Zirconocene-Mediated Intermolecular Coupling of Si-tethered Diynes with Alkynes, Ketones, Aldehydes, and Isocyanates by means of Novel Skeletal Rearrangement of Zirconacyclobutene–Silacyclobutene and Zirconacyclohexadiene–Silacyclobutene Fused-Ring Intermediates

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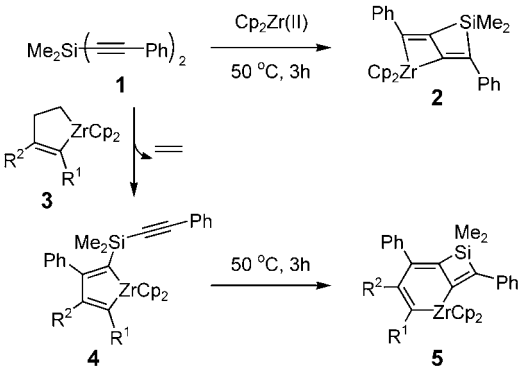
Abstract: Bis(alkynyl)silanes react with low valent zirconocene species to afford zirconacyclobutene intermediates. These in situ generated reactive organometallic intermediates can react with alkynes, ketones, aldehydes, and isocyanates by means of a novel skeletal rearrangement. When a zirconacyclobutene intermediate was treated with an alkyne, an α-alkynylsilyl zirconacyclopentadiene was formed. Addition of dimethyl acetylenedicarboxylate (DMAD) and CuCl resulted in one-pot formation of an alkynylsilyl–benzene derivative from three different alkynes. At a higher temperature, the α-alkynylsilylzirconacyclopentadiene was transformed by means of an intramolecular skeletal rearrangement to a zirconacyclohexadiene–silacyclobutene fused-ring compound, which reacted with DMAD in the presence of CuCl affording the same alkynylsilyl–benzene derivative. When treated with a ketone, an aldehdye, or an isocyanate, the zirconocyclobutene intermediate also underwent the above-mentioned skeletal rearrangement, generating zirconocene-mediated cross-coupling products.

Keywords: cross-coupling · rearrangement · silanes · zirconium

Introduction

The chemistry of metallacyclic compounds has attracted much attention because many synthetically important transition-metal-assisted reactions proceed via metallacyclic intermediates.[1] Compared with a large number of reports on five-membered metallacycles,[2,3] there are not many reports on preparation and reaction of four- and six-membered metallacyclic intermediates.[4–8] Thus, development of synthetic methods for four- and six-membered metallacycles and investigation into their reaction chemistry and applications in organic synthesis are demanding.

Several years ago,[9] Takahashi and co-workers reported an interesting zirconocene-mediated reaction of bis(alkynyl)silanes. As illustrated in Scheme 1, treatment of bis(al-



Scheme 1. Zirconocene-mediated skeleton rearrangement of bis(alkynyl)-silanes affording four- and six-membered zirconacycles.

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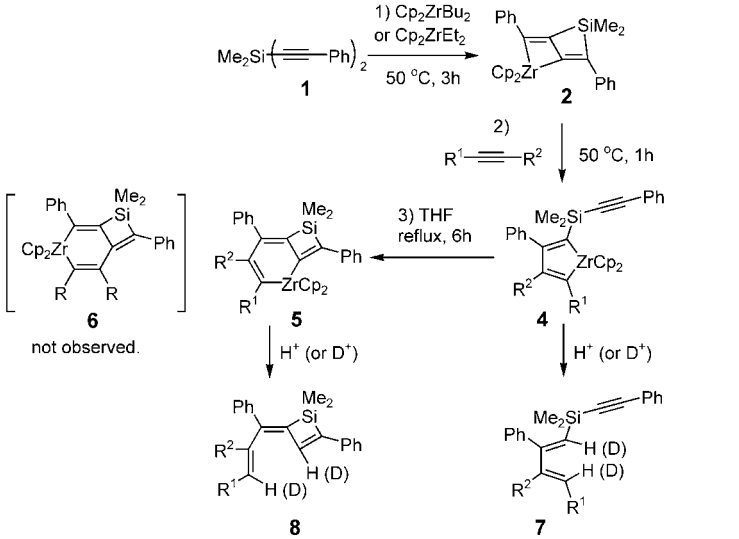
Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. Copies of ^{1}H and ^{13}C NMR spectra for new compounds and X-ray crystallography data for **14b** and **17a**.

 DOI: 10.1002/chem.200400697 © 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

kynyl)silanes **1** with low valent zirconocene species afforded four-membered zirconacyclobutene derivatives **2**, while reaction of **1** with zirconacyclopentenes **3** firstly resulted in the formation of zirconacyclopentadienes **4**, which subsequently transformed to six-membered zirconacyclohexadiene derivatives **5**. Both reactions proceeded by means of a novel intramolecular skeleton rearrangement. As we are interested in synthesis and applications of metallacycles, we have investigated the reaction chemistry of zirconacyclobutene derivatives **2**. Recently, we reported that reaction of **2** with three equivalents of organonitriles affords pyrrolo[3,2*c*]pyridine derivatives after hydrolysis.[10] Cleavage of one of the three C≡N triple bonds was observed. In this paper, we report reactions and synthetic applications of zirconacyclobutene derivatives **2** with alkynes, ketones, aldehydes, and isocyanates.[11] Novel skeletal rearrangement of **2** took place in these reactions.

