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Synthesis of Silafluorenes by Iridium-Catalyzed [2 + 2 + 2] Cycloaddition of Silicon-Bridged Diynes with Alkynes

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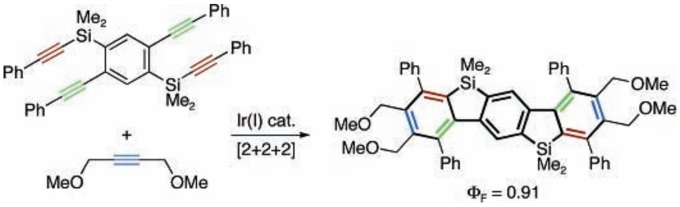
ABSTRACT

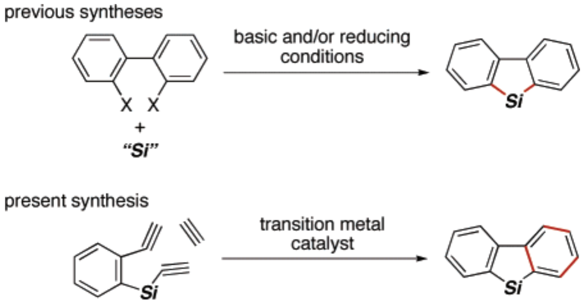


Silicon-bridged 1,6-diynes underwent [2 + 2 + 2] cycloaddition with alkynes in the presence of an iridium(I)–phosphine catalyst to afford densely substituted silafluorene derivatives. Extended silafluorene skeletons were constructed by the [2 + 2 + 2] cycloaddition of tetraynes.

Siloles (silacyclopentadienes) are members of an intriguing class of silicon-based π-conjugated molecules that possess unique photophysical and electronic properties owing to their low-lying LUMO associated with $\sigma^*-\pi^*$ conjugation.[1] For example, high electron-transporting performances have been reported for some of the siloles.[2] 9-Silafluorenes (dibenzosiloles), which embody a silicon-bridged biphenyl framework, are also considered to be a promising candidate for materials of such properties.[3] There are several methods reported for the syntheses of silafluorenes.[4] However, starting substances are limited to biaryl derivatives and the cyclization step requires strongly basic conditions and/or reducing conditions which require special precautions (Scheme 1). It is, therefore, highly desired to develop a new method for the synthesis of silafluorenes. Transition-metal-catalyzed [2 + 2 + 2] cycloaddition reactions of alkynes (cyclotrimerization) proceed under barely basic conditions and have been widely used for constructing benzene structures.[5] Herein, we report a new synthetic method for silafluorene derivatives by the iridium(I)-catalyzed [2 + 2 + 2] cycloaddition of silicon-bridged 1,6-diynes with alkynes.[6]

Dimethyl(phenylethynyl)[2-(phenylethynyl)phenyl]-silane (**1a**) was easily prepared by the chemoselective pal-

Scheme 1



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(1) Yamaguchi, S.; Tamao, K. *J. Chem. Soc., Dalton Trans.* **1998**, 3693.

(2) (a) Tamao, K.; Uchida, M.; Izumizawa, T.; Furukawa, K.; Yamaguchi, S. *J. Am. Chem. Soc.* **1996**, *118*, 11974. (b) Palilis, L. C.; Murata, H.; Uchida, M.; Kafafi, Z. H. *Org. Electron.* **2003**, *4*, 113. (c) Kulkarni, A. P.; Tonzola, C. J.; Babel, A.; Jenekhe, S. A. *Chem. Mater.* **2004**, *16*, 4556.

(3) (a) Chan, K. L.; McKiernan, M. J.; Towns, C. R.; Holmes, A. B. *J. Am. Chem. Soc.* **2005**, *127*, 7662. (b) Mo, Y.; Tian, R.; Shi, W.; Cao, Y. *Chem. Commun.* **2005**, 4925. (c) Usta, H.; Lu, G.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 9034.

