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Isolation and Synthetic Applications of 2,5-Bis(alkynylsilyl) Zirconacyclopentadienes

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2,5-Bis(alkynylsilyl)-1-zirconacyclopentadienes **3** were formed highly regio- and chemoselectively in excellent yield by the homocoupling reaction of 2 equiv of bis(alkynyl)silanes **1** mediated by a low-valent zirconocene species (Negishi reagent) generated in situ from Cp_2ZrBu_2. Single-crystal X-ray structural analysis of 2,5-bis(phenylalkynyldimethylsilyl)-1-zirconacyclopentadiene (**3a**) revealed a sandwich-type conformation. Hydrolysis or halogenation of these zirconacyclopentadienes **3** afforded multisubstituted stereodefined Si-bridged conjugated systems. Skeletal rearrangement of these 2,5-bis(alkynylsilyl)-1-zirconacyclopentadienes with aromatic substituents afforded zirconacyclohexadiene−silacyclobutene fused ring compounds **4**. Using these zirconacyclopentadienes **3** as starting reactive organometallic reagents, interesting cyclic compounds such as bis(alkynylsilyl)benzene derivatives and bis(alkynylsilyl)thiophene derivatives could be prepared in high yield. Further applications of these alkynylsilyl-substituted compounds for more complicated products and functional materials can be expected.

Introduction

Low-valent group 4 metallocene species such as "Cp_2Zr" and "Cp_2Ti" have played an important role in a variety of stoichiometric and catalytic reactions.[1–3] A large number of examples dealing with coupling and cyclization of alkynes by zirconocene "Cp_2Zr" and titanocene "Cp_2Ti" have been well documented in the literature.[1–3] Generally, the reaction pathway depends on the nature of the metallocene including the substitution pattern of the η^5-cyclopentadienyl rings, the substituents of the alkynes, and the metal-to-alkyne ratio.[2] The excellent work reported by Rosenthal and co-workers that described the reactivity of zirconocene "Cp_2Zr" and titanocene "Cp_2Ti" toward different diynes, especially 1,3-butadiynes, demonstrates how the combination of the metal, the substituent of the diynes, and the metal-to-diyne ratio could lead to fascinating compounds.[2,3] Si-tethered diynes, as reported by Takahashi, Mach, Rosenthal, et al., could also react with zirconocene "Cp_2Zr" and titanocene "Cp_2Ti" to afford unusual structures depending on the metal, the Cp ring, the substituents of the diynes, and the metal-to-diyne ratio.[4]

During our continued interest in the zirconocene-mediated reaction of Si-tethered diynes,[5] we realized that the metal-to-diyne ratio also played a key role in this case.[2,3] When the

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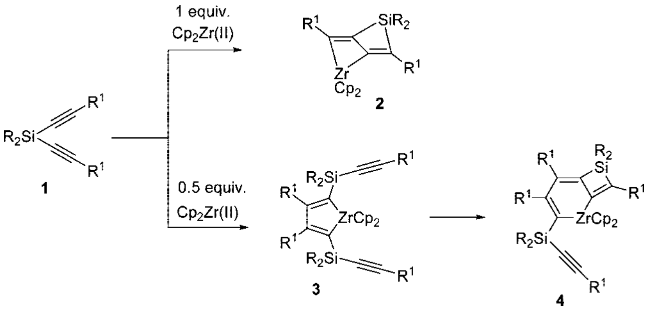
Scheme 1. Reaction Patterns between the Si-Tethered Diyne 1 and $Cp_2Zr(II)$



amount of the Si-tethered diyne **1** reported by Takahashi and co-workers[4b] was increased from 1 equiv to 2 equiv relative to Cp_2ZrBu_2, 2,5-bis(alkynylsilyl)zirconacyclopentadienes **3** were isolated in high yield with high regio- and chemoselectivity (Scheme 1). To the best of our knowledge, only one example of this type of potentially useful zirconacyclopentadienes had been reported, by Mathey and Le Floch.[6] These authors prepared 2,5-bis(1-propynyldimethylsilyl)-3,4-dimethylzirconacyclopentadiene and used it in a reaction with PCl_3 for the preparation of the interesting 2,5-bis(1-propynyldimethylsilyl)-3,4-dimethyl-1-chlorophosphole and its corresponding phospholide anion. However, a structurally characterized example of such a 2,5-bis(alkynylsilyl)zirconacyclopentadiene complex **3** has not been reported previously, and the study of their reactivities has also remained very limited.[6]

In this paper, we report the scope of this synthetic method for 2,5-bis(alkynylsilyl)-1-zirconacyclopentadienes **3**, X-ray single-crystal structural analysis, their reactivities including novel intramolecular skeletal rearrangement, and further synthetic applications leading to 1,4-bis(alkynylsilyl)benzene, 2,5-bis(alkynylsilyl)thiophene, and multisubstituted 1,3-butadiene derivatives.

Results and Discussion

Synthesis of 2,5-Bis(alkynylsilyl)zirconacyclopentadienes 3 and X-ray Single-Crystal Structural Analysis. Our previous work established that when unsaturated substrates such as alkynes were added to zirconacyclobutene−silacyclobutene fused ring compounds **2**, carbon−carbon triple bonds could coordinate to the Zr centers, facilitating skeletal rearrangement of the zirconacyclobutene−silacyclobutene fused ring system to form a new zirconacyclopentadiene ring system.[5] As shown in Scheme 1, the competition between formation of zirconacyclobutene−silacyclobutene fused ring compounds **2** via an intramolecular skeletal rearrangement and 2,5-bis(alkynylsilyl)zirconacyclopentadienes **3** via a homocoupling reaction was simply controlled by the metal-to-diyne ratio employed. Takahashi and co-workers[4b] have shown that a 1:1 molar ratio of diyne **1** to Cp_2ZrBu_2 generates zirconacyclobutene−silacyclobutene fused ring compounds **2**. When 2 equiv of diyne **1** and 1 equiv of Cp_2ZrBu_2 were used, 2,5-bis(alkynylsilyl)zirconacyclopentadiene **3** was formed. The zirconacyclobutene−silacyclobutene fused ring compounds **2** were found to undergo a novel skeletal rearrangement with diyne **1** to form 2,5-bis(alkynylsilyl)zirconacyclopentadienes **3**.

Scheme 2. Formation of Zirconacyclopentadiene Derivatives 3 and Si-Bridged Conjugated Systems 5

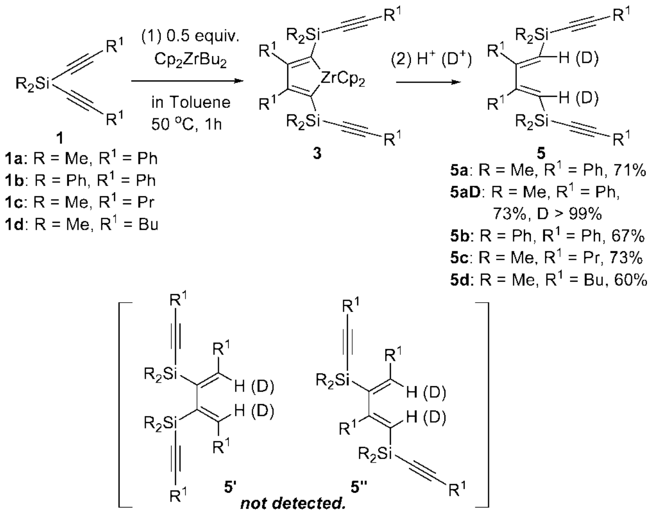
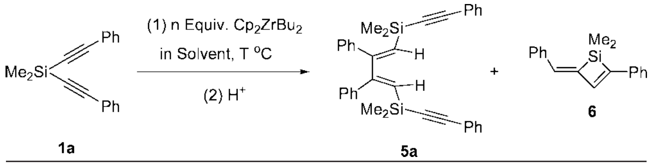