Results and Discussion

Alkyne-induced skeleton rearrangement of zirconacyclobutene derivatives 2 leading to the formation of six-membered zirconacyclohexadiene derivatives 5 via five-membered zirconacyclopentadienes 4: The four-membered zirconacyclobutene derivatives **2** can be easily prepared by following Takahashi's procedure.[9] Insertion reaction of an alkyne into one of the Zr–C bonds of **2** was expected to generate the six-membered zirconacycles **5** (Scheme 2). The reaction did proceed, affording **5** highly selectively in excellent yields. Formation of isomeric products **6** was not observed. However, surprisingly, experimental results demonstrated that products **5** were not formed through the expected insertion reaction path, but through a novel cleavage of a C–C bond in the zirconacyclobutene skeleton and a C–Si bond in the silacyclobutene skeleton (Scheme 2).



Scheme 2. Reaction of alkynes with **2** by means of skeleton rearrangement.

As illustrated in Scheme 2, after addition of one equivalent of 5-decyne to a solution of **2** in THF, the reaction mixture was warmed to 50 °C and stirred at this temperature for 1 h. Hydrolysis of the reaction mixture with 3% aqueous HCl afforded **7a** in 71% isolated yield (72% GC yield), along with <3% yield of **8a**. With longer reaction times and higher temperature, the concentration of **7a** decreased while that of **8a** increased. Finally, on prolonged heating at reflux, **7a** disappeared completely and **8a** was formed as the sole product in 80% isolated yield (90% GC yield). In similar fashions, products **7b** and **8b** were obtained in high yields. Deuteriolysis of the reaction mixtures instead of hydrolysis afforded the deuterated products [D_2]-**7b** and [D_2]-**8b** in 77% and 70% isolated yields, respectively, with more than 98% of deuterium incorporation. When an unsymmetrical alkyne such as 1-phenyl-1-butyne was used, both **7c** and **8c** were formed in excellent isolated yields with perfect regioselectivity. The phenyl substituent was always located at the terminal position. Interestingly, in case of 1-trimethylsilyl-1-propyne, only compound **7d** was formed with perfect regioselectivity, and product **8d** was not be formed even after a prolonged reaction time, probably due to the bulkiness of $SiMe_3$ group.

The above results indicate that intermediate **4** is kinetically favored, whilst intermediate **5** is thermodynamically favored.

It is still not clear how the zirconacyclobutene derivative **2** undergoes skeleton rearrangement in the presence of alkynes to finally afford zirconacyclopentadienes **4**. For the formation of **5** from **4**, Takahashi and co-workers have proposed a reaction path.[9] For the formation of **4** from the reaction of an alkyne with **2**, we assume that two pathways might be considered. One is the associative path (Scheme 3, path a), the other is a disassociative path (Scheme 3, path b). In path a, coordination of the alkyne onto the zirconium atom is assumed to be critical for inducing cleavage of the C–C bond and Si–C bond in **2**.

One-pot formation of alkynylsilyl–benzene derivatives from three molecules of alkynes including one Si-tethered diyne: Transition-metal-mediated selective aromatization of alkynes has attracted much attention.[1,12] The strategy of coupling a tethered diyne with a monoyne has been successfully applied to achieve preparation of bicyclic aromatic compounds from these three triple bonds [Eq. (1) in Scheme 4].[13] In recent years, one-pot construction of benzene derivatives from three different monoynes has also been developed [Eq. (2) in Scheme 4].[14–17] In this work, we found that three triple bonds out of four [shown in Eq. (3) in Scheme 4] could be highly selectively integrated into a benzene derivative; one of the triple bonds in bis(alkynyl)si-

