Novel Organosilicon Starburst Compounds Based on Ruthenium-Catalyzed Silylative Coupling Reactions of 1,3,5-Tris(dimethylvinylsilyl)benzene

Yujiro Itami, Bogdan Marciniec,* Mariusz Majchrzak, and Maciej Kubicki

Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

The highly stereo- and regioselective reaction of 1,3,5-tris(dimethylvinylsilyl)benzene (**1**) with *p*-substituted styrenes, *p*-XC₆H₄CH=CH₂, where X = H (**2**), Cl (**3**), Br (**4**), vinyl (**5**), catalyzed by RuHCl(CO)(PCy₃)₂ (**I**) appeared to be an efficient basis for new starburst compounds involving silylene−vinylene−arylene sequences. Attempts were made to synthesize the first generation of dendrimer (**12**), based on **1** as a core, via two methods: direct silylative coupling of 1,3,5-tris[dimethyl(4-vinylstyryl)silyl]benzene (**5**) with **1**, which gave a mixture of oligomers containing the SiCH=CHSi structure, and successfully via silylation of **5** with vinylsilyl-3,5-bis(isopropoxysilyl)benzene (**10**) followed by vinylation with Grignard reagent. Additionally, the double silylation of DVB with **10** followed by vinylation allowed the synthesis of an analogous starburst compound (**14**), which can be a new core for analogous dendritic compounds.

Introduction

Alkenylsilanes, in particular substituted vinylsilanes, are commonly used organosilicon reagents.[1] Recently a new efficient synthetic method based on the silylation of various olefins with vinylsilanes (called mainly "the silylative coupling reaction", or "silyl group transfer", and "*trans*-silylation"), catalyzed by various transition metal complexes (e.g. Ru[2], Rh[3], Ir,[4] Co,[5] and Fe[6]), has been developed. A range of novel silylated olefins, along with well-known ones, have been obtained via this reaction (for a review see ref 7). For example, *trans*-styrylsilanes, common organosilicon reagents, have been regio- and stereoselectively synthesized by the reaction between para-substituted styrenes with vinylsilanes, catalyzed by ruthenium[2] and rhodium[3] complexes (Scheme 1).

Scheme 1. Silylation of Styrene with Vinylsilanes[a]
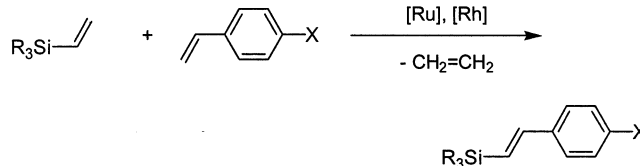
[a] R = alkyl, alkoxy, siloxy; X = H, CL, Br, Me, OMe.

Results of mechanistic studies have indicated that the process proceeds in the presence of catalytic species containing initially or generated in situ M−H or M−Si bonds via cleavage of the =C−Si bond of vinylsilanes and the =C−H bond of the olefins (e.g. styrene). It is worth noting that the cross-metathesis which starts and ends with the same substrates and products occurs through the cleavage of −C=C− double bonds of both olefin molecules.[8] The catalytic cycle of the silylative coupling reaction involves insertion of vinylsilanes into the M−H bond and styrene into the M−Si bond, followed by β-Si and β-H transfer to the metal center with elimination of productive *trans*-styrylsilanes and ethylene (Scheme 2).[2a]

The silylative coupling reaction catalyzed by ruthenium complexes has been applied to the synthesis of silicon-containing phenylene (arylene)−vinylene polymers with well-defined structure (Scheme 3), which are of growing interest due to their efficient photo- and electroluminescence.[9−11]

* To whom correspondence should be addressed. Tel: +48-61-8291366. Fax: +48-61-8291508. E-mail: marcinb@main.amu.edu.pl.

(1) (a) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988. (b) Thomas, S. E. *Organic Synthesis: The Role of Boron and Silicon*; Oxford University Press: New York, 1999.

(2) (a) Marciniec, B.; Pietraszuk, C. *Organometallics* **1997**, *16*, 4320 and references therein. (b) Marciniec, B.; Kujawa, M.; Pietraszuk, C. *Organometallics* **2000**, *19*, 1677 and references therein. (c) Wakatsuki, Y.; Yamazaki, H.; Nakano, M.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 703. (d) Yi, C.-S.; He, Z.; Lee, D.-W. *Organometallics* **2000**, *19*, 2036.

(3) (a) Marciniec, B.; Walczuk-Guściora, E.; Pietraszuk, C. *Organometallics* **2001**, *20*, 3423. Marciniec, B.; Walczuk-Guściora, E.; Błaże-jewska-Chadyniak, P. *J. Mol. Catal. A: Chem.* **2000**, *160*, 165. (b) Marciniec, B.; Walczuk-Gu_ciora, E.; Pietraszuk, C. *Catal. Lett.* **1998**, *55*, 125.

(4) Marciniec, B.; Kownacki, I.; Kubicki, M. *Organometallics* **2002**, *19*, 3263.

(5) Marciniec, B.; Kownacki, I.; Chadyniak, D. *Inorg. Chem. Commun.* **1999**, *2*, 581.

(6) Marciniec, B.; Majchrzak, M. *Inorg. Chem. Commun.* **2000**, *3*, 371.

(7) (a) Marciniec, B. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: Weinheim, Germany, 2002; Chapter 2.6. (b) Reichl, J. A.; Berry, D. H. *Adv. Organomet. Chem.* **1998**, *43*, 203. (c) Marciniec, B. *Appl. Organomet. Chem.* **2000**, *14*, 527. (d) Marciniec, B.; Pietraszuk, C. *Curr. Org. Chem.,* in press.

(8) Pietraszuk, C.; Marciniec, B.; Fischer, H. *Organometallics* **2000**, *19*, 913.

(9) Kwak, G.; Masuda, T. *Macromol. Rapid Commun.* **2001**, *22*, 1233. Mori, A.; Takahisa, E.; Kajiro, H.; Nishihara, Y.; Hiyama, T. *Macromolecules* **2000**, *33*, 1115. Kim, D.-S.; Shim, S.-C. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2263. Kim, H.-K.; Ryu, M.-K.; Kim, K.-D.; Lee, S.-M.; Cho, S.-W.; Park, J.-W. *Macromolecules* **1998**, *31*, 1114. Chen, R.-M.; Chien, K.-M.; Wong, K.-T.; Jin, B.-Y.; Luh, T.-Y.; Hsu, J.-H.; Fann, W. *J. Am. Chem. Soc.* **1997**, *119*, 11321.

Scheme 2.   Catalytic Cycle of the Silylative Coupling Reaction[a]
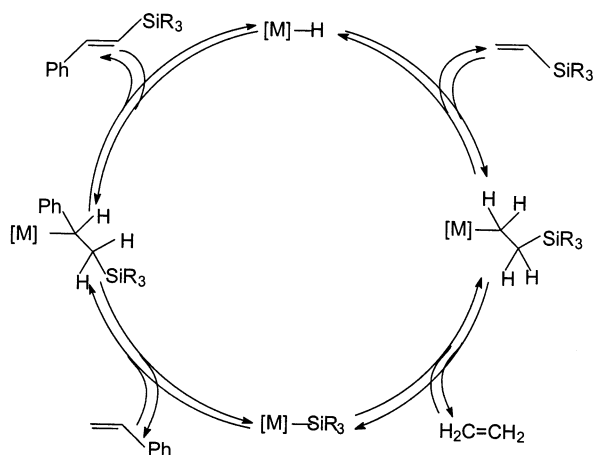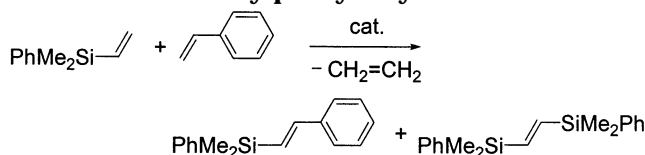

[a] M = Ru, Rh, Ir, Co.