Table 1. Formation of Butadiene 5a and Silacyclobutene 6 via Different Metal-to-Diyne Ratios



n (Zr/**1a**)	solvent	T, °C	**5a** (yield/%)	**6** (yield/%)
1.0	THF	50	0	67
0.67	THF	50	80	8
1.0	THF	50	85	0
1.0	toluene	50	0	80
1.0	toluene	50	56	14
1.0	toluene	50	71	0

As demonstrated in Scheme 2, when 2 equiv of Si-tethered diynes **1** in toluene were treated with 1 equiv of Cp_2ZrBu_2, only 2,5-bis(alkynylsilyl)zirconacyclopentadienes **3** were formed. Because intermediate **3a** is highly symmetric, the ^{1}H NMR spectra showed only one Cp signal at 6.59 ppm. Its ^{13}C NMR spectra revealed one Cp signal at 112.6 ppm and two carbon−carbon triple bond signals at 98.6 and 106.1 ppm. The chemical shifts in its ^{13}C NMR spectra at 201.1 and 157.0 ppm are assignable to the four carbon atoms of the zirconacyclopentadiene ring, Zr-C(2,5) and C(3,4), respectively. Upon hydrolysis, these zirconacycles **3** afforded the corresponding 1,4-bis(alkynylsilyl)-1,3-butadiene derivatives **5** in high yield. Deuterolysis of the reaction mixture with DCl/D_2O instead of aqueous HCl gave dideuterated butadiene **5aD** in 73% isolated yield with more than 99% D incorporation. This result indicates that before quenching the usual 2,5-bis(alkynylsilyl)zirconacyclopentadienes **3** really had been formed. Both aromatic and aliphatic substituents on Si and terminal alkynyl carbon atoms could be used to smoothly facilitate this synthetically useful reaction. This coupling reaction is highly regioselective; no isomers **5′** and **5″** were detected.

In addition to the metal-to-diyne ratio, we also tested many other variables, including solvents, concentration of reagents, and reaction temperatures. We found that only one product, either **2** or **3**, depending on the metal-to-diyne ratio of reagents used,[2,3] was formed highly selectively. This phenomenon was also demonstrated by the following experiments in which the metal-to-diyne ratio was changed (Table 1). These results clearly showed that the metal-to-diyne ratio of "Cp_2Zr" to Si-tethered

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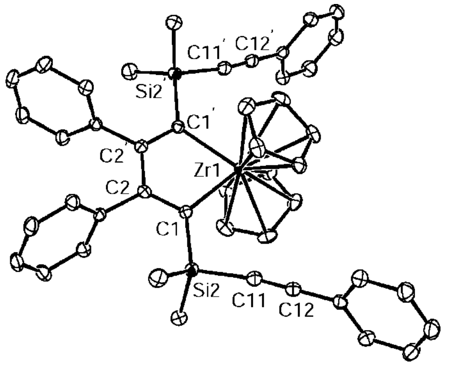
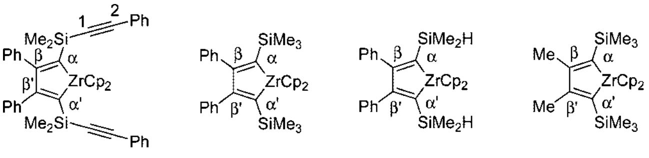


Figure 1. X-ray structure for **3a** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 2. Crystal Data and Structure Refinement for 3a

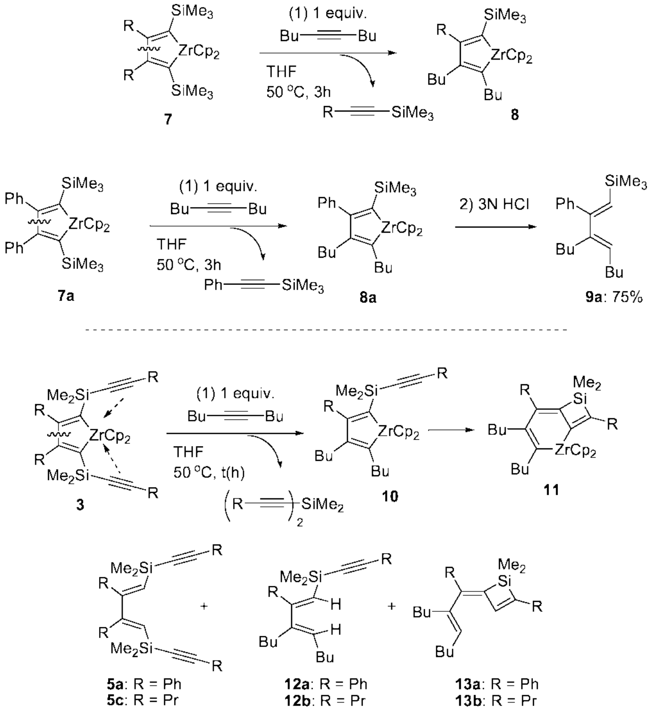
color	orange
formula	$C_{46}H_{42}Si_2Zr$
M_w	742.20
T (K)	173(2)
cryst syst	monoclinic
space group	*C*2/*c*
a (Å)	28.421(2)
b (Å)	11.091(1)
c (Å)	13.323(1)
β (deg)	115.210(1)
V (Å^3)	3799.7(6)
Z	4
ρ_{calcd} (g cm^{-3})	1.297
μ (mm^{-1})	0.384 mm^{-1}
θ range (deg)	2.00−25.05
no. of reflns collected	9642
no. of indep reflns	3353 [$R_{int} = 0.0216$]
completeness to $\theta = 25.05°$	99.5%
GOF	1.042
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0274$, $wR_2 = 0.0688$
R indices (all data)	$R_1 = 0.0341$, $wR_2 = 0.0704$
largest diff peak and hole (e·Å^{-3})	0.397 and −0.197

Table 3. Selected Bond Lengths [Å] and Angles [deg] for 3a, 7a,[7b] 7b,[7e] and 7c[7f]



	3a	7a	7b	7c
Zr−C(α)	2.275(2)	2.265(2)	2.270(3)	2.248(2)
Zr−C(α′)	2.275(2)	2.265(2)	2.270(3)	2.244(3)
C(α)−C(β)	1.358(3)	1.363(3)	1.358(4)	1.351(4)
C(β)−C(β′)	1.504(4)	1.511(3)	1.488(6)	1.519(4)
C(β′)−C(α′)	1.358(3)	1.363(3)	1.358(4)	1.351(4)
C(α)−Zr−C(α′)	79.6(1)	82.6(1)	78.6(2)	81.8(1)
C(1)−C(2)	1.204(3)			

Scheme 3. *β,β′* C−C Bond Cleavage of Zirconacyclopentadienes



diynes **1** determined formation of either zirconacyclobutene−silacyclobutene fused ring compounds **2** or 2,5-bis(alkynylsilyl)zirconacyclopentadienes **3**.

The formation of zirconacyclopentadienes **3** was further confirmed by using X-ray single-crystal structural analysis. The structure of **3a** shows that two phenylalkynyl moieties are on the same orientation, making a sandwich with the Zr atom at the center (Figure 1). The C−C triple bond length for **3a** is 1.204(3) Å, which is longer than reported lengths (1.197(3) and 1.186(4) Å).[5c] The distances between Zr and the triple-bond carbon atoms are 3.941 Å for Zr−C11 and 4.649 Å for Zr−C12, respectively. The angle Si−C11−C12 is 170.48(19)°. Table 2 shows crystallographic data for the X-ray structure of **3a**. Crystal structures of several zirconacyclopentadienes have been reported.[7] As a comparison given in Table 3 shows, the *β*,*β′* C−C bond of **3a** is shorter than those of **7a**[7b] and **7c**.[7f] The Zr−C bonds of **3a**, comparable to **7b**,[7e] are much longer than those of **7c**.