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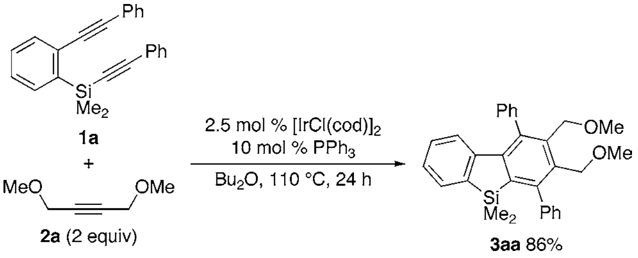
ladium-catalyzed coupling reaction of 1-bromo-2-iodobenzene with phenylacetylene and the following installation of alkynylsilane moieties.[7] Diyne **1a** and 1,4-dimethoxybut-2-yne (**2a**, 2 equiv) in dibutyl ether were heated at 110 °C for 24 h in the presence of $[IrCl(cod)]_2$ (2.5 mol %; cod = cycloocta-1,5-diene) and triphenylphosphine (10 mol %). A cross [2 + 2 + 2] cycloaddition between **1a** and **2a** selectively took place to give 2,3-bis(methoxymethyl)-1,4-diphenylsilafluorene **3aa** in 86% isolated yield (Scheme 2).

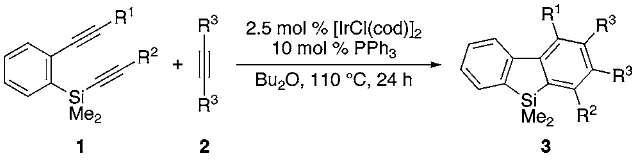
Scheme 2. Iridium-Catalyzed [2 + 2 + 2] Cycloaddition of Silicon-Bridged 1,6-Diyne **1a** with Monoyne **2a**



Iridium acts as a template to assemble the three carbon−carbon triple bonds into the six-membered aromatic ring on it. Dibutyl ether afforded a better yield of **3aa** than other solvents (toluene, 110 °C, 64%; 1,4-dioxane, 100 °C, 52%). The use of a similar rhodium catalyst (2.5 mol % of $[RhCl(CH_2{=}CH_2)_2]_2$ and 10 mol % of PPh_3) under identical conditions gave 73% yield of **3aa**.

Various diynes **1** and monoynes **2** were subjected to the iridium(I)-catalyzed [2 + 2 + 2] cycloaddition reaction (Table 1). Diyne **1a** reacted with 1,4-dibenzyloxybut-2-yne (**2b**) to provide silafluorene **3ab** in 93% yield (entry 1). Unprotected but-2-yne-1,4-diol also participated in the cycloaddition (entry 2). Oct-4-yne (**2d**) required 10 mol % of the iridium catalyst to get a good yield (entry 3). The reaction of **1a** with dimethyl acetylenedicarboxylate (**2e**) was sluggish even at 145 °C giving only 7% yield of product **3ae** (entry 4). Diphenylacetylene failed to react with **1a**. Diynes (**1b** and **1c**) having functionalized aromatic rings on the alkyne termini gave the corresponding silafluorenes (**3ba** and **3ca**) in good yields (entries 5 and 6). The functionalized silafluorenes obtained are potential candidates for the monomer for the synthesis of silafluorene-containing polymers.[3] Alkyl groups on the alkyne termini of the diynes were also tolerated (entries 7 and 8). Diyne **1f** possessing an unsubstituted terminal alkyne moiety afforded 25% yield of silafluorene **3fa** (entry 9).

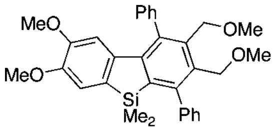
Table 1. Iridium-Catalyzed [2 + 2 + 2] Cycloaddition of Diynes **1** with Monoynes **2**[a]