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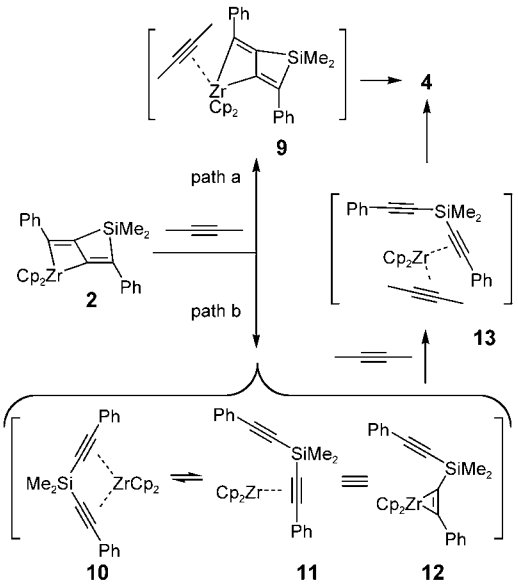
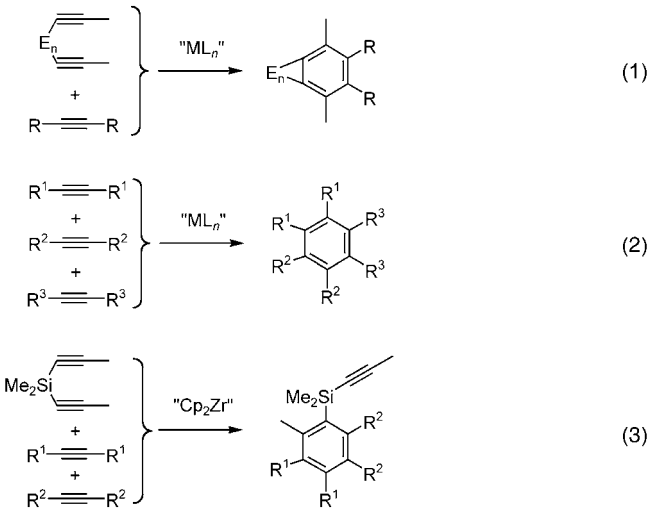
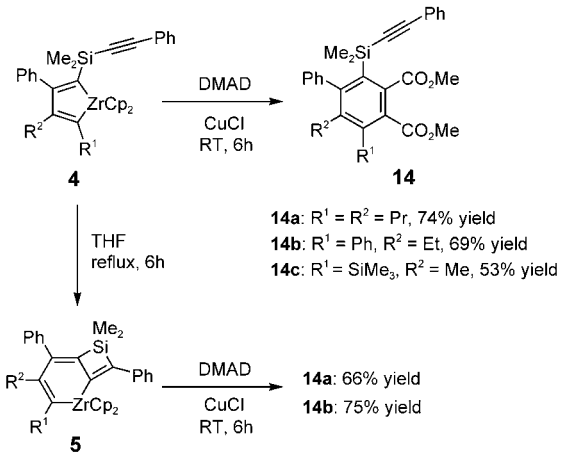


Scheme 3. Proposed reaction mechanisms from **2** to **4**.



Scheme 4. Types of one-pot aromatization of alkynes.



Scheme 5. Reactions of **4** and **5** with DMAD in the presence of CuCl.

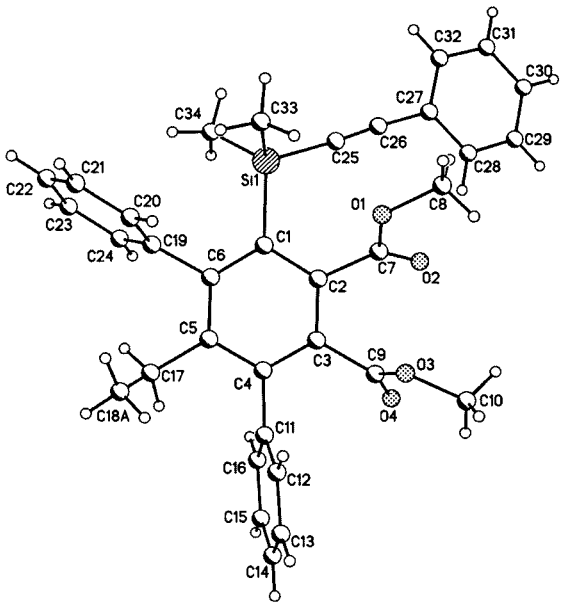


Figure 1. X-ray structure of **14b**. Selected bond lengths [Å]: C1–C2 1.425 (3), C2–C3 1.399 (3), C3–C4 1.381 (3), C4–C5 1.409 (3), C5–C6 1.409 (3), C1–C6 1.400 (3), C25–C26 1.197 (3).

lanes **1** remains unreacted as a functional group attached to the products.

Takahashi and co-workers have reported the CuCl-mediated formation of benzene derivatives from reaction of zirconacyclopentadienes with dimethyl acetylenedicarboxylate (DMAD).[2,14,16] In our work, treatment of zirconacyclopentadiene derivatives **4**, generated in situ from bis(alkynyl)silane **1** and monoalkynes via zirconacyclobutene intermediates **2**, with one equivalent of DMAD in the presence of CuCl afforded benzene derivatives **14** in high isolated yields (Scheme 5). The structure of **14b** has been determined by single-crystal X-ray structural analysis (Figure 1).[18] These benzene derivatives are formed chemo- and regioselectively from three different alkynes.

Interestingly, the in situ generated zirconacyclohexadiene–silacyclobutene fused-ring compounds **5** reacted with DMAD in the presence of CuCl to give the same alkynylsilyl–benzene derivatives **14**.

The reaction mechanism for CuCl-mediated formation of benzene derivatives from zirconacyclopentadienes and DMAD has been previously discussed in the literature.[16] However, formation of benzene derivatives **14** from the six-membered zirconacycles **5** is not clear yet. A novel skeletal rearrangement must be involved in this CuCl-mediated benzene formation reaction.