***β*,*β′* C−C Bond Cleavage of 2,5-Bis(alkynylsilyl)zirconacyclopentadienes 3.** Certain types of zirconacyclopentadienes, such as those possessing trimethylsilyl groups at their α and/or α′ positions, have been reported to undergo *β*,*β′* C−C bond cleavage when treated with alkynes such as 5-decyne at higher reaction temperatures.[8] As given in Scheme 3, zirconacyclopentadienes **7** (R = aromatic or aliphatic substituents) reacted with 1 equiv of 5-decyne in THF at 50 °C within 3 h to afford

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(7) (a) Crystal structures of several zirconacyclopentadienes have been reported; see: Wielstra, Y.; Gambarotta, S.; Meetsma, A.; de Boer, J. L. *Organometallics* **1989**, *8*, 2696–2702. (b) Erker, G.; Zwettler, R.; Kruger, C.; Kryspin, I. H.; Gleiter, R. *Organometallics* **1990**, *9*, 524–530. (c) Du, B.; Farona, M. F. *Tetrahedron* **1995**, *51*, 4359–4370. (d) Mao, S. S. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1995**, *117*, 7031–7032. (e) Kempe, R.; Spannenberg, A.; Kosse, P.; Peulecke, N.; Rosenthal, U. Z. *Krist.−New Cryst. Struct.* **1998**, 789–804. (f) Westerhausen, M.; Digeser, M. H.; Guckel, C.; Noth, H.; Knizek, J.; Ponikwar, W. *Organometallics* **1999**, *18*, 2491–2496. (g) Kulsomphob, V.; Harvey, B. G.; Arif, A. M.; Ernst, R. D. *Inorg. Chim. Acta* **2002**, *334*, 17–24. (h) Buzin, F. X.; Nief, F.; Ricard, L.; Mathey, F. *Organometallics* **2002**, *21*, 259–263. (i) Connor, P.; Berg, D. J.; Twamley, B. *Organometallics* **2005**, *24*, 2836. (. (j)) Hilton, C. L.; King, B. T. *Organometallics* **2006**, *25*, 4058–4061.

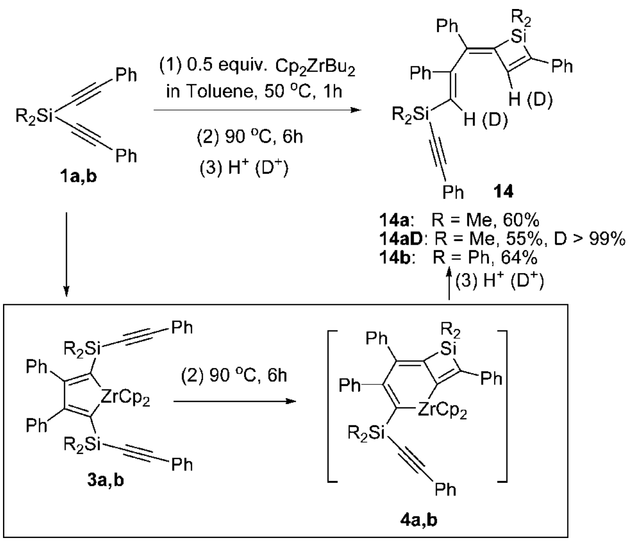
(8) (a) Cleavage of the *β*,*β*' C−C bond of zirconacyclopentadienes, see: Buchwald, S. L.; Nielsen, R. B. J. *Am. Chem. Soc.* **1989**, *111*, 2870–2874. (b) Smith, D. P.; Stricker, J. R.; Gray, S. D.; Bruck, M. A.; Holmes, R. S.; Wigley, D. E. *Organometallics* **1992**, *11*, 1275–1288. (c) Balaich, G. ; Hill, J. E.; Fanwich, P. E.; Rothwell, I. P. *Organometallics* **1993**, *12*, 2911–2924. (d) Suzuki, N.; Kondakov, D. Y.; Kageyama, M.; Kotora, M.; Hara, R.; Takahashi, T. *Tetrahedron* **1995**, *51*, 4519–4540. (e) Hara, R.; Xi, Z.; Kotora, M.; Xi, C.; Takahashi, T. *Chem. Lett.* **1996**, 1003–1004. (f) Johnson, E. S.; Balaich, G. J.; Rothwell, I. P. *J. Am. Chem. Soc.* **1997**, *119*, 7685–7693.

Table 4. β,β' C−C Bond Cleavage of 2,5-Bis(alkynylsilyl)zirconacyclopentadienes 3

R	*t* (h)	**5** (yield/%)	**12** (yield/%)[a]	**13** (yield/%)[a]
Ph	3	63[b]	7	0
	6	51[b]	16	7
	9	37[b]	19	14
Pr	3	54	27	0
	6	39	36	3
	9	31	45	5

[a] Yields determined by GC. [b] Isolated yields.

Scheme 4. Skeletal Rearrangement of 2,5-Bis(alkynylsilyl)zirconacyclopentadienes 3

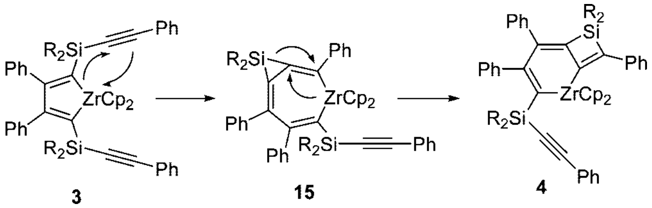


new zirconacyclopentadienes **8** via β,β' C−C bond cleavage. For example, β,β' C−C bond cleavage of zirconacyclopentadienes **7a** was complete within 3 h to afford **9a** in 75% isolated yield upon hydrolysis of **8a**. Surprisingly, as shown in Scheme 3, when the above experiment was applied to zirconacyclopentadienes **3**, it was found that β,β' C−C bond cleavage was much slower than in the case of **7**, probably due to the existence of two carbon−carbon triple bonds near the Zr atom. Reaction of **3** with 5-decyne gave zirconacyclopentadiene **10**, which underwent skeletal rearrangement to afford **11**.[4b,5a,c] Hydrolysis of the reaction mixture gave a mixture of three products: **5**, **12**, and **13**.

Although these data (given in Table 3 and Table 4) and experimental results mentioned above cannot show obvious interaction or coordination between the Zr atom and two triple bonds, this type of conformation is very interesting for further theoretical and experimental study.

Intramolecular Skeletal Rearrangement of 2,5-Bis(alkynylsilyl)zirconacyclopentadienes 3. Very interestingly, when **3a** and **3b** were further heated at elevated temperatures such as 90 °C for several hours, the intermediates **3a**,**b** disappeared completely and new products were obtained in good isolated yield. As shown in Scheme 4, products **14a** and **14b** were isolated in 60% and 64% yields, respectively. Deuterolysis of the reaction mixture with DCl/D$_2$O instead of aqueous HCl gave dideuterated butadiene **6aD** in 55% isolated yield with more than 99% D incorporation. These results indicated that, at higher temperatures, the intermediate compounds **3** undergo a novel intramolecular skeletal rearrangement to afford the zirconacyclohexadiene−silacyclobutene fused ring compounds **4**. Quenching of **4** with 1 N HCl gave **14**. Although we expected further skeletal rearrangement of **4** via insertion of the remaining triple bond into the Zr−C bond, no change was detected even after prolonged reaction time at higher temperatures such as refluxing toluene.

Scheme 5. Proposed Mechanism for Intramolecular Skeletal Rearrangement of 3



However, it is surprising to find that, unlike the aromatic substituted **3a** and **3b**, aliphatic substituted **3c** (R^1 = *n*-Pr) and **3d** (R^1 = *n*-Bu) did not undergo the above skeletal rearrangement.