In view of the experience thus far, it seems promising to use the silylative-coupling reaction for syntheses of other types of unsaturated organosilicon compounds—dendrimers (or starburst compounds),[12,13] which up to now have been synthesized mostly via the hydrosilylation process.[12a,13]

Therefore, the aim of this paper is to extend this reaction to the synthesis of novel organosilicon starburst compounds with the silicon-bridged π-conjugated structure (expected to have potential optoelectronic properties) by the respective reactions of trivinyl-substituted silane (1,3,5-tris(dimethylvinylsilyl)benzene (**1**)[13]) with conjugated diene (1,4-divinylbenzene).[14]

Results and Discussion

Catalytic Tests. Although various ruthenium complexes have been used for the silylative coupling reaction, their reactivity and selectivity have not been directly compared, since the reactions have been performed under different conditions (solvent, temperature, ratio of substrates, substituents at silicon, etc.).

Therefore, to selectively synthesize dendritic (starburst) compounds based on the reaction of 1,3,5-tris-(dimethylvinylsilyl)benzene (**1**) with 1,4-divinylbenzene, catalytic screenings have been applied in the model catalytic process of dimethylphenylvinylsilane with styrene. Many ruthenium complexes as well as the dimeric siloxide complex [Rh(cod)(μ-OSiMe$_3$)]$_2$[3a] and the first-generation Grubbs catalyst **II** have been tested in

(10) Majchrzak, M.; Itami, Y.; Marciniec, B.; Pawluc, P. *Tetrahedron Lett.* **2000**, *41*, 10303.
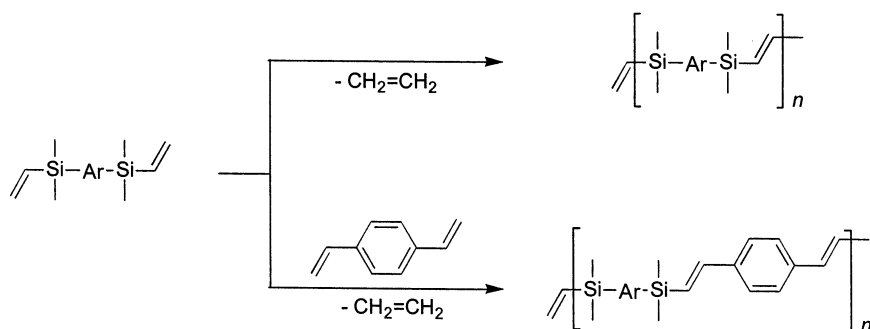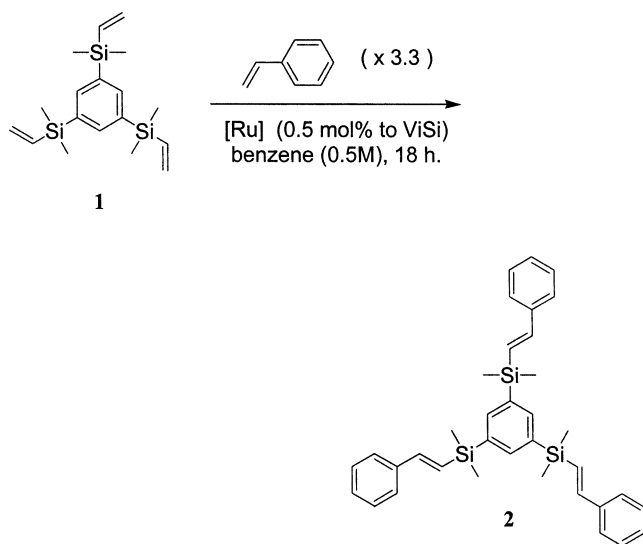
(11) Majchrzak, M.; Itami, Y.; Marciniec, B.; Pawluc, P. *Macromol. Rapid Commun.* **2001**, *22*, 202.

(12) (a) Kim, C.; Jeong, K.; Jung, I. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2749. Kim, C.; Kim, M. *J. Organomet. Chem.* **1998**, *563*, 43. Kim, C.; Jung, I. *Inorg. Chem. Commun.* **1998**, *1*, 427. Kim, C.; Son, S. *J. Organomet. Chem.* **2000**, *599*, 123. (b) Nakayama, J.; Lin, J.-S. *Tetrahedron Lett.* **1997**, *38*, 6043. Matsuo, T.; Uchida, K.; Sekiguchi, A. *Chem. Commun.* **1999**, 1799. (c) For general information about the organosilicon dendrimer, see the following review: Frey, H.; Schlenk, C. *Top. Curr. Chem.* **2000**, *210*, 70. Majoral, J.-P.; Caminade, A.-M. *Chem. Rev.* **1999**, *99*, 845.

(13) Organosilicon dendrimers based on **1** as a core, with the vinylene group between silicon atoms and the *partial saturated chain*, have been prepared recently. See: Kim, C.; Jung, I. *J. Organomet. Chem.* **2000**, *599*, 208.

(14) A preliminary communication was reported previously. See: Marciniec, B.; Małecka, E.; Majchrzak, M.; Itami, Y. *Macromol. Symp.* **2001**, *174*, 137−144.

Table 1. Silylation of Styrene with Dimethylphenylvinylsilane

entry	catalyst	cross[a] (%)	homo[a] (%)	ref
1	RuHCl(CO)(PPh$_3$)$_3$	47 (69*)	trace (6*)	2a,c
2	RuHCl(CO)$_2$(PPh$_3$)$_2$	33 (75*)	trace (7*)	
3	RuH(OAc)(CO)(PPh$_3$)$_2$	12	b	
4	RuH(OAc)(PPh$_3$)$_3$	trace	b	
5	RuH(acac)(CO)(PPh$_3$)$_2$	trace	b	
6	Ru(SiMe$_3$)Cl(CO)(PPh$_3$)$_2$	97 (69**)	3 (2**)	2a
7	RuHCl(CO)(PCy$_3$)$_2$ (**I**)	>99 (84**)	b (b**)	2d
8	RuHCl (PCy$_3$)$_2$	8	b	
9	RuH(OAc)(CO)(PCy$_3$)$_2$	12	b	
10	RuH(acac)(CO)(PCy$_3$)$_2$	8	b	
11	RuHI(CO)(PCy$_3$)$_2$	>99	b	
12	CpRuH(PPh$_3$)$_2$	trace	b	
13	[Rh(cod)(μ-OSiMe$_3$)]$_2$	69	30	3a
14	[Ru=] cat. (catalyst **II**)	20***	b***	

[a] Conversion calculated from GC. [b] Not observed. Unless otherwise stated, the conditions are as follows: [ViSi]:[styrene]:[cat] = 100:100:1, in toluene (1 M), under Ar, 18 h, 80 °C. Legend: (*) under air; (**) [ViSi]:[styrene]:[cat] = 2000:2000:1; (***) in CH$_2$Cl$_2$ at room temperature.

the silylative cross-coupling reaction and cross-metathesis, respectively. Since the synthetic procedure requires the absence of byproducts of the homo-coupling (disproportionation) of vinylsilanes (or homo-metathesis of styrene), all the screening tests have been performed at the 1:1 ratio of substrates. The results are presented in Table 1 along with those reported earlier on silylative coupling and/or cross-metathesis occurring in the presence of different catalysts and under different conditions.