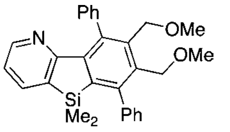
entry	**1** (R^1, R^2)	**2** (R^3)	**3** (% yield[b])
1	**1a** (Ph, Ph)	**2b** (CH_2OBn)	**3ab** (93)
2	**1a** (Ph, Ph)	**2c** (CH_2OH)	**3ac** (42)
3[c]	**1a** (Ph, Ph)	**2d** (Pr)	**3ad** (75)
4[d]	**1a** (Ph, Ph)	**2e** (CO_2Me)	**3ae** (7)
5	**1b** (4-($CH_2{=}CH$)C_6H_4, Ph)	**2a**	**3ba** (79)
6	**1c** (4-$MeOC_6H_4$, 4-$MeOC_6H_4$)	**2a**	**3ca** (77)
7	**1d** (Ph, n-C_5H_{11})	**2a**	**3da** (81)
8[d]	**1e** (n-C_5H_{11}, n-C_5H_{11})	**2a**	**3ea** (69)
9[c]	**1f** (Ph, H)	**2a**	**3fa** (25)

[a] Unless otherwise noted, diyne **1** and monoyne **2** (2 equiv) were heated in Bu_2O at 110 °C in the presence of $[IrCl(cod)]_2$ (2.5 mol %) and PPh_3 (10 mol %) for 24 h. [b] Isolated yield. [c] $[IrCl(cod)]_2$ (5 mol %) and PPh_3 (20 mol %) were used. [d] 145 °C.

Structural modification of the *o*-phenylene linker was also studied. A diyne having two methoxy groups on the *o*-phenylene tether gave hexasubstituted silafluorene **3ga** in 76% yield. Pyridine-fused product **3ha** was obtained by the reaction of the corresponding pyridine-tethered diyne with a higher catalyst loading (5 mol % of $[IrCl(cod)]_2$ and 20 mol % of PPh_3) at a higher reaction temperature (145 °C).



3ga 76%



3ha 48%

The core skeleton required for the present [2 + 2 + 2] cycloaddition reaction is an *o*-phenylene-tethered siladiyne unit. The core unit can be multiply embodied in the starting substances. This advantageous feature rendered it possible to synthesize various types of arrayed silafluorenes.

Ladder-type π-conjugated molecules have received considerable attention due to effective conjugation by the rigid coplanar structures.[8] Tetrayne **4** was readily prepared starting

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(4) (a) Gilman, H.; Gorsich, R. D. *J. Am. Chem. Soc.* **1955**, *77*, 6380. (b) Ishikawa, M.; Tabohashi, T.; Sugisawa, H.; Nishimura, K.; Kumada, M. *J. Organomet. Chem.* **1983**, *250*, 109. (c) van Klink, G. P. M.; de Boer, H. J. R.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F.; Spek, A. L. *Organometallics* **2002**, *21*, 2119. (d) Liu, Y.; Stringfellow, T. C.; Ballweg, D.; Guzei, I. A.; West, R. *J. Am. Chem. Soc.* **2002**, *124*, 49. (e) Wang, Z.; Fang, H.; Xi, Z. *Tetrahedron Lett.* **2005**, *46*, 499. (f) Chen, R.-F.; Fan, Q.-L.; Zheng, C.; Huang, W. *Org. Lett.* **2006**, *8*, 203. (g) Hudrlik, P. F.; Dai, D.; Hudrlik, A. M. *J. Organomet. Chem.* **2006**, *691*, 1257.

(5) For recent examples of [2 + 2 + 2] cycloaddition forming benzene derivatives, see: (a) Miljanić, O. Š.; Holmes, D.; Vollhardt, K. P. C. *Org. Lett.* **2005**, *7*, 4001. (b) Yamamoto, Y.; Ishii, J.; Nishiyama, H.; Itoh, K. *J. Am. Chem. Soc.* **2005**, *127*, 9625. (c) Shibata, T.; Tsuchikama, K.; Otsuka, M. *Tetrahedron: Asymmetry* **2006**, *17*, 614. (d) Kezuka, S.; Tanaka, S.; Ohe, T.; Nakaya, Y.; Takeuchi, R. *J. Org. Chem.* **2006**, *71*, 543. (e) Tanaka, K.; Takeishi, K.; Noguchi, K. *J. Am. Chem. Soc.* **2006**, *128*, 4586. (f) Tracey, M. R.; Oppenheimer, J.; Hsung, R. P. *J. Org. Chem.* **2006**, *71*, 8629. For reviews, see: (g) Saito, S.; Yamamoto, Y. *Chem. Rev.* **2000**, *100*, 2901. (h) Gandon, V.; Aubert, C.; Malacria, M. *Chem. Commun.* **2006**, 2209.