For the skeletal rearrangement of **3** to **4**, a proposed mechanism is given in Scheme 5.[4,9,10] Insertion of one of the carbon−carbon triple bonds into the Zr−C bond of **3** leads to zirconacycloheptatriene-fused silacyclopropane intermediates **15**, or a "R$_2$Si-complex" of seven-membered zirconacyclocumulene intermediates,[4a,c] before rearranging to the final products **4**. Several reports demonstrated that intermediates with an alkynyl group as a substituent on the position α to the zirconium atom could lead to ring enlargement of the metallacycle.[9] Complexes of metallacyclocumulenes with "Ni(PPh$_3$)$_2$",[10a] "Cp$_2$V",[10b,d] and "R−P"[10e] were isolated and characterized.

Synthetic Applications of 2,5-Bis(alkynylsilyl)zirconacyclopentadienes 3. Zirconacyclopentadienes have been demonstrated to be very useful precursors for various linear and cyclic compounds.[11,12] Since 2,5-bis(alkynylsilyl)zirconacyclopentadienes **3** are readily available in high yield, we have attempted

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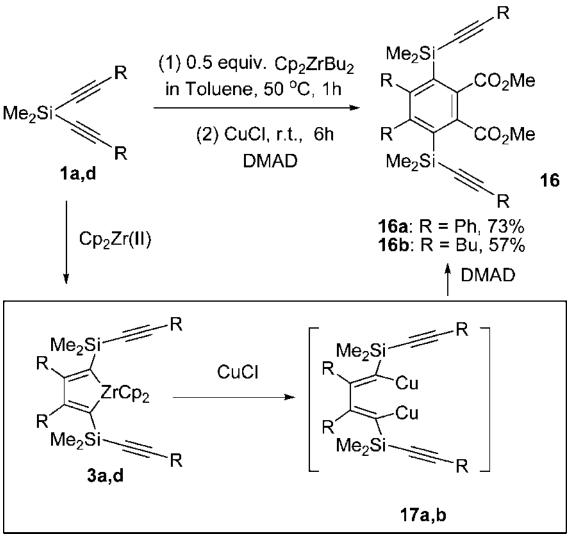
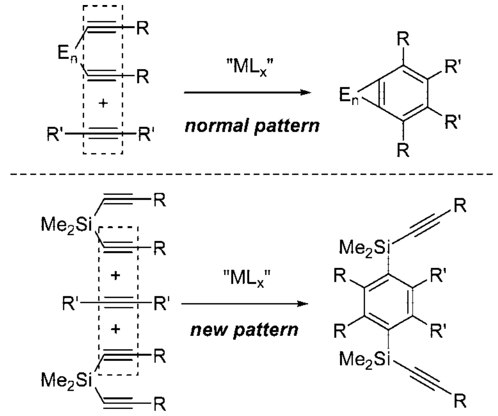
Scheme 6. Formation of *para*-Bis(alkynylsilyl)benzene Derivatives 16



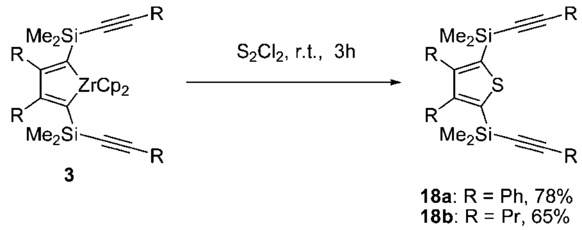
to use them as starting materials for preparation of more complicated and interesting products to demonstrate their usefulness. As we mentioned previously, the only example of applications of this type of zirconacyclopentadienes was reported by Mathey and Le Floch to prepare 2,5-bis(1-propynyldimethylsilyl)-3,4-dimethyl-1-chlorophosphole by its reaction with PCl_3.[6] As this type of zirconacyclopentadienes possess two alkynylsilyl groups, their derivatives can be further functionalized. Thus, we applied strategies reported for applications of simple zirconacyclopentadienes in this work.[11,12] Interesting cyclic and linear products bearing two alkynylsilyl groups were prepared in good to excellent yield.

First, as shown in Scheme 6, we treated the in situ generated 2,5-bis(alkynylsilyl) zirconacyclopentadienes **3** with dimethyl acetylenedicarboxylate (DMAD) in the presence of CuCl, using the procedure reported by Takahashi and co-workers, expecting formation of bis(alkynylsilyl)benzene derivatives.[5c,12e,f,1,13] Indeed, products **16a** (R = Ph) and **16b** (R = Bu) were obtained in 73% and 57% isolated yields, respectively. As proposed previously, transmetalation of 2,5-bis(alkynylsilyl)zirconacyclopentadienes **3** with CuCl to form the corresponding di-Cu intermediates **17a**,**b** might be the key step for this transformation. From the viewpoint of strategy of transition metal mediated alkyne trimerization leading to benzene derivatives, this work represents a new pattern of one-pot aromatization involving two diynes and one monoyne (Scheme 7).

Scheme 7. Types of One-Pot Aromatization from Diynes and Monoynes



Scheme 8. Formation of 2,5-Bis(alkynylsilyl)thiophene Derivatives 18



Functionalized thiophene derivatives are interesting and useful compounds for organic materials and biological applications. Several reports by Fagan, Nugent, and Takahashi et al. have been involved in the synthesis of heterocycles of main group elements via metallacycle transfer of the carbon fragments from a zirconacyclopentadiene to a main group element halide.[14,15] We treated our 2,5-bis(alkynylsilyl)zirconacyclopentadienes **3** with S_2Cl_2 and obtained the corresponding thiophene derivatives **18a**,**b** in high isolated yield (Scheme 8). Obviously, these functionalized thiophene derivatives can be further manipulated to generate more complicated compounds.

Our major research program on the synthesis and applications of 1,4-dihalo-1,3-dienes has demonstrated that 1,4-dihalo-1,3-dienes are very useful precursors for organic synthesis.[16–18]

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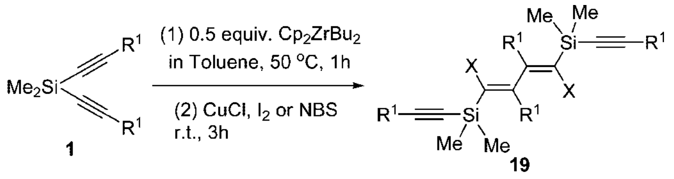
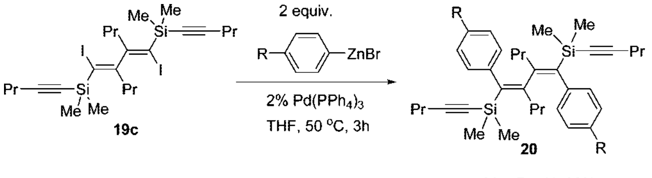
Scheme 9. Formation of Stereodefined 1,4-Bis(alkynylsilyl)-1,4-dihalo-1,3-butadienes 19



19a: R^1 = Ph, X = I, 69%
19b: R^1 = Ph, X = Br, 63%
19c: R^1 = Pr, X = I, 80%
19d: R^1 = Bu, X = I, 74%
19e: R^1 = Pr, X = Br, 82%
19f: R^1 = Bu, X = Br, 75%

Scheme 10. Formation of Fully Substituted Stereodefined 1,3-Butadiene Derivatives 20



20a: R = H, 86%
20b: R = OMe, 64%

Therefore, we then terminated the reaction mixture containing 2,5-bis(alkynylsilyl)zirconacyclopentadienes **3** with halogenation reagents such as I_2 and NBS and obtained in high isolated yield stereodefined 1,4-bis(alkynylsilyl)-1,4-dihalo-1,3-butadienes **19** (Scheme 9).

