes within ± 0.5 ns error. [f] Ref 10.

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(12) Crystallographic data. **5a**: $C_{26}H_{26}Si_2$, FW = 394.65, crystal dimensions 0.40 × 0.40 × 0.40 mm^3, monoclinic, space group $P21/n$, a = 9.9095(5) Å, b = 9.850(5) Å, c = 24.523(5) Å, β = 92.510(5)°, V = 2194.8(17) Å^3, Z = 4, D_c = 1.194 Mg m^{-3}, μ(Mo Kα) = 0.170 mm^{-1}, T = 100(2) K, F(000) = 840, 2θ_{max} = 50°. 10 740 reflections measured, of which 3856 were unique (R_{int} = 0.0284). Final R_1 = 0.0451 with wR_2 = 0.1092 for 3856 observed reflections with $I > 2\sigma(I)$. **7a**: $C_{26}H_{26}Si_2$, FW = 394.65, crystal dimensions 0.20 × 0.20 × 0.20 mm^3, orthorhombic, space group Pbca, a = 6.750(4) Å, b = 16.542(10) Å, c = 20.635(12) Å, V = 2304(2) Å^3, Z = 4, D_c = 1.138 Mg m^{-3}, μ(Mo Kα) = 0.162 mm^{-1}, T = 173(2) K, F(000) = 840, 2θ_{max} = 55°. 16 155 reflections measured, of which 2622 were unique (R_{int} = 0.0407). Final R_1 = 0.0574 with wR_2 = 0.1533 for 2622 observed reflections with $I > 2\sigma(I)$.

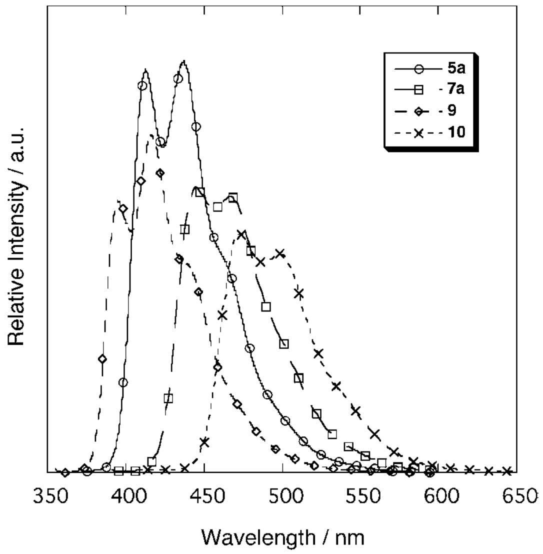
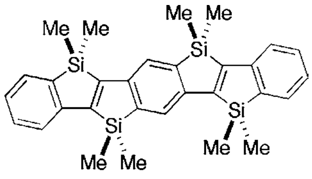


Figure 2. Fluorescence spectra of compounds **5a**, **7a**, **9**, and **10** in THF.



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tetrakis-silicon-bridged bis(styryl)benezene **10**,[10] for comparison, and Figure 2 shows their fluorescence spectra. Since compounds **5a**, **7a**, and **10** have identical π-conjugation lengths but have a different number of silicon bridges at the different positions, the comparison among these compounds provides some crucial information about the effect of the silicon moieties: (1) Compounds **5a**, **7a**, and **10** have their absorption maxima at 376−424 nm and emission maxima at 413−473 nm. Notably, these values are rather longer than those of the nonbridged parent 1,4-bis(styryl)benzene ($\lambda_{\text{abs,max}} = 350$ nm and $\lambda_{\text{em,max}} = 405$ nm).[13] (2) Compound **7a**, bearing the two silicon-bridges on the internal benzene ring, has longer absorption and emission maxima by 22 and 32 nm, respectively, compared to compound **5a**, which has the two silicon-bridges on the external benzene rings. (3) From the bis-silicon-bridged **5a** and **7a** to the tetrakis-silicon-bridged **10**, the absorption and emission maxima further shifts to longer wavelengths. The red shifts in the absorption and emission maxima from **5a** to **10** reach 48 and 60 nm, respectively. (4) Accompanied with these differences, the fluorescence quantum yields (Φ_F) tend to decrease from **5a** to **7a** to **10**, while the fluorescence lifetime increases in this order. These observations clearly demonstrate not only the significant contribution of the silicon bridges to the photophysical properties and thus to the electronic structures but also the strong dependence of the properties on the position of the silicon-bridges. In a view of the application as a blue-emitting material, the bis-silicon-bridged derivatives may be promising because of their high fluorescence quantum yields as well as the color purity.

In summary, we have developed a new intramolecular reductive cyclization that is a complement of the conventional heteroannulation for the synthesis of heteroindenes. This cyclization methodology allows us to synthesize a series of fluorescent silaindene- and disilaindacene-containing π-electron systems and to disclose the significant effect of the silicon bridges on their photophysical properties. The readily accessible functionalization and structural modification are other notable advantages of the present methodology. On the basis of this synthesis, further structural optimization toward more promising silicon-containing π-electron materials is now in progress in our laboratory.

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Supporting Information Available: Spectral and analytical data for silaindene derivatives and CIF data for **5a** and **7a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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