Reactions of ketones, aldehydes, and isocyanates with zirconacyclobutene derivatives 2 affording allylic alcohols and

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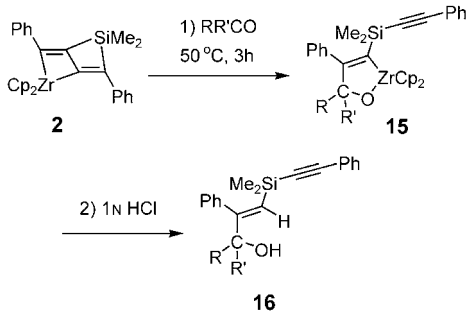
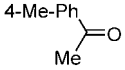
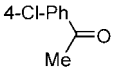
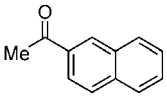
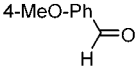
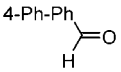
unsaturated amides: In addition to alkynes, ketones, aldehydes, and isocyanates were also found to be able to induce the novel cleavage of C–C and C–Si bond (Scheme 6). Five-membered oxazirconacyclopentenes **15**[19,20] are proposed to be formed as the organometallic intermediates, probably by similar reaction paths shown in Scheme 3. Allylic alcohols **16** were isolated in good yields after hydrolysis of the reaction mixtures (Scheme 6). The results are listed in Table 1.



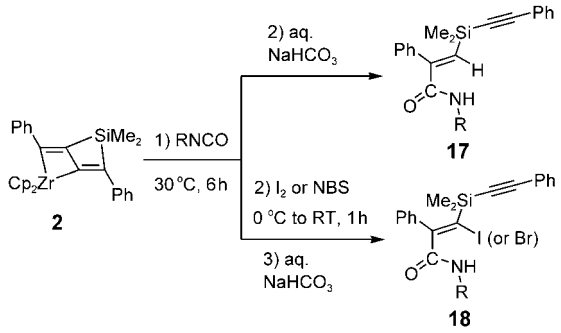
Scheme 6. Reactions of **2** with ketones and aldehydes affording alkynylsilyl-substituted allylic alcohols.

Table 1. Zirconocene-mediated intermolecular coupling of a Si-tethered diyne with a ketone or an aldehyde by means of novel skeletal rearrangement of zirconacyclobutene–silacyclobutene fused-ring intermediates affording allylic alcohols after hydrolysis.[a]

Entry	Ketone or aldehyde RR′CO	Product **16**	Yield [%][b]
1		**16a**	(75)
2		**16b**	(65)
3		**16c**	(80)
4		**16d**	86 (82)
5		**16e**	83 (63)
6		**16f**	72 (63)
7		**16g**	71 (69)
8		**16h**	81 (81)
9		**16i**	93 (79)
10		**16j**	(79)

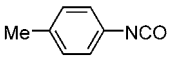
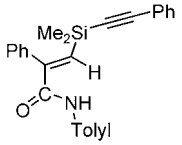
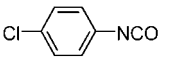
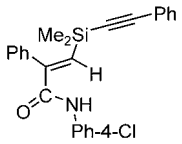
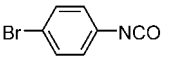
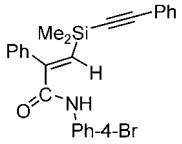
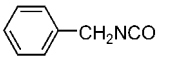
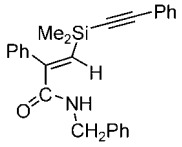
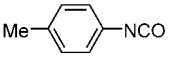
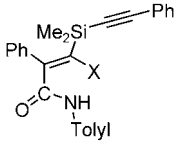
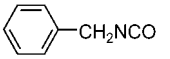
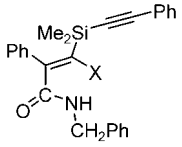
[a] Reaction conditions are given in Scheme 6. [b] GC yields. Isolated yields are given in parentheses.

When **2** was treated with isocyanates, alkynylsilyl amides were obtained in good yields upon hydrolysis or halogenation of the reaction mixtures with I_2 or NBS (Scheme 7). Table 2 shows the results obtained. The structure of **17a** has been determined by single-crystal X-ray structural analysis (Figure 2).[21] Proposed reaction intermediates are given in Scheme 8.[22]



Scheme 7. Reaction of **2** with isocyanates.

Table 2. Isolation of alkynylsilyl amides from zirconocene-mediated intermolecular coupling reaction of a Si-tethered diyne with an isocyanate.[a]

RNCO	Products **17** and **18**		Yield [%][b]
		**17a**	62
		**17b**	55
		**17c**	43
		**17d**	64
		**18a**: X = I **18b**: X = Br	53 67
		**18c**: X = I **18d**: X = Br	60 55

[a] Reaction conditions are given in Scheme 7. [b] Isolated yields.