In order to further demonstrate the usefulness of these readily available 1,4-bis(alkynylsilyl)-1,4-dihalo-1,3-butadienes **19**, we used them as starting materials for Negishi coupling reactions to obtain fully substituted functionalized 1,3-butadienes **20** (Scheme 10).[19]

In summary, we have reported synthesis, crystal structure analysis, and skeletal rearrangement of 2,5-bis(alkynylsilyl)zirconacyclopentadienes and their synthetic applications as reactive organometallic reagents for the preparation of 1,4-bis(alkynylsilyl)benzenes, 2,5-bis(alkynylsilyl)thiophenes, and 1,4-bis(alkynylsilyl)-1,3-butadiene derivatives. Further applications of these alkynylsilyl-substituted compounds for more complicated products and functional materials are in progress.

Experimental Section

General Methods. All reactions were conducted under a slightly positive pressure of dry, prepurified nitrogen using standard Schlenk line techniques when appropriate. Unless otherwise noted, all starting materials were commercially available and were used without further purification. THF and toluene were refluxed and distilled from sodium/benzophenone ketyl under a nitrogen atmosphere. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75.4 MHz, respectively, in $CDCl_3$ unless stated otherwise.

Typical Procedure for Synthesis of 1,4-Bis(alkynylsilyl)-1,3-butadiene Derivatives 5 from Si-Tethered Diynes 1. To a toluene (2 mL) solution of Cp_2ZrCl_2 (280 mg, 0.96 mmol) at −78 °C in a 20 mL Schlenk tube was added dropwise *n*-BuLi (1.92 mmol, 1.6 M, 1.2 mL) by syringe. After the addition was complete, the reaction mixture was stirred at −78 °C for 1 h. Then 1.92 mmol of **1** was added, and the reaction mixture was allowed to warm gradually to 50 °C and stirred at this temperature for 1 h. The corresponding 2,5-bis(alkynylsilyl)-1-zirconacyclopentadiene **3** was thus formed. The resulting reaction mixture containing **3** was quenched with 3 N HCl, and the organic layer was washed successively with water and brine and then dried over $MgSO_4$. After evaporation of the solvent, column chromatography (silica gel, hexane/ether = 20:1) afforded 1,4-bis(alkynylsilyl) 1,3-butadiene derivatives **5**.

5a: white solid, mp 140–142 °C, isolated yield 71% (371 mg); ^{1}H NMR ($CDCl_3$, Me_4Si) δ −0.12 (s, 12H, CH_3), 5.63 (s, 2H, CH), 7.26–7.36 (m, 20H, CH); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −0.45 (4 CH_3), 93.71 (2 quart C), 105.32 (2 quart C), 123.25 (2 quart C), 127.37 (2 CH), 127.77 (4 CH), 128.11 (4 CH), 128.38 (2 CH), 130.04 (4 CH), 131.05 (2 CH), 131.92 (4 CH), 141.21 (2 quart C), 161.03 (2 quart C); HRMS calcd for $C_{36}H_{34}Si_2$ 522.2199, found 522.2190. Anal. Calcd for $C_{36}H_{34}Si_2$: C, 82.70, H, 6.55. Found: C, 82.57, H, 6.59.

5aD: white solid, isolated yield 73% (382 mg); ^{1}H NMR ($CDCl_3$, Me_4Si) δ −0.12 (s, 12H, CH_3), 7.27–7.36 (m, 20H, CH); ^{13}C NMR ($CDCl_3$, Me_4Si): δ −0.45 (4 CH_3), 93.71 (2 quart C), 105.34 (2 quart C), 123.26 (2 quart C), 127.38 (2 CH), 127.78 (4 CH), 128.11 (4 CH), 131.08 (2 CD, J = 21 Hz), 128.38 (2 CH), 130.03 (4 CH), 131.92 (4 CH), 141.21 (2 quart C), 160.98 (2 quart C); HRMS calcd for $C_{36}H_{32}D_2Si_2$ 524.2325, found 524.2319. Anal. Calcd for $C_{36}H_{32}D_2Si_2$: C, 82.38, H, 6.91. Found: C, 82.20, H, 6.67.

5b: white solid, mp 138–140 °C, isolated yield 67% (516 mg); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 6.04 (s, 2H, CH), 7.08–7.45 (m, 40H, CH); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 89.30 (2 quart C), 108.62 (2 quart C), 123.00 (2 quart C), 127.51 (6 CH), 127.64 (8 CH), 127.79 (2 CH), 128.05 (4 CH), 128.66 (2 CH), 129.23 (4 CH), 130.13 (4 CH), 132.16 (4 CH), 134.76 (8 CH), 135.05 (4 quart C), 140.36 (2 quart C), 164.07 (2 quart C); HRMS calcd for $C_{56}H_{42}Si_2$ 770.2825, found 770.2816. Anal. Calcd for $C_{56}H_{42}Si_2$: C, 87.23, H, 5.49. Found: C, 87.17, H, 5.48.

5c: colorless oil, isolated yield 73% (282 mg); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.25 (s, 12H, CH_3), 0.88–1.01 (m, 12H, CH_3), 1.34–1.60 (m, 8H, CH_2), 2.18–2.42 (m, 8H, CH_2), 5.45 (s, 2H, CH); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 0.60 (4 CH_3), 13.43 (2 CH_3), 14.14 (2 CH_3), 21.96 (2 CH_2), 22.06 (2 CH_2), 22.55 (2 CH_2), 35.88 (2 CH_2), 83.99 (2 quart C), 107.86 (2 quart C), 122.79 (2 CH), 161.97 (2 quart C); HRMS calcd for $C_{24}H_{42}Si_2$ 386.2825, found 386.2832.

5d: colorless oil, isolated yield 60% (265 mg); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.24 (s, 12H, CH_3), 0.89–0.93 (t, J = 7.2 Hz, 12H, CH_3), 1.33–1.51 (m, 16H, CH_2), 2.21–2.41 (m, 8H, CH_2), 5.45 (s, 2H, CH); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 0.58 (4 CH_3), 13.62 (2 CH_3), 14.07 (2 CH_3), 19.69 (2 CH_2), 21.96 (2 CH_2), 22.94 (2 CH_2), 30.72 (2 CH_2), 31.51 (2 CH_2), 33.64 (2 CH_2), 83.79 (2 quart C), 108.01

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(2 quart C), 122.61 (2 CH), 162.11 (2 quart C); HRMS calcd for $C_{28}H_{50}Si_2$ 442.3451, found 442.3456.

Isolation of Crystal 3a. To a toluene (1 mL) solution of Cp_2ZrCl_2 (140 mg, 0.48 mmol) at −78 °C (dry ice/acetone bath) in a 20 mL Schlenk tube was added dropwise *n*-BuLi (0.96 mmol, 1.6 M, 0.6 mL) by syringe. After the addition was complete, the reaction mixture was stirred at −78 °C for 1 h. Then **1a** (238 mg, 0.915 mmol) was added, and the reaction mixture was allowed to warm gradually to 50 °C and stirred at this temperature for 1 h. The resulting reaction mixture was dried under vacuum, and the residue was extracted with hexane. The precipitated LiCl was separated using a frit under a nitrogen atmosphere. The clear filtrate was reduced under vacuum to precipitate **3a** as an orange powder (306 mg, 0.412 mmol, 90% isolated yield). Single crystals of **3a** suitable for X-ray analysis were grown in hexane at −40 °C overnight: ^{1}H NMR (C_6D_6) δ 0.11 (s, 12H, $SiMe_2$), 6.59 (s, 10H, C_5H_4), 6.79−6.80 (m, 6H, C_6H_5), 6.89 (t, *J* 7.2 Hz, 4H, C_6H_5),7.01−7.03 (m, 6H, C_6H_5), 7.44−7.47 (m, 4H, C_6H_5); ^{13}C NMR (C_6D_6) δ 2.48 (4 CH_3), 98.60 (2 quart C), 106.12 (2 quart C), 112.64 (10 CH), 124.22 (2 quart C), 125.43 (2 CH), 127.02 (4 CH), 128.59 (2 CH), 128.75 (4 CH), 129.69 (4 CH), 131.87 (4 CH), 145.79 (2 quart C), 156.99 (2 quart C), 201.12 (2 quart C). Anal. Calcd for $C_{46}H_{42}Si_2Zr$: C, 74.44; H, 5.70. Found: C, 74.15; H, 5.43. CCDC 652662.