The catalysis of the initial hexacovalent ruthenium hydride complexes containing triphenylphosphine (entries 1 and 2) was less efficient when the reaction was performed under argon, but its rate increased when it was performed in air, as a result of the elimination and oxidation of phosphine by the atmospheric oxygen, generating in situ coordinatively unsaturated (pentacoordinated) and catalytically active species. The reaction also proceeds effectively when a coordinatively unsaturated, pentacoordinated silyl ruthenium complex is used directly (entry 6), but therefore it catalyzes also the homo-coupling of vinylsilanes. The complexes involving chelating ligands such as OAc and acac (entries 3−5, 9, and 10) are inactive under the conditions examined due to strong bidentate coordination effects of the groups coordinated to the complexes, preventing the insertion−elimination mechanism. Since the ruthenium complexes without carbonyl ligands (entries 4, 8, and 12), even the coordinatively unsaturated tetracoordinated complex (entry 8), have been found inactive, one carbonyl ligand seems necessary to ensure increased catalytic activity. The cyclopentadienyl ruthenium catalyst (entry 9) has also been found quite inactive under the conditions examined. In the presence of the rhodium siloxide complex, the process occurs readily but via a preliminary activation of the =C−H bond of the olefin or vinylsilane (hydrovinylation), yielding also some undesirable homo-coupling products.

Scheme 3.   Synthesis of Silicon-Containing Phenylene (Arylene)−Vinylene Polymers

Scheme 4.   Silylative Coupling Reaction of 1 with Styrene

[Ru]	temp.	conv.	yield
I	80°C	100% (tri-)	95%
(Cy$_3$P)$_2$RuCl$_2$(=CHPh) (**II**)	r.t.	25% (mono-)	–

The Grubbs catalyst **II** appeared inactive (entry 14), as it has been reported that the ruthenium-catalyzed cross-metathesis of olefins (also styrene) with vinylsilanes containing one or more alkyl substituents on the silicon atom gave only traces or no cross-metathesis products due to non-productive decomposition of the ruthenacyclobutanes by β-elimination.[15] Finally, pentacoordinated monocarbonyl bis(tricyclohexylphosphine) complexes (entries 7 and 11) appeared to be the most active and selective catalysts, of which RuHCl(CO)(PCy$_3$)$_2$ (**I**) has shown high catalytic activity under the conditions of low catalyst loadings, even at 0.05 mol %. Therefore, catalyst **I** has been selected for the synthetic procedures.

Silylative-Coupling Reaction of Polyvinyl-Substituted Organosilicon Compounds. The silylative coupling reaction of 1,3,5-tris(dimethylvinylsilyl)benzene (**1**) with styrene catalyzed by **I** proceeds fairly well, giving stereoselectively product **2** at a high conversion, while the reaction in the presence of the ruthenium carbene complex **II** gave low conversion due to the aforementioned decomposition of ruthenium carbene species with vinylsilane (Scheme 4). Product **2** was

(15) Pietraszuk, C.; Fischer, H. *Chem. Commun.* **2000**, 2463.

Scheme 5.   Silylative Coupling Reaction of 1 with Para-Substituted Styrenes

X = H	(**2**)	96%
X = Cl	(**3**)	91%
X = Br	(**4**)	99%
X = CH=CH$_2$	(**5**)	96%
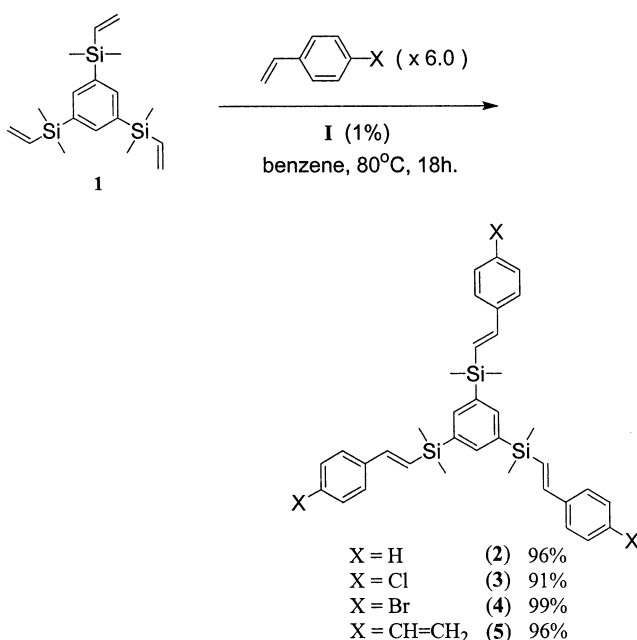
isolated easily in high yield, and its X-ray crystal structure was determined (Figure 1).

Catalyst **I** was also used in the reaction of **1** with para-substituted styrenes to give the products **3**−**5** with high yield and selectivity (Scheme 5). The effective silylative coupling of **1** with 1,4-divinylbenzene (DVB) enabled us to synthesize compound **5**, containing opto-electronically active DVB groups and terminating styryl groups which can be functionalized by further silylative coupling reaction with vinylsilanes.

Although compounds **3** and **4** have electron-withdrawing halogen substituents on the para position, they have similar absorption wavelength (264 and 265 nm, respectively) to that of compound **2** (263 nm). In contrast, **5** is characterized by a longer (by 30 nm) absorption wavelength (294 nm) than the other compounds because it contains the DVB fragment with a greater conjugation length (Figure 2).

Silylation of compound **5** with various vinylsilanes in the presence of catalyst **I** gave compounds **6**−**8** (Scheme 6). Although in the presence of Grubbs catalyst **II**, the cross-metathesis of vinyltriethoxysilane with styrene occurs readily and efficiently,[8] in the presence of **5** it does not proceed at all, which seems to be due to the lower activity of catalyst **II** toward the conjugated system.
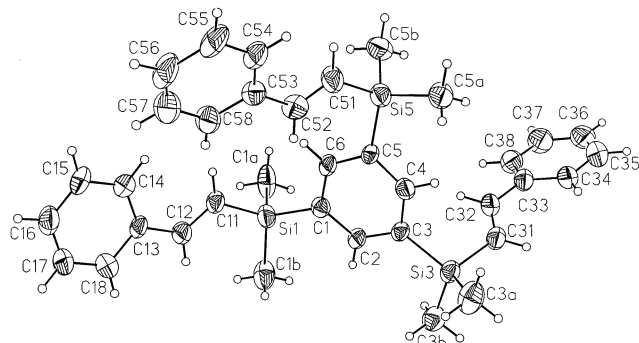
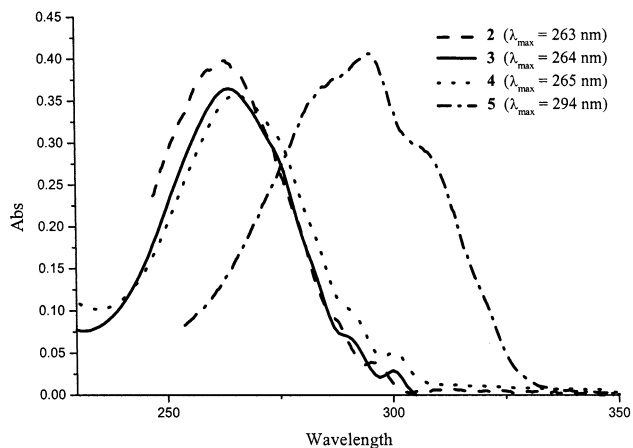**Figure 1.** X-ray crystal structure of **2**.