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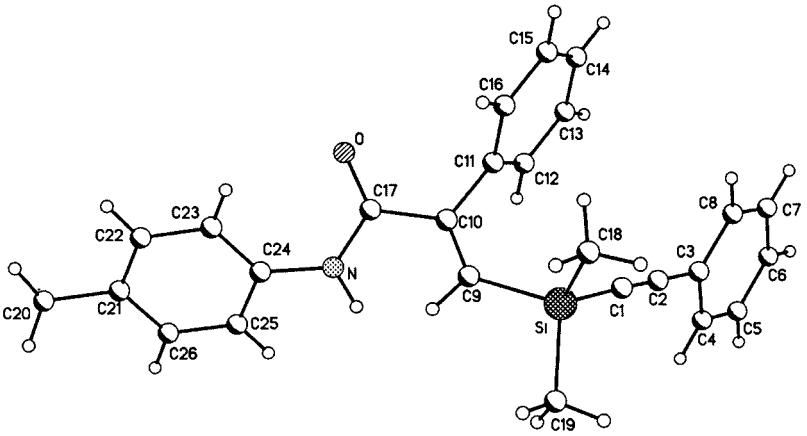
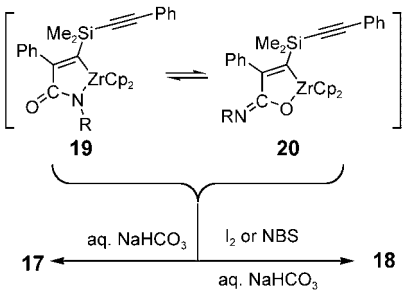


Figure 2. X-ray structure of **17a**. Selected bond lengths [Å]: C1–C2 1.186 (4), C9–C10 1.329 (3), C10–C17 1.502 (3), C17–O 1.228 (3), C17–N 1.353 (3).



Scheme 8. Proposed reaction intermediates in the reaction of **2** with isocyanates.

Conclusion

Investigation into the reaction chemistry of isolable reactive organometallic intermediates and applications of these intermediates in organic synthesis have been of great interest. In this work, we have studied on the reaction chemistry of zirconacyclobutene–silacyclobutene and zirconacyclohexadiene–silacyclobutene fused-ring compounds. Novel skeletal rearrangements, though their mechanisms are not clear yet, take place in all the reactions involving the zirconacyclobutene and zirconacyclohexadiene derivatives. Through novel skeletal rearrangement mechanisms, several synthetically useful methods have been developed, including selective cross-coupling of bis(alkynyl)silanes with monoynes, aldehydes, ketones, and isocyanates, and a new one-pot procedure for the formation of alkynylsilyl–benzene derivatives from four C≡C triple bonds.

Experimental Section

General: Unless otherwise noted, all starting materials were commercially available and were used without further purification. All reactions involving organometallic compounds were run under a slightly positive pressure of dry N_2 with use of standard Schlenk techniques. Zirconocene dichloride was obtained from Nichia Co. THF was refluxed and distilled from sodium benzophenone ketyl under a nitrogen atmosphere.

^{1}H and ^{13}C NMR spectra were recorded on a JEOL-300 MHz spectrometer. GLC analysis was performed on a gas chromatograph (Shimadzu 14B) equipped with a flame ionization detector using a capillary column (CBP1 M25–25). GLC yields were determined by using suitable hydrocarbons as internal standards.

General procedure for the reaction of compounds 2 with alkynes leading to alkynylsilyl butadienes (7a–d): *n*BuLi (2.1 mmol, 1.6 M, 1.32 mL) was added dropwise with a syringe to a solution of Cp_2ZrCl_2 (1.05 mmol, 307 mg) in THF (10 mL) at −78 °C (dry ice/acetone) in a 20 mL Schlenk tube. After the addition was complete, the reaction mixture was stirred at −78 °C for 1 h. Then 1 mmol of bis(phenylethynyl)dimethylsilane (**1**) was added, and the reaction mixture was warmed up to 50 °C and stirred at this temperature for 3 h. After an alkyne (1.0 mmol) was added, the reaction mixture was stirred at this temperature for 1 h. The reaction mixture was quenched with aqueous HCl (1 N), extracted with diethyl ether, then washed with saturated aqueous $NaHCO_3$, water, and brine. The extract was dried over anhydrous $MgSO_4$. The solvent was evaporated in vacuo to give the crude product, which was further purified by column chromatography.

Alkynylsilyl butadiene 7a: Colorless liquid, GC yield 72%, isolated yield 71% (284 mg); ^{1}H NMR ($CDCl_3$, TMS): $\delta = -0.07$ (s, 6H), 0.87 (t, $J =$ 6.9 Hz, 3H), 0.94 (t, $J = 6.9$ Hz, 3H), 1.26–1.60 (m, 8H), 2.07 (t, $J =$ 7.2 Hz, 2H), 2.32 (t, $J = 7.2$ Hz, 2H), 5.21 (t, $J = 7.5$ Hz, 1H), 5.85 (s, 1H), 7.17–7.45 ppm (m, 10H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = -0.17$, 13.95, 14.03, 22.47, 22.85, 27.39, 28.55, 31.23, 31.76, 94.47, 105.01, 122.17, 123.43, 126.98, 127.51, 128.11, 128.30, 129.77, 131.92, 134.12, 142.46, 142.85, 160.45 ppm; HRMS: *m*/*z* calcd for $C_{28}H_{36}Si$: 400.2586; found: 400.2600.