Replacement of Alkyne Moieties of Zirconacyclopentadienes via C−C Bond Cleavage Reaction. To a THF (10 mL) solution of Cp_2ZrCl_2 (280 mg, 0.96 mmol) at −78 °C (dry ice/acetone bath) in a 20 mL Schlenk tube was added dropwise *n*-BuLi (1.92 mmol, 1.6 M, 1.2 mL) by syringe. After stirring at −78 °C for 1 h, 2 equiv of phenylethynyltrimethylsilane (348 mg, 1.92 mmol) was added by syringe, and the resulting solution was warmed to 50 °C for 1 h. Then 5-decyne (132 mg, 0.96 mmol) was added and stirred at 50 °C for 3 h. The resulting mixture was quenched by 3 N HCl. The organic layer was washed successively with water and brine and then dried over $MgSO_4$. After evaporation of the solvent, column chromatography (silica gel, hexane/ether = 50:1) afforded **9a** as colorless oil (235 mg, 75% isolated yield). **9a**: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.25 (s, 12H, CH_3), 0.88–1.01 (m, 12H, CH_3), 1.34–1.60 (m, 8H, CH_2), 2.18–2.42 (m, 8H, CH_2), 5.45 (s, 2H, CH); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 0.00 (3 CH_3), 14.01 (1 CH_3), 14.09 (1 CH_3), 22.54 (1 CH_2), 22.92 (1 CH_2), 27.37 (1 CH_2), 28.59 (1 CH_2), 31.35 (1 CH_2), 31.89 (1 CH_2), 125.79 (1 CH), 126.65 (1 CH), 127.42 (2 CH), 129.72 (2 CH), 133.23 (1 CH), 142.99 (1 quart C), 143.16 (1 quart C), 158.77 (1 quart C); HRMS calcd for $C_{21}H_{34}Si$ 314.2430, found 314.2412.

To a THF (10 mL) solution of **3a** (0.96 mmol) was added 5-decyne (132 mg, 0.96 mmol), and the mixture was stirred at 50 °C for 3, 6, and 9 h; **12a**, and **13a** were determined by GC. The resulting mixture was then quenched by 3 N HCl. The organic layer was washed successively with water and brine and then dried over $MgSO_4$. After evaporation of the solvent, column chromatography (silica gel, hexane/ether = 50:1) afforded **12a** and **13a** as colorless oils, whose NMR spectra are consistent with our published results.[5c]

To a THF (10 mL) solution of **3c** (0.96 mmol) was added 5-decyne (132 mg, 0.96 mmol), and the mixture was stirred at 50 °C for 3, 6, and 9 h; **5c**, **12b**, and **13b** were determined by GC. The resulting mixture was quenched by 3 N HCl. The organic layer was washed successively with water and brine and then dried over $MgSO_4$. After evaporation of the solvent, column chromatography (silica gel, hexane/ether = 50:1) afforded **12b** and **13b**.

12b: colorless oil, isolated yield 30% (100 mg); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.25 (s, 6H, CH_3), 0.88–1.01 (m, 12H, CH_3), 1.27–1.60 (m, 12H, CH_2), 2.05–2.42 (m, 8H, CH_2), 5.35 (s, 1H, CH), 5.50 (t, $J = 7.5$ Hz, 1H, CH); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −0.73 (2 CH_3), 13.45 (1 CH_3), 14.04 (1 CH_3), 14.07 (1 CH_2), 14.16 (1 CH_2), 22.01 (1 CH_2), 22.11 (1 CH_2), 22.55 (1 CH_2), 22.85 (1 CH_2), 22.90 (1 CH_2), 27.82 (1 CH_2), 28.16 (1 CH_2), 31.16 (1 CH_2), 32.16 (1 CH_2), 35.91 (1 CH_2), 84.31 (1 quart C), 107.61 (1 quart C), 120.86 (1 CH), 127.98 (1 CH), 142.16 (1 quart C), 160.86 (1 quart C); HRMS calcd for $C_{22}H_{40}Si$: 332.2899, found 332.2906.

13b: colorless oil, isolated yield 3% (10 mg); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.33 (s, 6H, CH_3), 0.81–0.93(m, 12H, CH_3), 1.26–1.46 (m, 12H, CH_2), 1.97–2.24 (m, 8H, CH_2), 5.18 (t, $J = 7.5$ Hz, 1H, CH) 7.15 (s, 1H, CH); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −0.70 (2 CH_3), 13.76 (1 CH_3), 14.06 (3 CH_3), 21.90 (1 CH_2), 22.49 (1 CH_2), 22.71 (1 CH_2), 22.72 (1 CH_2), 27.58 (1 CH_2), 28.41 (1 CH_2), 30.77 (1 CH_2), 32.41 (1 CH_2), 34.48 (1 CH_2), 38.43 (1 CH_2), 128.54 (1 CH), 139.02 (1 quart C), 139.13 (1 quart C), 140.05 (1 quart C), 149.68 (1 CH), 160.08 (1 quart C); HRMS calcd for $C_{22}H_{40}Si$: 332.2899, found 332.2890.

Typical Procedure for Intramolecular Skeletal Rearrangement of 2,5-Bis(alkynylsilyl)zirconacyclopentadienes 3 Leading to Silacyclobutene Derivatives 14. To a toluene (2 mL) solution of Cp_2ZrCl_2 (280 mg, 0.96 mmol) at −78 °C (dry ice/acetone bath) in a 20 mL Schlenk tube was added dropwise *n*-BuLi (1.92 mmol, 1.6 M, 1.2 mL) with a syringe. After the addition was complete, the reaction mixture was stirred at −78 °C for 1 h. Then 1.92 mmol of Si-tethered diynes **1** was added, and the reaction mixture was allowed to warm gradually to 50 °C, stirred at this temperature for 1 h and then 90 °C for 6 h, and quenched with 1 N HCl at 0 °C. The organic layer was washed successively with water and brine and then dried over $MgSO_4$. After evaporation of the solvent, column chromatography (silica gel, hexane/ether = 20:1) afforded **14**.

When the above reaction mixture was quenched with 3 mL of 1 N DCl, **14aD** was obtained.

14a: colorless oil, isolated yield 60% (313 mg); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.13 (s, 6H, CH_3), 0.45 (s, 6H, CH_3), 5.89 (s, 1H, CH), 7.18–7.46 (m, 21H, CH); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −0.73 (2 CH_3), 0.22 (2 CH_3), 94.05 (1 quart C), 105.63 (1 quart C), 123.27 (1 quart C), 126.58 (1 CH), 126.88 (1 quart C), 127.59 (1 CH), 127.67 (3 CH), 127.71 (1 quart C), 127.89 (2 CH), 127.98 (2 CH), 128.14 (3 CH), 128.41 (1 CH), 128.56 (2 CH), 129.10 (2 CH), 130.27 (1 CH), 131.97 (3 CH), 137.31 (1 quart C), 142.32 (1 quart C), 142.52 (1 quart C), 142.86 (1 quart C), 145.97 (1 quart C), 148.00 (1 CH), 158.05 (1 quart C), 159.46 (1 quart C); HRMS calcd. for $C_{36}H_{34}Si_2$ 522.2199, found 522.2187.