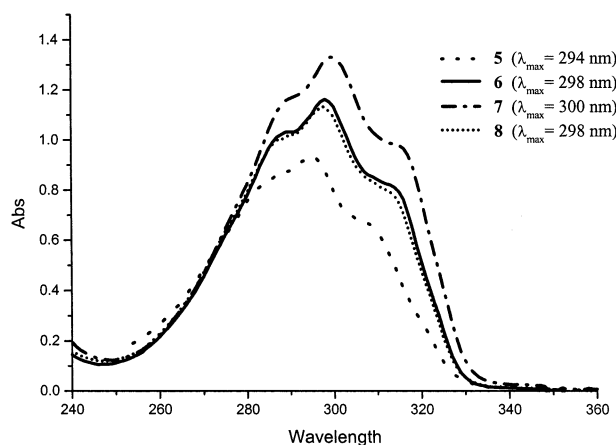**Figure 2.** UV−vis absorption spectra of **2**−**5**.

**Figure 3.** UV−vis absorption spectra of **5**−**8**.

The isolated compounds **6**−**8** show absorption wavelengths similar to those of **5**, with a small (4−6 nm) blue shift due to the induction effect of silyl groups (Figure 3).

To synthesize the starburst compound, the first generation of dendrimer **G1**, via direct silylation of **5** with tris(vinyldimethylsilyl)benzene (**1**), was applied using catalyst **I**. However, the presence of a terminal vinylsilyl group caused silylative homo-coupling of **G1** itself or of **G1** with another amount of tris(vinylsilyl)-benzene (**1**) to give a polymeric compound. Even the use of the six-coordinated ruthenium hydride [RuH(OAc)-(CO)(PPh₃)₂], being much less active toward a silylative homo-coupling reaction, furnishes a mixture of oligomeric compounds **9** containing the SiCH=CHSi struc-

Scheme 6. Silylation of 5 with Various Vinylsilanes

R₃ = Me₃ (**6**) 32%
R₃ = Me₂Ph (**7**) 36%
R₃ = (OEt)₃ (**8**) 27%
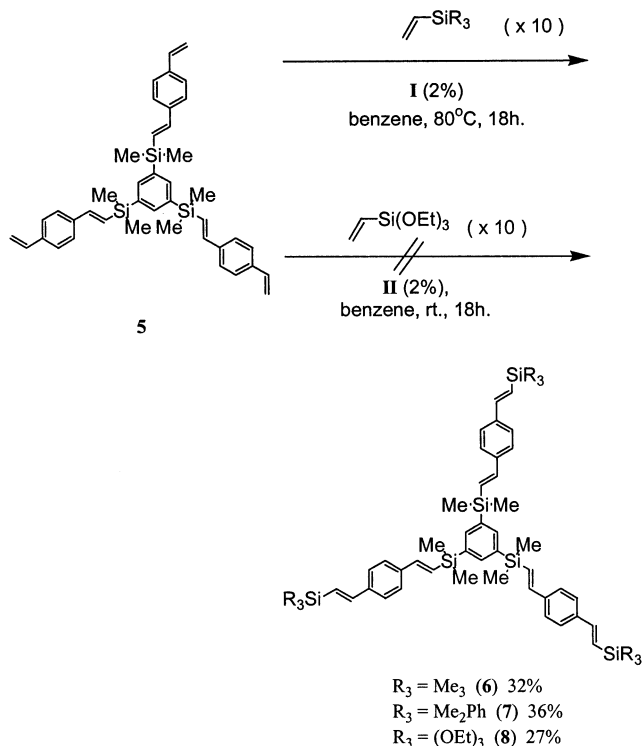
**Scheme 7. Formation of Oligomeric Compound 9**
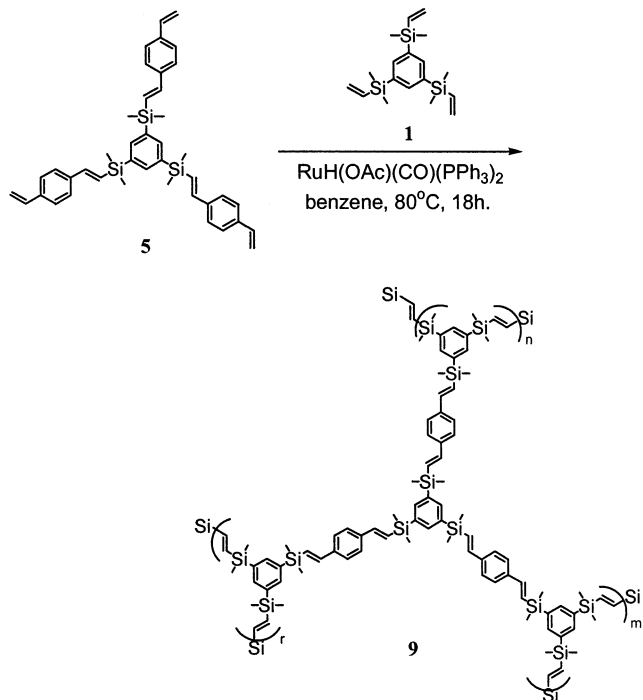
ture (Scheme 7), manifested in the NMR spectrum as a broad singlet at 6.8 ppm.

We have therefore finally succeeded in synthesizing **G1** (**12**), via a preliminary formation of an isopropoxy-dimethylsilyl-terminated precursor (**11**). The silylation of **5** with 1-(vinylsilyl)-3,5-bis(isopropoxysilyl)benzene (**10**) was examined to synthesize **12**, followed by vinylation with vinyl Grignard reagent and a catalytic amount (3% in relation to the isopropoxysilyl group) of CuCN (Scheme 8).