Alkynylsilyl butadiene 7b: Colorless liquid, isolated yield 75% (279 mg); ^{1}H NMR ($CDCl_3$, TMS): $\delta = -0.14$ (s, 6H), 0.77 (t, $J = 7.5$ Hz, 3H), 0.88 (t, $J = 7.2$ Hz, 3H), 1.18–1.28 (m, 2H), 1.37–1.49 (m, 2H), 1.99 (q, $J =$ 7.2 Hz, 2H), 2.24 (t, $J = 7.2$ Hz, 2H), 5.16 (t, $J = 7.5$ Hz, 1H), 5.78 (s, 1H), 7.10–7.38 ppm (m, 10H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = -0.17$, 12.89, 13.21, 21.16, 21.73, 28.68, 29.88, 93.45, 103.99, 121.19, 122.39, 125.97, 126.52, 127.10, 127.30, 128.75, 130.92, 133.19, 141.44, 141.78, 159.43 ppm; HRMS: *m*/*z* calcd for $C_{26}H_{32}Si$: 372.2273; found: 372.2266.

Alkynylsilyl butadiene [D_2]-7b: Obtained when the reaction mixture was quenched with DCl/D_2O instead of 1 N aqueous HCl. Colorless liquid, isolated yield 77% (288 mg); ^{1}H NMR ($CDCl_3$, TMS): $\delta = -0.07$ (s, 6H), 0.84 (t, $J = 7.2$ Hz, 3H), 0.95 (t, $J = 7.5$ Hz, 3H), 1.10–1.65 (m, 4H), 2.05 (t, $J = 7.5$ Hz, 2H), 2.31 (t, $J = 7.5$ Hz, 2H), 6.96–7.65 ppm (m, 10H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = -0.15$, 13.89, 14.22, 22.17, 22.72, 29.67, 30.78, 94.46, 105.03, 121.84 (t, $J = 21$ Hz), 123.43, 126.99, 127.53, 128.11, 128.30, 129.26, 131.92, 133.79 (t, $J = 21$ Hz), 142.46, 142.70, 160.40 ppm; HRMS: *m*/*z* calcd for $C_{26}H_{30}D_2Si$: 374.2402; found: 374.2399.

Alkynylsilyl butadiene 7c: Colorless liquid, GC yield 84%, isolated yield 77% (302 mg); ^{1}H NMR ($CDCl_3$, TMS): $\delta = -0.20$ (s, 6H), 1.00 (t, $J =$ 7.5 Hz, 3H), 2.35 (q, $J = 7.5$ Hz, 2H), 5.91 (s, 1H), 6.10 (s, 1H), 6.99–7.27 ppm (m, 15H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = -0.19$, 13.98, 21.29, 94.08, 105.27, 125.03, 126.60, 127.31, 127.75, 127.91, 128.08, 128.12, 128.38, 128.68, 129.78, 131.56, 131.92, 138.13, 141.93, 146.71, 159.91 ppm; HRMS: *m*/*z* calcd for $C_{28}H_{28}Si$: 392.1960; found: 392.1957.

Alkynylsilyl butadiene 7d: Colorless liquid, GC yield 81%, isolated yield 77% (288 mg); ^{1}H NMR ($CDCl_3$, TMS): $\delta = -0.07$ (s, 6H), 0.08 (s, 9H), 2.08 (s, 3H), 5.34 (s, 1H), 6.01 (s, 1H), 7.16–7.44 ppm (m, 10H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = -0.33$, −0.05, 19.77, 94.04, 105.24, 124.41, 126.36, 127.09, 127.56, 128.13, 128.38, 129.86, 131.95, 132.94, 141.85,

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153.20, 161.88 ppm; HRMS: *m*/*z* calcd for $C_{24}H_{30}Si_2$: 374.1886; found: 374.1877.

General procedure for the reaction compounds 2 with alkynes leading to alkylidene silacyclobutenes (8a–c): After an alkyne (1.0 mmol) was added to **2**, the reaction mixture was stirred at reflux for 6 h. The reaction mixture was quenched with aqueous HCl (1 N), extracted with diethyl ether, then washed with saturated aqueous $NaHCO_3$, water, and brine. The extract was dried over anhydrous $MgSO_4$. The solvent was evaporated in vacuo to give the crude product, which was further purified by column chromatography.

Alkylidene silacyclobutene 8a: Colorless liquid, GC yield 90%, isolated yield 80% (320 mg); ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.49$ (s, 6H), 0.83 (t, $J = 6.6$ Hz, 3H), 0.99 (t, $J = 6.9$ Hz, 3H), 1.26–1.52 (m, 8H), 2.12 (t, $J = 7.5$ Hz, 2H), 2.26 (t, $J = 6.9$ Hz, 2H), 5.46 (t, $J = 7.5$ Hz, 1H), 7.19–7.36 (m, 10H), 7.88 ppm (s, 1H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = -0.58$, 13.96, 14.03, 22.55, 22.61, 27.76, 29.57, 30.60, 32.26, 126.53, 126.67, 126.86, 127.34, 128.00, 128.54, 131.84, 137.66, 138.63, 142.14, 142.89, 143.36, 148.55, 156.99 ppm; HRMS: *m*/*z* calcd for $C_{28}H_{36}Si$: 400.2586; found: 400.2594.