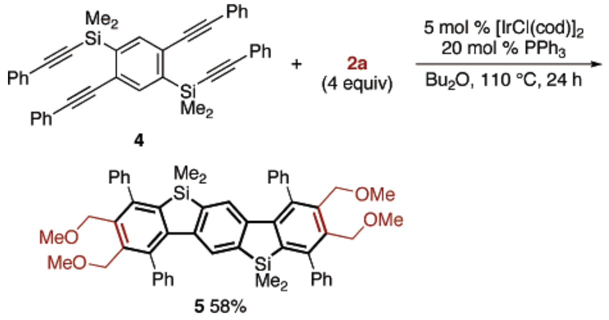
(6) Synthesis of carbazoles by an analogous rhodium-catalyzed [2 + 2 + 2] cycloaddition of nitrogen-bridged diynes and alkynes has been reported. Witulski, B.; Alayrac, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 3281.

(7) See Supporting Information for details.

(8) (a) Scherf, U. *J. Mater. Chem.* **1999**, *9*, 1853. (b) Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350. (c) Wong, K.-T.; Chi, L.-C.; Huang, S.-C.; Liao, Y.-L.; Liu, Y.-H.; Wang, Y. *Org. Lett.* **2006**, *8*, 5029.

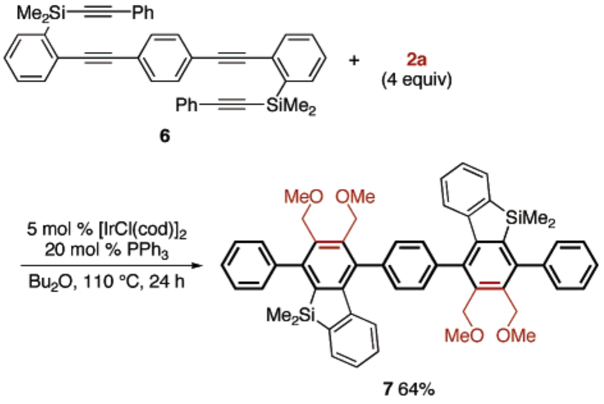
from 1,4-dibromo-2,5-diiodobenzene by sequential installation of two alkyne parts. On heating **4** in the presence of the iridium catalyst, double [2 + 2 + 2] cycloaddition with **2a** occurred on both sides of **4** to furnish ladder-type silafluorene **5**[9] in 58% yield (Scheme 3).

Scheme 3. Synthesis of Ladder-Type Silafluorene **5**



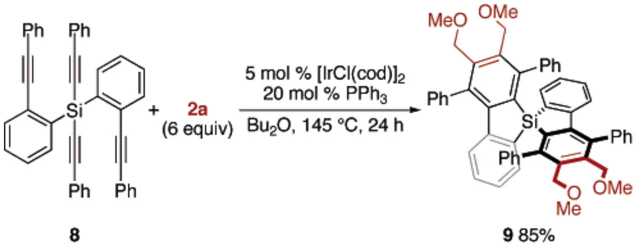
Poly(*p*-phenylene)s (PPPs) have been the focus of much study because they act as organic conductors upon doping and as light-emitting materials.[10] Tetrayne **6** was prepared from 1,4-diethynylbenzene through the palladium-catalyzed coupling reaction with 1-bromo-2-iodobenzene followed by installation of the alkynylsilane moieties. Cycloaddition of **6** with **2a** gave *p*-phenylenebis(silafluorene) **7** carrying a *p*-quinquephenyl moiety, in which three phenyl rings and two aromatic groups of silafluorene skeletons were alternatively arrayed (Scheme 4).[11]

Scheme 4. Synthesis of *p*-Phenylenebis(silafluorene) **7**



Spiro-linked molecules have many favorable properties such as high glass transition temperatures and high morphological stabilities.[12] Tetrayne **8** was prepared by the reaction of dichlorobis[2-(phenylethynyl)phenyl]silane and (phenylethynyl)lithium. The iridium-catalyzed reaction of **8** with **2a** produced asymmetrically substituted spirosilabifluorene **9** in good yield (Scheme 5).[13]