Scheme 8. Synthesis of G1 (12)
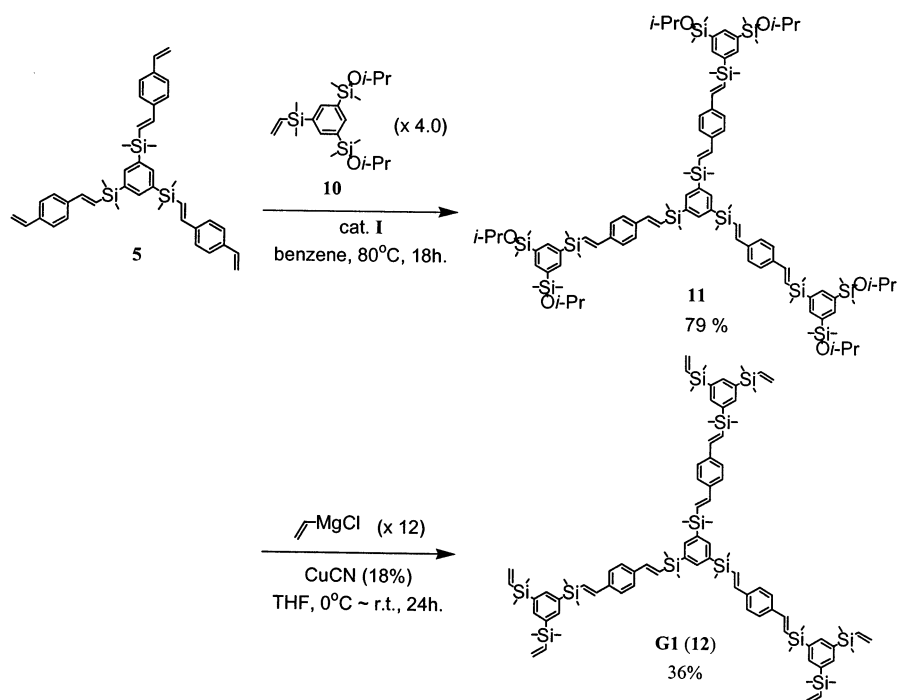
Scheme 9. Synthesis of 14
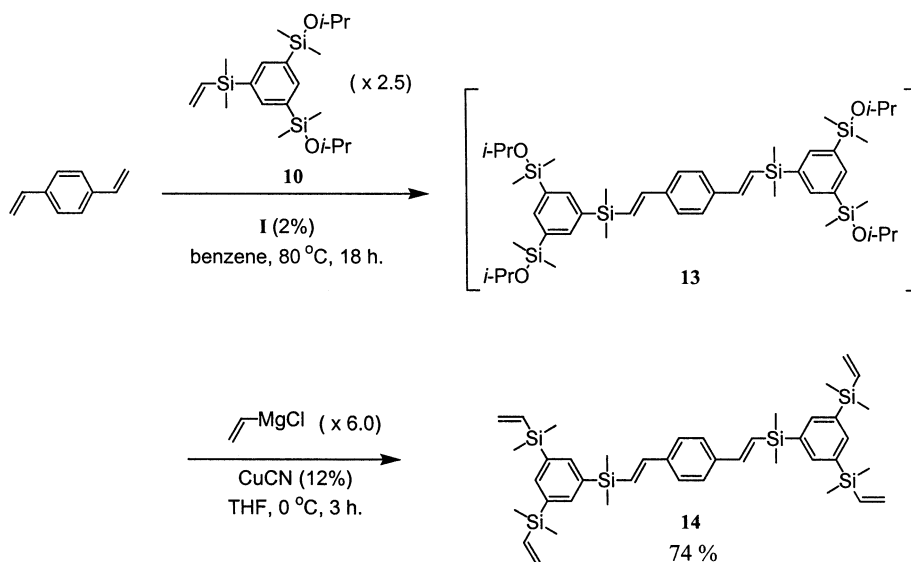
G1 (**12**) was identified by NMR spectroscopy, FAB-mass spectroscopy, and elemental analysis. NMR spectroscopy showed high regio- and stereoregularity on vinylene groups (*trans*), while the respective components obtained from the hydrosilylation of alkynes contained usually small amounts of *cis* and *gem* isomers.[9]

By analogy, compound **14**, which has an analogous starburst structure and can be potentially used as a novel core for an analogous dendritic compound, was also successfully synthesized in high yield via silylation of DVB with **10** followed by vinylation without isolation of intermediate **13** (Scheme 9). The UV−vis absorption spectra of compounds **12** and **14** have absorption wavelengths similar to that of compound **7**, with a maximum at 301 nm.

Conclusions

(a) The highly stereo- and regioselective reaction of 1,3,5-tris(dimethylvinylsilyl)benzene (**1**) with para-substituted styrenes (*p*-$XC_6H_4CH=CH_2$, where X = H, Cl, Br, vinyl) catalyzed by $RuHCl(CO)(PCy_3)_2$ (**I**) appeared to be an efficient basis for new starburst compounds involving silylene−vinylene−arylene sequences (compounds **2**−**5** and **6**−**8**).

(b) Attempts were made to synthesize the first generation of dendrimer **G1** (**12**), based on **1** as a core, via two methods: direct silylative coupling of **5** with **1**, which gave a mixture of oligomers containing the SiCH=CHSi structure (**9**), and successfully via silylation of **5** with 1-(vinylsilyl)-3,5-bis(isopropoxysilyl)-benzene (**10**) followed by vinylation with Grignard reagent.

(c) Double silylation of divinylbenzene (DVB) with **10** followed by vinylation with Grignard reagents allowed the synthesis of compound **14**, which can be potentially used as a novel core for analogous dendritic compounds.

(d) **G1** (**12**) and all the compounds with the DVB component (**5**−**10** and **14**) are characterized by longer absorption wavelengths than the other compounds (**1**−**4**), due to their longer conjugation lengths in the DVB fragment. All the compounds are also characterized by relatively strong blue-light fluorescence, but details about the fluorescence spectra will be reported in a separate paper, and further photophysical investigations are under way.

Experimental Section

General Procedure. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Varian XL 300 MHz spectrometer in CDCl₃ solution. Chemical shifts are reported in δ (ppm) with reference to the residual protio solvent (CHCl₃) peak for ^{1}H and ^{13}C and to TMS for [29]Si. Analytical gas chromatographic analyses were carried out on a Varian Star 3400CX gas chromatograph equipped with a DB-5 fused silica capillary column (30 m × 0.15 mm; Restock Inc.). High-resolution desorption electron impact (DEI) mass spectra were recorded on a AMD 402 mass spectrometer and FAB mass spectra on an AMD 604 instrument (AMD Intectra GmbH). MALDI-TOF mass spectra were recorded on a Voyager-Elite instrument (PerSeptive Biosystems Inc.), and 2,5-dihydroxybenzoic acid (DHB) or silver trifluoroacetate (AgTFA) was used as matrix. Ultraviolet absorption spectra were recorded on a Varian Cary 300 Bios UV−vis spectrometer, using spectral grade hexane (Merck) as a solvent. Thin-layer chromatography (TLC) was performed on plates coated with 250 μm thick silica gel (Aldrich), and column chromatography was performed with silica gel 60 (70−230 mesh; Fluka). Recycling gel permeation chromatography was performed with a JAI LC-908 instrument equipped with JAIGEL-1H and JAIGEL-2H columns. Diethyl ether and tetrahydrofuran (THF) were dried, having been distilled from sodium/benzophenone; similarly, benzene and toluene were distilled from sodium hydride and methanol and 2-propanol from magnesium under argon. All the other substrates were also dried and degassed by bulb-to-bulb distillation over molecular sieves 4A. All the reactions were carried out under an argon atmosphere.

1,3,5-tris(dimethylvinyl)silylbenzene (**1**),[13] diethyl(chlorodimethylsilyl)amine,[16] and the complexes RuHCl(CO)(PPh₃)₃,[17] RuHCl(CO)₂(PPh₃)₂,[18] RuH(OAc)(CO)(PPh₃)₂,[19] RuH(OAc)-(PPh₃)₃,[20] RuH(acac)(CO)(PPh₃)₂,[18] Ru(SiMe₃)Cl(CO)(PPh₃)₂,[2a] RuHCl(CO)(PCy₃)₂ (**I**),[21] RuHCl(PCy₃)₂,[22] RuH(OAc)(CO)-(PCy₃)₂,[18] RuH(acac)(CO)(PCy₃)₂,[18] RuHI(CO)(PCy₃)₂,[18] CpRu-H(PPh₃)₂,[23] and [Rh(cod)(μ-OSiMe₃)]₂[24] were prepared according to the literature procedures. Pure 1,4-divinylbenzene was synthesized by an Ni-catalyzed coupling reaction[25] between vinyl bromide and 1,4-bis(bromomagnesium)benzene.

Catalytic Screenings. Catalytic screenings were basically performed under Ar using an earlier prepared toluene solution (1 M) of a 1:1 mixture of dimethylphenylvinylsilane and styrene with 1 mol % of catalyst at 80 °C for 18 h, unless otherwise stated.