Alkylidene silacyclobutene 8b: Colorless liquid, isolated yield 66% (246 mg); ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.42$ (s, 6H), 0.76 (t, $J = 7.2$ Hz, 3H), 0.95 (t, $J = 7.5$ Hz, 3H), 1.19–1.27 (m, 2H), 1.42–1.49 (m, 2H), 2.02 (t, $J = 6.9$ Hz, 2H), 2.17 (q, $J = 7.5$ Hz, 2H), 5.39 (t, $J = 7.2$ Hz, 1H), 7.14–7.28 (m, 10H), 7.80 ppm (s, 1H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = -1.55$, 13.09, 13.14, 20.65, 22.25, 29.23, 30.98, 125.55, 125.69, 125.87, 126.37, 127.03, 127.56, 130.90, 136.65, 137.66, 141.14, 141.95, 142.33, 147.60, 156.00 ppm; HRMS: *m*/*z* calcd for $C_{26}H_{32}Si$: 372.2273; found: 372.2275.

Alkylidene silacyclobutene [D_2]-8b: Obtained when the reaction mixture was quenched with DCl/D_2O instead of 1 N aqueous HCl. Colorless liquid, GC yield 70%, isolated yield 66% (247 mg); ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.49$ (s, 6H), 0.83 (t, $J = 7.2$ Hz, 3H), 1.03 (t, $J = 7.5$ Hz, 3H), 1.27–1.32 (m, 2H), 1.49–1.57 (m, 2H), 2.10 (t, $J = 7.5$ Hz, 2H), 2.24 (t, $J = 7.2$ Hz, 2H), 7.17–7.37 ppm (m, 10H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = -0.55$, 14.10, 14.14, 21.67, 23.25, 30.14, 31.96, 126.57, 126.71, 126.89, 127.36, 128.04, 128.57, 131.51 (t, $J = 21$ Hz), 137.67, 138.64, 142.17, 142.90, 143.30, 148.34 (t, $J = 21$ Hz), 156.92 ppm; HRMS: *m*/*z* calcd for $C_{26}H_{30}D_2Si$: 374.2399; found: 374.2397.

Alkylidene silacyclobutene 8c: Colorless liquid, isolated yield 77% (302 mg); ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.54$ (s, 6H), 1.01 (t, $J = 7.2$ Hz, 3H), 2.41 (q, $J = 7.2$ Hz, 2H), 6.53 (s, 1H), 7.21–7.43 (m, 15H), 7.95 ppm (s, 1H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = -0.51$, 12.96, 23.74, 126.51, 126.81, 126.85, 126.95, 127.60, 128.21, 128.27, 128.59, 128.85, 130.18, 137.46, 137.97, 141.68, 142.27, 143.38, 144.34, 148.13, 158.30 ppm; HRMS: *m*/*z* calcd for $C_{28}H_{28}Si$: 392.1960; found: 392.1967.

General procedure for the preparation of alkynylsilyl–benzene derivatives (14a-c) from reaction of five-membered zirconacyclopentadienes 4 or six-membered zirconacyclohexadienes 5 with DMAD in the presence of CuCl: Five-membered zirconacyclopentadienes **4** were generated in situ as described above. After the reaction mixture was cooled to 0°C, DMAD (2 mmol) and CuCl (2 mmol) were added. The reaction mixture was then warmed up to room temperature and stirred at room temperature for 6 h. The reaction mixture was quenched with aqueous HCl (1 N), extracted with diethyl ether, then washed with saturated aqueous $NaHCO_3$, water and brine. The extract was dried over anhydrous $MgSO_4$. The solvent was evaporated in vacuo to give the crude product, which was further purified by column chromatography.

Six-membered zirconacyclohexadienes **5** were generated in situ as described above. After the reaction mixture was cooled to 0°C, DMAD (2 mmol) and CuCl (2 mmol) were added. The reaction mixture was then warmed up to room temperature and stirred at room temperature for 6 h. Normal workup afforded the same alkynylsilyl–benzene derivatives **14**.