Scheme 5. Synthesis of Spirosilabifluorene **9**



Photophysical and thermal data for the produced silafluorenes are summarized in Table 2. The silafluorenes exhibited their absorption maxima at 323−362 nm and their fluorescence maxima at 349−396 nm. For comparison, a UV−vis spectrum of 9,9-dimethyl-9-silafluorene was measured. It showed a fluorescence maximum at 339 nm (10% quantum yield). Introduction of the substituents at the 1, 2, 3, and 4 positions of the silafluorene cores caused a bathochromic shift of 10−15 nm. Of particular note is that ladder-type **5** has a longer absorption wavelength and exceptionally high fluorescence efficiency (91%). The two silafluorene cores share the internal benzene ring. The extension of the π-conjugation shifted the absorption and fluorescence maxima to longer wavelengths, which still lay within the UV region. The photophysical data of *p*-phenylenebis(silafluorene) **7** were very similar to those of **3aa**. Spirosilabifluorene **9** has longer absorption and fluorescence maxima by ca. 10 nm compared to **3aa**. As for the thermal properties, the glass transition temperatures (T_g) and melting points (T_m) were

Table 2. Photophysical and Thermal Properties of Silafluorenes

	UV−vis[a]	fluorescence[b]		
silafluorene	λ_{abs} (log ϵ)	λ_{em} (Φ_F)	T_g	T_m
3aa	323 nm (3.60)	354 nm (0.12)	37 °C	151 °C
3ea	323 nm (3.75)	349 nm (0.29)	−40 °C	–
5	362 nm (4.37)	396 nm (0.91)	–	64 °C
7	323 nm (3.53)	356 nm (0.10)	74 °C	296 °C
9	334 nm (3.72)	364 nm (0.16)	91 °C	215 °C

[a] Measured in $CHCl_3$. [b] Measured in hexane. Determined with reference to quinine sulfate in 0.1 N H_2SO_4 and anthracene in EtOH (excited at 250 nm).

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[9] For ladder-type siloles, see: (a) Yamaguchi, S.; Xu, C.; Tamao, K. *J. Am. Chem. Soc.* **2003**, *125*, 13662. (b) Xu, C.; Wakamiya, A.; Yamaguchi, S. *J. Am. Chem. Soc.* **2005**, *127*, 1638.

[10] (a) Tour, J. M. *Adv. Mater.* **1994**, *6*, 190. (b) Berresheim, A. J.; Müller, M.; Müllen, K. *Chem. Rev.* **1999**, *99*, 1747.

[11] Synthesis of oligo-*p*-phenylenes by [2 + 2 + 2] cycloaddition has been reported. McDonald, F. E.; Smolentsev, V. *Org. Lett.* **2002**, *4*, 745.

[12] Steuber, F.; Staudigel, J.; Stössel, M.; Simmerer, J.; Winnacker, A.; Spreitzer, H.; Weissörtel, F.; Salbeck, J. *Adv. Mater.* **2000**, *12*, 130.

[13] For spirosilabifluorenes, see: (a) Gilman, H.; Gorsich, R. D. *J. Am. Chem. Soc.* **1958**, *80*, 1883. (b) Russell, A. G.; Spencer, N. S.; Philp, D.; Kariuki, B. M.; Snaith, J. S. *Organometallics* **2003**, *22*, 5589. (c) Lee, S. H.; Jang, B.-B.; Kafafi, Z. H. *J. Am. Chem. Soc.* **2005**, *127*, 9071.

investigated. Silafluorenes **7** and **9** melted above 200 °C, and the T_g values were higher than 70 °C. Silafluorenes **3aa**, **3ea**, and **5** exhibited inferior thermal properties.

In summary, densely substituted silafluorenes have been synthesized by the iridium-catalyzed [2 + 2 + 2] cycloaddition of silicon-bridged 1,6-diynes with alkynes. Structurally intriguing extended silafluorenes have also been prepared by the cycloaddition.

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Supporting Information Available: Experimental procedures and characterization data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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