14aD: colorless oil isolated yield 55% (288 mg); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.13 (s, 6H, CH_3), 0.44 (s, 6H, CH_3), 7.16–7.45 (m, 20H, CH); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −0.73 (2 CH_3), 0.21 (2 CH_3), 94.06 (1 quart C), 105.63 (1 quart C), 123.29 (1 quart C), 126.58 (1 CH), 126.90 (2 CH), 127.59 (1 CH), 127.70 (3 CH), 127.77 (1 CH), 127.91 (2 CH), 127.98 (2 CH), 128.16 (2 CH), 128.41 (1 CH), 128.57 (2 CH), 129.12 (2 CH), 130.03 (1 CH), 131.99 (2 CH), 137.33 (1 quart C), 142.37 (1 quart C), 142.55 (1 quart C), 142.80 (1 quart C), 145.98 (1 quart C), 158.05 (1 quart C), 159.36 (1 quart C); HRMS calcd for $C_{36}H_{32}D_2Si_2$ 524.2325, found 524.2307.

14b: colorless oil, isolated yield 64% (493 mg); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 6.33 (s, 1H, CH), 7.00–7.73 (m, 40H, CH), 7.97 (s, 1H, CH); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 89.55 (1 quart C), 108.93 (1 quart C), 122.87 (1 quart C), 126.63 (1 CH), 126.91 (1 CH), 127.26 (2 CH), 127.64 (2 CH), 127.76 (1 CH), 127.88 (4 CH), 127.94 (2 CH), 128.04 (3 CH), 128.13 (6 CH), 128.56 (2 CH), 128.70 (1 CH), 129.39 (2 CH), 130.33 (2 CH), 132.20 (2 CH), 133.09 (2 quart C), 134.86 (4 CH), 135.37 (2 quart C), 135.41 (4 CH), 136.65 (1 quart C), 141.32 (1 quart C), 141.95 (1 quart C), 143.96 (1 quart C), 144.34 (1 quart C), 151.85 (1 CH), 157.75 (1 quart C), 160.34 (1 quart C); HRMS calcd for $C_{56}H_{42}Si_2$ 770.2825, found 770.2815.

Typical Procedure for Synthesis of 1,4-Bis(alkynylsilyl)benzene Derivatives 16. A toluene (2 mL) solution of **3c** (0.96 mmol) was cooled to 0 °C, and DMAD (1.92 mmol, 0. 24 mL) and CuCl (1.92 mmol, 190 mg) were added. The reaction mixture was then warmed to room temperature and stirred at room temperature for 6 h. The organic layer was washed successively with water and brine and then dried over $MgSO_4$. After evaporation of the solvent, column chromatography (silica gel, hexane/ether = 4: 1) afforded **16**.

16a: white solid, mp 220–222 °C, isolated yield 73% (483 mg); ^{1}H NMR ($CDCl_3$, Me_4Si) δ −0.01 (s, 12H, CH_3), 3.84 (s, 6H, CH_3), 6.82–7.44 (m, 20H, CH); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 1.69 (4 CH_3), 52.47 (2 CH_3), 93.30 (2 quart C), 105.76 (2 quart C), 123.17 (2 quart C), 127.16 (2 CH), 127.28 (4 CH), 128.13 (4 CH), 128.44 (2 CH), 131.17 (4 CH), 131.90 (4 CH), 135.73 (2 quart C), 139.07 (2 quart C), 141.32 (2 quart C), 149.42 (2 quart C), 170.02 (2 quart C); IR (neat) v(C=O) = 1735 cm^{-1}; HRMS calcd for $C_{42}H_{38}O_4Si_2$ 662.2309, found 662.2304. Anal. Calcd for $C_{42}H_{38}O_4Si_2$: C, 76.10, H, 5.78. Found: C, 75.93, H, 5.89.

16b: colorless oil, isolated yield 57% (332 mg); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.46 (s, 12H, CH_3), 0.87–0.98 (m, 12H, CH_3), 1.35–1.51 (m, 16H, CH_2), 2.19–2.23 (t,J = 6.9 Hz, 4H, CH_2), 3.03–3.08 (t,J = 7.5 Hz, 4H, CH_2), 3.80 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 2.31 (4 CH_3), 13.58 (2 CH_3), 13.90 (2 CH_3), 19.73 (2 CH_2), 21.96 (2 CH_2), 23.37 (2 CH_2), 30.52 (2 CH_2), 33.72 (2 CH_2), 35.62 (2 CH_2), 52.16 (2 CH_3), 84.14 (2 quart C), 108.73 (2 quart C), 135.90 (2 quart C), 136.26 (2 quart C), 150.63 (2 quart C), 170.44 (2 quart C); IR (neat) v(C=O) = 1736 cm^{-1}; HRMS calcd for $C_{34}H_{54}O_4Si_2$ 582.3561, found 582.3558.

Typical Procedure for Synthesis of 2,5-Bis(alkynylsilyl)thiophene Derivatives 18. A toluene (2 mL) solution of **3c** (0.96 mmol) was cooled to 0 °C, and S_2Cl_2 (0.96 mmol, 0.08 mL) was then added. The reaction mixture was warmed to room temperature and stirred at room temperature for 3 h. The organic layer was washed successively with water and brine and then dried over $MgSO_4$. After evaporation of the solvent, column chromatography (silica gel, hexane/ether = 50:1) afforded **18**.

18a: colorless oil, isolated yield 78% (431 mg); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.27 (s, 12H, CH_3), 7.17–7.49 (m, 20H, CH); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 0.20 (4 CH_3), 92.61 (2 quart C), 106.72 (2 quart C), 122.96 (2 quart C), 126.85 (2 CH), 127.42 (4 CH), 128.17 (4 CH), 128.65 (2 CH), 130.49 (4 CH), 132.00 (4 CH), 137.89 (2 quart C), 138.80 (2 quart C), 152.45 (2 quart C); HRMS calcd for $C_{36}H_{32}SSi_2$ 552.1763, found 552.1759.

18b: colorless oil, isolated yield 65% (270 mg); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.44 (s, 12H, CH_3), 0.97–1.04 (m, 12H, CH_3), 1.49–1.63 (m, 8H, CH_2), 2.20–2.72 (m, 8H, CH_2); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 0.88 (4 CH_3), 13.48 (2 CH_3), 14.75 (2 CH_3), 21.92 (2 CH_2), 21.99 (2 CH_2), 25.34 (2 CH_2), 31.90 (2 CH_2), 82.65 (2 quart C), 109.10 (2 quart C), 136.33 (2 quart C), 152.16 (2 quart C); HRMS calcd for $C_{24}H_{40}SSi_2$ 416.2389, found 416.2382.

Typical Procedure for the Preparation of 1,4-Bis(alkynylsilyl)-1,4-dihalo-1,3-butadienes 19. A toluene (2 mL) solution of **3c** (0.96 mmol) was cooled to 0 °C, and CuCl (1.92 mmol, 190 mg) and I_2 (2.88 mmol, 731 mg) or NBS (2.88 mmol) were added. The reaction mixture was then warmed to room temperature and stirred at room temperature for 3 h. The organic layer was washed successively with water and brine and then dried over $MgSO_4$. After evaporation of the solvent, column chromatography (silica gel, hexane/ether = 50:1) afforded **19**.

19a: colorless oil, isolated yield 69% (534 mg); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.11 (s, 6H, CH_3), 0.23 (s, 6H, CH_3), 7.19–7.43 (m, 20H, CH); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 0.89 (2 CH_3), 1.48 (2 CH_3), 92.38 (2 quart C), 106.81 (2 quart C), 107.45 (2 quart C), 122.98 (2 quart C), 127.87 (4 CH), 128.06 (2 H), 128.56 (4 CH), 128.60 (2 CH), 129.44 (4 CH), 131.99 (4 CH), 138.87 (2 quart C), 164.51 (2 quart C); MS (EI) m/z (rel int) 647 (M^+ − 127, 10), 159 (100).