Synthesis of 1,3,5-Tris[dimethyl(2-phenylvinyl)silyl]-benzene (2). To a benzene solution (2.4 mL) of RuHCl(CO)-(PCy₃)₂ (26 mg, 0.036 mmol) was added styrene (0.9 mL, 8 mmol), followed by 1,3,5-tris(dimethylvinylsilyl)benzene (1 mL, 2.4 mmol), and the mixture was heated at 80 °C under an Ar flow for 18 h. After the substrate disappearance was confirmed by GC analysis, the solvent was evaporated under vacuum and the product was isolated from styrene by flash column chromatography to afford 1.28 g of **2** (2.28 mmol) in 95% yield as a white powder. ^{1}H NMR (CDCl₃; δ (ppm)): 0.50 (s, 18H), 6.65 (d, J = 19.2 Hz, 3H), 7.01 (d, J = 19.2 Hz, 3H), 7.27−7.37 (m, 9H), 7.46 (d, J = 7.8 Hz, 3H), 7.88 (s, 3H). ^{13}C NMR (CDCl₃; δ (ppm)): −2.46, 126.48, 127.25, 128.08, 128.52, 136.74, 138.23, 140.26, 145.30. ^{29}Si NMR (CDCl₃; δ (ppm)): −9.22. HRMS: calcd for C₃₆H₄₂Si₃, 558.25943; found, 558.25626. Anal. Calcd for C₃₆H₄₂Si₃: C, 77.35; H, 7.57. Found: C, 77.10; H 7.81. UV−vis absorption spectrum: λ_{max} 263 nm (log ϵ = 4.92). Single crystals of **2** suitable for an X-ray crystal structure analysis were obtained by recrystallization from hexane.

X-ray Crystal Structure Analysis. Crystal data for **2**: crystal 0.2 × 0.2 × 0.3 mm, monoclinic, space group *P*c, a = 18.2951(17) Å, b = 7.2694(11) Å, c = 27.035(4) Å, β = 109.378(12)°, V = 3391.8(8) Å, Z = 4, ρ_{calcd} = 1.095 Mg m⁻³. Data were collected at 293(2) K on a KUMA KM4 diffractometer,[25] with Cu Kα radiation (λ = 1.541 78 Å); 5159 unique reflections were measured to $2\theta_{max}$ = 150° using the $\omega/2\theta$ scan mode. Data were corected for Lorentz and polarization effects with the KUMA RED program.[26] The structure was solved by direct methods with SHELXS97[27] and refined by full-matrix least-squares methods (against F^2, using all 51 559 data, 704 parameters) with SHELXL97.[28] The final discrepancy indices were R1 = 0.0440, wR2 = 0.0837, and S = 1.11. The largest difference peak and hole in final difference Fourier maps were 0.237 and −0.220 e Å⁻³. CCDC-198212 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.; fax (+44) 1223-336-033 or deposit@ccdc.cam.ac.uk).

Reaction of 1,3,5-Tris(dimethylvinyl)silylbenzene (1) with Para-Substituted Styrenes. Compounds **3**−**5** were synthesized by analogous reactions with 4-chlorostyrene for **3**, with 4-bromostyrene for **4**, and with 1,4-divinylbenzene for **5** and isolated by a procedure similar to that mentioned above for the synthesis of 1,3,5-tris[(2-phenylvinyl)dimethylsilyl]-benzene (**2**).

3 was obtained in 91% yield as a white powder. ^{1}H NMR (CDCl₃; δ (ppm)): 0.43 (s, 18H), 6.54 (d, J = 19.2 Hz, 3H), 6.87 (d, J = 19.2 Hz, 3H), 7.25 (d, J = 8.7 Hz, 6H), 7.30 (d, J = 8.7 Hz, 6H), 7.70 (s, 3H). ^{13}C NMR (CDCl₃; δ (ppm)): 2.56, 127.63, 128.13, 128.70, 133.83, 136.65, 140.26, 143.94. ^{29}Si NMR (CDCl₃; δ (ppm)): −10.18. HRMS: calcd for C₃₆H₃₉Cl₃-Si₃, 660.14251, found, 660.14231. Anal. Calcd for C₃₆H₃₉Cl₃-Si₃: C, 65.28; H, 5.94. Found: C, 65.30; H, 5.97. UV−vis absorption spectrum: λ_{max} = 264 nm (log ϵ = 4.90).

4 was obtained in 99% yield as a white powder. ^{1}H NMR (CDCl₃; δ (ppm)): 0.32 (s, 18H), 6.45 (d, J = 19.2 Hz, 3H),

(16) Wannagat, U.; Schreiner, G. *Monatsh. Chem.* **1965**, *96*, 1889.
(17) Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 45.
(18) Itami, Y.; Majchrzak, M.; Marciniec, B. Unpublished results.
(19) Esterulas, M. A.; Werner, H. *J. Organomet. Chem.* **1986**, *303*, 221.
(20) Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Dalton Trans.* **1973**, 1912.
(21) Yi, C. S.; Lee, D. W.; Chen, Y. *Organometallics* **1999**, *18*, 2043.
(22) van der Schaaf, P. A.; Kolly, R.; Hafner, A. *J. Chem. Soc., Chem. Commun.* **2000**, 1045.
(23) Wilczewski, T.; Bochenska, M.; Biernat, J. F. *J. Organomet. Chem.* **1981**, *215*, 87.
(24) Marciniec, B.; Krzyżanowski, P. *J. Organomet. Chem.* **1995**, *493*, 261.
(25) Tamao, K.; Sumitani, K.; Kiso, Y.; Zenbayashi, M.; Fujioka, A.; Kodama, S.; Nakajima, I.; Minato, A.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1976**, 1958.

(26) CrysAlis CCD Program System; KUMA Diffraction, Wrocław, Poland, 1999.
(27) CrysAlis Red: CCD Data Reduction Program System; KUMA Diffraction, Wrocław, Poland, 1999.
(28) Sheldrick, G. M. SHELXL-97, Program for Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1997.
(29) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1969; Vol. IV, pp 293−309.

6.75 (d, $J = 19.2$ Hz, 3H), 7.24 (d, $J = 8.4$ Hz, 6H), 7.30 (d, $J = 8.4$ Hz, 6H), 7.66 (s, 3H). ^{13}C NMR (CDCl$_3$; δ (ppm)): -2.59, 122.03, 127.93, 128.28, 131.65, 136.62, 137.06, 140.25, 143.97. ^{29}Si NMR (CDCl$_3$; δ (ppm)): -10.19. MS (FAB): 791 (M$^+$). Anal. Calcd for C$_{36}$H$_{39}$Br$_3$Si$_3$: C, 54.34; H, 4.94. Found: C, 54.32; H, 5.09. UV$-$vis absorption spectrum: $\lambda_{max} = 265$ nm (log $\epsilon = 4.87$).

5 was obtained in 96% yield as a white powder. ^{1}H NMR (C$_6$D$_6$; δ (ppm)): 0.49 (s, 18H), 5.09 (dd, $J = 11.1$, 2.4 Hz, 3H), 5.63 (d, $J = 17.4$ Hz, 3H), 6.58 (ddd, $J = 17.4$, 11.1, 2.4 Hz, 3H), 6.69 (d, $J = 19.2$ Hz, 3H), 7.09 (d, $J = 19.2$ Hz, 3H), 7.02$-$7.27 (m, 12H), 8.24 (s, 3H). ^{13}C NMR (CDCl$_3$; δ (ppm)): -2.28, 113.78, 126.30, 126.56, 127.12, 136.35, 136.63, 137.19, 137.62, 140.14, 144.68. ^{29}Si NMR (CDCl$_3$; δ (ppm)): -9.94. HRM: calcd for C$_{42}$H$_{48}$Si$_3$, 636.30638; found, 636.30250. Anal. Calcd for C$_{42}$H$_{48}$Si$_3$: C, 79.18; H, 7.59. Found: C, 78.67; H, 7.89. UV$-$vis absorption spectrum: $\lambda_{max} = 294$ nm (log $\epsilon = 4.93$).

Silylation of 5 with Vinylsilanes. Trimethylvinylsilane (0.27 mL, 1.8 mmol) was added to a benzene solution (2 mL) of **5** (0.116 g, 0.18 mmol) and RuH(Cl)(CO)(PCy$_3$)$_2$ (2.8 mg, 0.0036 mmol), and the mixture was heated at 80 °C for 18 h. After disappearance of the signal from the styryl group of **5** was confirmed by NMR spectroscopy, volatiles were removed in vacuo, and the mixture was injected onto a silica gel column (hexane/EtOAc = 50/1, R_f = 0.20) and isolated by preparative GPC to afford 49 mg (0.057 mmol) of **6** in 32% yield as a white powder. ^{1}H NMR (CDCl$_3$; δ (ppm)): 0.15 (s, 27H), 0.42 (s, 18H), 6.46 (d, $J = 19.0$ Hz, 3H), 6.56 (d, $J = 19.0$ Hz, 3H), 6.84 (d, $J = 19.0$ Hz, 3H), 6.91 (d, $J = 19.0$ Hz, 3H), 7.35 (s, 12H), 7.78 (s, 3H). ^{13}C NMR (CDCl$_3$; δ (ppm)): -2.33, -1.08, 126.45, 126.60, 127.19, 129.59, 136.60, 137.72, 137.98, 140.12, 143.02, 144.70. ^{29}Si NMR (CDCl$_3$; δ (ppm)): -10.29, -6.19. MS (FAB): 853 (M$^+$), 838 ([M $-$ CH$_3$]$^+$). MS (MALDI-TOF/DHB): 875 ([M + Na]$^+$). Anal. Calcd for C$_{51}$H$_{72}$Si$_6$: C, 71.76; H, 8.50. Found: C, 71.62; H, 8.64. UV$-$vis absorption spectrum: λ_{max} 298 nm (log $\epsilon = 5.06$).

Compound **7** was prepared in essentially the same manner as **6** and isolated by flash column chromatography and preparative GPC in 36% yield as a white powder. ^{1}H NMR (CDCl$_3$; δ (ppm)): 0.51 (s, 18H), 0.52 (s, 18H), 6.67 (d, $J = 19.0$ Hz, 6H), 7.00 (d, $J = 19.0$ Hz, 3H), 7.01 (d, $J = 19.0$ Hz, 3H), 7.42$-$7.48 (m, 9H), 7.46 (s, 12H), 7.63$-$7.66 (m, 6H), 7.89 (s, 3H). ^{13}C NMR (CDCl$_3$; δ (ppm)): -2.33, -2.38, 126.61, 127.17, 127.39, 127.73, 128.95, 133.80, 136.58, 137.79, 137.93, 138.38, 140.12, 144.62, 144.68. ^{29}Si NMR (CDCl$_3$; δ (ppm)): -9.87. MS (FAB): 1039 (M$^+$). MS (MALDI-TOF/AgTFA): 1148 ([M + Ag]$^+$). Anal. Calcd for C$_{66}$H$_{78}$Si$_6$: C, 76.23; H, 7.56. Found: C, 75.97; H, 7.68. UV$-$vis absorption spectrum: λ_{max} = 300 nm (log $\epsilon = 5.12$).

Compound **8** was prepared in essentially the same manner as **6**, in the reaction between **5** and triethoxyvinylsilane, and isolated by preparative GPC in 27% yield as a white solid. ^{1}H NMR (CDCl$_3$; δ (ppm)): 0.44 (s, 18H), 1.27 (t, $J = 6.9$ Hz, 27H), 3.89 (q, $J = 6.9$ Hz, 18H), 6.18 (d, $J = 19.0$ Hz, 3H), 6.62 (d, $J = 19.0$ Hz, 3H), 6.94 (d, $J = 19.0$ Hz, 3H), 7.20 (d, $J = 19.0$ Hz, 3H), 7.41 (s, 6H), 7.42 (s, 6H), 7.79 (s, 3H). ^{13}C NMR (CDCl$_3$; δ (ppm)): -2.38, 18.39, 58.64, 117.60, 126.93, 127.85, 136.55, 137.21, 138.44, 140.11, 144.45, 148.47. ^{29}Si NMR (CDCl$_3$; δ (ppm)): -9.89, -68.90. MS (FAB): 1122 (M$^+$). MS (MALDI-TOF/DHB): 1145 ([M + Na]$^+$). Anal. Calcd for C$_{60}$H$_{90}$O$_9$Si$_6$: C, 64.12; H, 8.07. Found: C, 63.82; H, 7.79. UV$-$vis absorption spectrum: λ_{max} = 298 nm (log $\epsilon = 5.05$).

Synthesis of 1,3-Dibromo-5-(dimethylvinylsilyl)benzene. To the ether (450 mL) suspension of 1,3,5-tribromobenzene (15.75 g, 50 mmol) was added dropwise *n*-BuLi (1.15 M solution in hexanes, 46 mL, 52.5 mmol) at -78 °C, and the mixture was stirred for 30 min at the same temperature. Then chlorodimethylvinylsilane (8.1 mL, 60 mmol) was added dropwise at -78 °C, and the mixture was warmed to room temperature and stirred for 1.5 h. The resulting salt was filtered off, the volatiles were removed in vacuo, and distilla-

tion under reduced pressure (83$-$86 °C/0.4 mmHg) afforded 13.5 g of 1,3-dibromo-5-(dimethylvinyl)silylbenzene (42.5 mmol) in 85% yield as a colorless liquid. ^{1}H NMR (CDCl$_3$; δ (ppm)): 0.39 (s, 6H), 5.82 (dd, $J = 14.2$, 19.2 Hz, 1H), 6.13 (dd, $J = 4.2$, 14.0 Hz, 1H), 6.27 (dd, $J = 14.0$, 19.2 Hz, 1H), 7.58 (s, 2H), 7.67 (s, 1H). ^{13}C NMR (CDCl$_3$; δ (ppm)): -3.15, 123.18, 134.10, 134.32, 134.83, 136.10, 143.86. ^{29}Si NMR (CDCl$_3$; δ (ppm)): -9.34. HRMS: calcd for C$_{10}$H$_{12}$SiBr$_2$, 317.90750; found, 317.90971. Anal. Calcd for C$_{10}$H$_{12}$Br$_2$Si: C, 37.52; H, 3.78. Found: C, 37.35; H, 3.98.