19b: colorless oil, isolated yield 63% (427 mg); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.11 (s, 6H, CH_3), 0.26 (s, 6H, CH_3), 7.26–7.39 (m, 20H, CH); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 0.23 (2 CH_3), 0.58 (2 CH_3), 91.55 (2 quart C), 106.64 (2 quart C), 122.88 (2 quart C), 124.04 (2 quart C), 127.92 (4 CH), 128.04 (2 H), 128.52 (4 CH), 128.58 (2 CH), 129.54 (4 CH), 132.04 (4 CH), 138.35 (2 quart C), 156.72 (2 quart C); HRMS calcd for $C_{36}H_{32}Br_2Si_2$: 678.0409, found 678.0401.

19c: colorless oil, isolated yield 80% (510 mg); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.43 (s, 12H, CH_3), 0.89–1.02 (m, 12H, CH_3), 1.52–1.67 (m, 8H, CH_2), 2.21–2.89 (m, 8H, CH_2); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 1.73 (2 CH_3), 2.52 (2 CH_3), 13.52 (2 CH_3), 14.52 (2 CH_3), 21.87 (2 CH_2), 22.04 (2 CH_2), 22.29 (2 CH_2), 38.78 (2 CH_2), 82.73 (2 quart C), 104.31 (2 quart C), 109.52 (2 quart C), 165.20 (2 quart C); MS (EI) m/z (rel int) 511 (M^+ − 127, 7), 177 (100).

19d: colorless oil, isolated yield 74% (514 mg); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.43 (s, 12H, CH_3), 0.89–0.95 (m, 12H, CH_3), 1.29–1.59 (m, 16H, CH_2), 2.23–2.89 (m, 8H, CH_2); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 1.79 (2 CH_3), 2.60 (2 CH_3), 13.59 (2 CH_3), 13.87 (2 CH_3), 19.76 (2 CH_2), 21.98 (2 CH_2), 23.22 (2 CH_2), 30.51 (2 CH_2), 30.72 (2 CH_2), 36.51 (2 CH_2), 82.60 (2 quart C), 104.15 (2 quart C), 109.68 (2 quart C), 165.07 (2 quart C); MS (EI) m/z (rel int) 567 (M^+ − 127, 5), 125 (100).

19e: colorless oil, isolated yield 82% (444 mg); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.40 (s, 6H, CH_3), 0.41 (s, 6H, CH_3), 0.90–1.02 (m, 12H, CH_3), 1.52–1.61 (m, 8H, CH_2), 2.21–2.95 (m, 8H, CH_2); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 0.84 (2 CH_3), 1.02 (2 CH_3), 13.48 (2 CH_3), 14.46 (2 CH_3), 21.68 (2 CH_2), 21.86 (2 CH_2), 22.00 (2 CH_2), 37.46 (2 CH_2), 82.72 (2 quart C), 109.56 (2 quart C), 121.52 (2 quart C), 156.27 (2 quart C); HRMS calcd for $C_{24}H_{40}Br_2Si_2$ 542.1035, found 542.1029.

19f: colorless oil, isolated yield 75% (449 mg); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.40 (s, 12H, CH_3), 0.89–0.94 (m, 12H, CH_3), 1.33–1.52 (m, 16H, CH_2), 2.23–2.97 (m, 8H, CH_2); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 0.89 (2 CH_3), 1.07 (2 CH_3), 13.59 (2 CH_3), 13.95 (2 CH_3), 19.73 (2 CH_2), 21.96 (2 CH_2), 23.15 (2 CH_2), 30.16 (2 CH_2), 30.49 (2 CH_2), 35.19 (2 CH_2), 82.57 (2 quart C), 109.72 (2 quart C), 121.41 (2 quart C), 156.20 (2 quart C); HRMS calcd for $C_{28}H_{48}Br_2Si_2$ 598.1661, found 598.1647.

Synthesis of 1,3-Butadiene Derivatives 20 via Negishi Coupling Reaction. To a solution of phenylmagnesium bromide (2 M, THF, 0.5 mL) in 5 mL of THF at 0 °C was added anhydrous zinc bromide (222 mg, 1.0 mmol) in 3 mL of THF followed by $Pd(PPh_3)_4$ (23 mg, 0.02 mmol) and **19c** (319 mg, 0.5 mmol). The cooling bath was removed, and the temperature was allowed to rise to 50 °C. After an additional 3 h the solution was cooled to rt and quenched by a saturated aqueous solution of ammonium chloride. The organic layer was washed successively with water and brine and then dried over $MgSO_4$. After evaporation of the solvent, column chromatography (silica gel, hexane/ether = 50:1) afforded **20a** as a colorless oil (462 mg, 86% isolated yield). **20a**: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.00 (s, 6H, CH_3), 0.03 (s, 6H, CH_3), 0.71–0.93 (m, 12H, CH_3), 1.18–1.53 (m, 8H, CH_2), 2.08–2.32 (m, 8H, CH_2), 7.08–7.25 (m, 10H, CH); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 0.61 (2 CH_3), 1.03 (2 CH_3), 13.43 (2 CH_3), 14.56 (2 CH_3), 21.91 (2 CH_2), 21.92 (2 CH_2), 22.08 (2 CH_2), 38.89 (2 CH_2), 83.95 (2 quart C), 108.10 (2 quart C), 125.23 (2 CH), 127.46 (4 CH), 128.14 (4 CH), 135.42 (2 quart C), 144.08 (2 quart C), 155.99 (2 quart C); HRMS calcd for $C_{36}H_{50}Si_2$ 538.3451, found 538.3446.

To a solution of 4-iodoanisole (234 mg, 1.0 mmol) in 5 mL of THF at −78 °C was added 1 equiv of *n*-BuLi (0.625 mL, 1.6 M in hexanes, 1.0 mmol). After stirring at −78 °C for 1 h, the resulting solution was warmed to 0 °C, and 1 equiv of anhydrous zinc bromide (222 mg, 1.0 mmol) was added, followed by $Pd(PPh_3)_4$ (23 mg, 0.02 mmol) and **19c** (319 mg, 0.5 mmol). The cooling bath was removed, and the temperature was allowed to rise to 50 °C. After an additional 3 h the solution was cooled to rt and quenched by a saturated aqueous solution of ammonium chloride. The organic layer was washed successively with water and brine and then dried over $MgSO_4$. After evaporation of the solvent, column chromatography (silica gel, hexane/ether = 10:1) afforded **20b** as a colorless oil (383 mg, 64% isolated yield). **20b**: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.02 (s, 6H, CH_3), 0.04 (s, 6H, CH_3), 0.71–0.93 (m, 12H, CH_3), 1.20–1.47 (m, 8H, CH_2), 2.10–2.29 (m, 8H, CH_2), 3.80 (s, 6H, CH_3) 6.77–7.01 (m, 8H, CH); ^{13}C NMR ($CDCl_3$, Me_4Si) δ0.75 (2 CH_3), 1.15 (2 CH_3), 13.40 (2 CH_3), 14.61 (2 CH_3), 21.93 (2 CH_2), 21.95 (2 CH_2), 22.11 (2 CH_2), 38.81 (2 CH_2), 55.14 (2 CH_3), 84.16 (2 quart C), 108.10 (2 quart C), 112.87 (4 CH), 129.14 (4 CH), 134.78 (2 quart C), 136.42 (2 quart C), 156.41 (2 quart C), 157.37 (2 quart C); HRMS calcd for $C_{38}H_{54}O_2Si_2$ 598.3662, found 598.3671.

X-ray Crystallographic Studies of 3a. Crystals for X-ray analyses of **3a** were obtained as described in the preparations. The crystals were manipulated under a nitrogen atmosphere and were sealed in thin-walled glass capillaries. Data collections were performed at −110 °C on a Bruker CCD APEX diffractometer with a CCD area detector, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file.[20] The structures were solved by use of the SHELXTL program.[21] Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data and processing parameters are summarized in Table 2.

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Supporting Information Available: Copies of ^{1}H and ^{13}C NMR spectra for all isolated compounds and X-ray structure and crystallographic data for **3a**. This material is available free of charge via the internet at http//pubs.acs.org.

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