Synthesis of 1-(Dimethylvinylsilyl)-3,5-bis(isopropoxydimethylsilyl)benzene (10). A mixture solution of 1,3-dibromo-5-(dimethylvinyl)silylbenzene (5.8 g, 18.1 mmol) and (diethylamino)chlorodimethylsilane (11.1 mL, 60 mmol) in 50 mL of THF was slowly added dropwise to a suspension of Mg turnings (1.6 g, 66 mmol), and the reaction mixture was refluxed for 18 h. After the reaction mixture was cooled to 0°C, a mixture of 2-propanol (11 mL, 145 mmol) and triethylamine (8.5 mL, 60 mmol) was added dropwise. Then the suspension of the reaction mixture was filtered and the volatiles were evaporated in vacuo. The oil left was washed with dry pentane, the suspended salt was filtered off, and the volatiles were evaporated in vacuo, and distillation under reduced pressure (110$-$115 °C/0.6 mmHg) afforded 3.2 g of **10** in 46% yield as a colorless liquid. ^{1}H NMR (CDCl$_3$; δ (ppm)): 0.43 (s, 6H), 0.46 (s, 12H), 1.22 (d, $J = 6.1$ Hz, 12H), 4.06 (quint, $J = 6.1$ Hz, 2H), 5.82 (dd, $J = 14.2$, 19.2 Hz, 1H), 6.11 (dd, $J = 4.2$, 14.0 Hz, 1H), 6.37 (dd, $J = 14.0$, 19.2 Hz, 1H), 7.85 (s, 2H), 7.89 (s, 1H). ^{13}C NMR (CDCl$_3$; δ (ppm)): -2.92, -1.06, 25.62, 65.23, 132.70, 136.19, 136.45, 137.93, 139.31, 140.04. ^{29}Si NMR (CDCl$_3$; δ (ppm)): -10.53, 5.51. HRMS: calcd for C$_{19}$H$_{35}$O$_2$Si$_3$ ([M $-$ CH$_3$]$^+$), 379.19449; found, 379.19784. Anal. Calcd for C$_{20}$H$_{38}$O$_2$Si$_3$: C, 60.85; H, 9.70. Found: C, 60.60; H, 9.89.

Synthesis of 11. To the benzene solution (2 mL) of **5** (80 mg, 0.126 mmol) and RuH(Cl)(CO)(PCy$_3$)$_2$ (**I**; 4.1 mg, 5.0 × 10^{-3} mmol) was added 1-(dimethylvinylsilyl)-3,5-bis-(isopropoxydimethylsilyl) benzene (**10**; 0.24 g, 0.50 mmol), and the mixture was heated to 80 °C for 18 h. After disappearance of the signal from the styryl group of **5** was confirmed by NMR spectroscopy, volatiles were removed in vacuo, and the mixture was passed through a silica gel column (hexane/EtOAc = 50/1, R_f = 0.19) and isolated by preparative GPC to afford 173 mg (0.1 mmol) of **11** in 79% yield as a colorless oil. ^{1}H NMR (CDCl$_3$; δ (ppm)): 0.39 (s, 36H), 0.44 (s, 18H), 0.45 (s, 18H), 1.14 (d, $J = 6.1$ Hz, 36H), 3.99 (q, $J = 6.1$ Hz, 6H), 6.59 (d, $J = 19.1$ Hz, 6H), 6.92 (d, $J = 19.0$ Hz, 3H), 6.93 (d, $J = 19.0$ Hz, 3H), 7.80 (s, 3H), 7.81 (s, 3H), 7.83 (s, 6H). ^{13}C NMR (CDCl$_3$; δ (ppm)): -2.36, -0.87, -0.80, 25.76, 65.33, 126.58, 127.35, 136.42, 136.49, 137.85, 139.30, 140.06, 144.62. ^{29}Si NMR (CDCl$_3$; δ (ppm)): -9.92, 5.73. Anal. Calcd for C$_{96}$H$_{150}$O$_6$Si$_{12}$: C, 66.37; H, 8.70. Found: C, 66.64; H, 8.79.

Synthesis of G1 (12). To a THF solution (2 mL) of **11** (70 mg, 0.04 mmol) and CuCN (0.6 mg, 0.007 mmol) was added a THF solution of CH$_2$=CHMgCl (1.7 M, 0.3 mL, 0.48 mmol), and the mixture was heated at room temperature for 18 h. The excess amount of Grignard reagent was quenched by adding MeOH/THF solution, and the mixture was extracted from ether/H$_2$O. The ethereal phase was dried over MgSO$_4$ and filtered, the volatiles were removed in vacuo, and the mixture was passed through a silica gel column (hexane/EtOAc = 50/1, R_f = 0.20). After isolation by preparative GPC, 22 mg (0.014 mmol) of **12** was afforded in 36% yield as a colorless oil. ^{1}H NMR (CDCl$_3$; δ (ppm)): 0.37 (s, 36H), 0.39 (s, 18H), 0.45 (s, 18H), 5.76 (dd, $J = 20.0$, 3.9 Hz, 6H), 6.05 (dd, $J = 14.7$, 3.9 Hz, 6H), 6.28 (dd, $J = 20.0$, 14.7 Hz, 6H), 6.59 (d, $J = 19.0$ Hz, 6H), 6.93 (d, $J = 19.0$ Hz, 6H), 7.40 (s, 12H), 7.72 (s, 3H), 7.73 (s, 3H), 7.77 (s, 3H). ^{13}C NMR (CDCl$_3$; δ (ppm)): -2.70, -2.33, 126.61, 127.39, 132.67, 136.38, 136.60, 137.89, 139.07, 139.82, 140.02, 144.62, 150.34. ^{29}Si NMR (CDCl$_3$; δ (ppm)): -11.50, -10.10. MS (FAB): 1544 ([M + H]$^+$). Anal. Calcd for

$C_{90}H_{126}Si_{12}$: C, 69.97; H, 8.22. Found: C, 70.07; H, 8.43. UV−vis absorption spectrum: λ_{max} = 301 nm (log ϵ = 5.15).

Synthesis of 13. The title compound was synthesized in essentially the same manner as **11**, by the reaction between DVB and **10**, and was used for the further synthesis of **14** without isolation. ^{1}H NMR (CDCl$_3$; δ (ppm)): 0.40 (s, 24H), 0.46 (s, 12H), 1.16 (d, J = 6.1 Hz, 24H), 4.01 (quint, J = 6.1 Hz, 6H), 6.61 (d, J = 19.1 Hz, 2H), 6.94 (d, J = 19.0 Hz, 2H), 7.41 (s, 4H), 7.84 (s, 6H). ^{13}C NMR (CDCl$_3$; δ (ppm)): −2.36, −0.86, 25.78, 65.33, 126.56, 127.37, 136.26, 136.50, 137.87, 139.30, 140.06, 144.63. ^{29}Si NMR (CDCl$_3$; δ (ppm)): −9.87, 5.71.

Synthesis of 14. This compound was synthesized and isolated in essentially the same manner as **12**, in 74% yield as a colorless oil. ^{1}H NMR (CDCl$_3$; δ (ppm)): 0.38 (s, 24H), 0.48 (s, 12H), 5.81 (dd, J = 20.0, 3.9 Hz, 4H), 6.09 (dd, J = 14.7, 3.9 Hz, 4H), 6.38 (dd, J = 20.0, 14.7 Hz, 4H), 6.63 (d, J = 19.0 Hz, 2H), 6.97 (d, J = 19.0 Hz, 2H), 7.45 (s, 4H), 7.75 (s, 2H), 7.78 (s, 4H). ^{13}C NMR (CDCl$_3$; δ (ppm)): −2.69, −2.33, 126.60, 127.44, 132.68, 136.35, 136.39, 137.88, 137.92, 139.94, 139.99, 144.60. ^{29}Si NMR (CDCl$_3$; δ (ppm)): −10.50, −9.89. MS (MALDI-TOF): 843 ([M + Ag]$^+$). Anal. Calcd for $C_{42}H_{62}Si_6$: C,

68.59; H, 8.50. Found: C, 68.70; H, 8.65. UV−vis absorption spectrum: λ_{max} = 301 nm (log ϵ = 4.70).

Supporting Information Available: Figures giving the MALDI-TOF mass spectra of **6**−**8** and **14**, FAB mass spectrum of **12**, NMR spectrum of **9**, **12**, and **14**, and UV−vis spectra of **12**, **14** and tables giving X-ray crystallographic data for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020986G