Alkynylsilyl–benzene 14a: Colorless solid, m.p. 114–116°C, isolated yield 74% (378 mg) from **4**, isolated yield 66% from **5**; ^{1}H NMR ($CDCl_3$, TMS): $\delta = -0.02$ (s, 6H), 0.68 (t, $J = 7.5$ Hz, 3H), 0.99 (t, $J = 7.5$ Hz, 3H), 1.14–1.40 (m, 2H), 1.60–1.77 (m, 2H), 2.32–2.50 (m, 2H), 2.60–2.75 (m, 2H), 3.79 (s, 3H), 3.89 (s, 3H), 7.11–7.62 ppm (m, 10H); ^{13}C NMR ($CDCl_3$): $\delta = 1.83$, 14.63, 14.92, 24.07, 24.87, 32.15, 33.43, 52.11, 52.37, 93.83, 105.24, 123.27, 127.86, 127.93, 128.12, 128.36, 130.71, 131.94, 133.27, 133.58, 136.36, 139.70, 141.66, 142.00, 150.51, 169.73, 170.11 ppm; HRMS: *m*/*z* calcd for $C_{32}H_{36}O_4Si$: 512.2383; found: 512.2367.

Alkynylsilyl–benzene 14b: Colorless solid, isolated yield 69% (367 mg) from **4**, isolated yield 75% from **5**; ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.02$ (s, 6H), 0.53 (t, $J = 7.2$ Hz, 3H), 2.29–2.36 (q, $J = 7.2$ Hz, 2H), 3.43 (s, 3H), 3.80 (s, 3H), 7.26–7.47 ppm (m, 15H); ^{13}C NMR ($CDCl_3$): $\delta = 1.74$, 14.46, 23.78, 51.98, 52.23, 93.52, 105.38, 123.10, 127.46, 127.77, 127.97, 128.02, 128.11, 128.39, 129.36, 130.74, 131.90, 134.12, 135.22, 135.69, 138.30, 140.81, 141.09, 143.10, 150.29, 169.27, 169.45 ppm; HRMS: *m*/*z* calcd for $C_{34}H_{32}O_4Si$: 532.2070; found: 532.2033.

Alkynylsilyl–benzene 14c: Colorless solid, isolated yield 53% (273 mg) from **4**; ^{1}H NMR ($CDCl_3$, TMS): $\delta = -0.04$ (s, 6H), 0.34 (s, 9H), 2.14 (s, 3H), 3.79 (s, 3H), 3.87 (s, 3H), 7.14–7.45 ppm (m, 10H); ^{13}C NMR ($CDCl_3$): $\delta = 1.71$, 1.75, 23.02, 52.19, 52.41, 93.32, 105.51, 123.15, 127.77, 128.12, 128.35, 128.39, 130.22, 131.88, 135.10, 135.55, 137.95, 138.45, 141.99, 144.45, 149.77, 169.83, 170.67 ppm; HRMS: *m*/*z* calcd for $C_{30}H_{34}O_4Si_2$: 514.1996 found 514.1963.

General procedure for the reaction of compounds 2 with ketones and aldehydes leading to alkynylsilyl allylic alcohols (16a–j): After a ketone or an aldehyde (1.0 mmol) was added to **2**, the reaction mixture was stirred at 50°C for 3 h. The reaction mixture was quenched with aqueous HCl (1 N), extracted with diethyl ether, and then washed with saturated aqueous $NaHCO_3$, water and brine. The extract was dried over anhydrous $MgSO_4$. The solvent was evaporated in vacuo to give the crude product, which was further purified by column chromatography.

Alkynylsilyl allylic alcohol 16a: Colorless liquid, isolated yield 75% (270 mg); ^{1}H NMR ($CDCl_3$, TMS): $\delta = -0.11$ (s, 6H), 1.44–1.63 (m, 4H), 1.83–2.04 (m, 4H), 2.32–2.38 (m, 2H), 5.41–5.46 (br, 1H), 6.12 (s, 1H), 7.16–7.44 ppm (m, 10H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = -0.37$, 21.86, 25.27, 36.11, 74.82, 93.91, 105.09, 121.75, 123.23, 127.08, 127.41, 128.07, 128.32, 129.85, 131.85, 140.50, 166.97 ppm; HRMS: *m*/*z* calcd for $C_{24}H_{28}OSi$: 360.1909; found: 360.1900.

Alkynylsilyl allylic alcohol 16b: Pale yellow liquid, isolated yield 65% (244 mg); ^{1}H NMR ($CDCl_3$, TMS): $\delta = -0.09$ (s, 6H), 0.73–1.13 (m, 6H), 1.23–1.89 (m, 8H), 1.96–2.00 (br, 1H), 6.02 (s, 1H), 7.14–7.66 ppm (m, 10H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = -0.32$, 14.33,16.76, 41.49, 78.90, 93.94, 105.09, 123.26, 123.75, 127.18, 127.57, 128.06, 128.29, 129.15, 131.81, 140.68, 163.83 ppm; HRMS: *m*/*z* calcd for $C_{25}H_{32}OSi$: 376.2222; found: 376.2217.

Alkynylsilyl allylic alcohol 16c: Yellow liquid, isolated yield 80% (306 mg); ^{1}H NMR ($CDCl_3$, TMS): $\delta = -0.09$ (s, 6H), 1.69 (s, 3H), 2.20–2.26 (br, 1H), 6.27 (s, 1H), 6.29–6.49 ppm (m, 15H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = -0.42$, −0.38, 28.47, 77.95, 93.66, 105.31, 122.77, 123.10, 125.80, 126.85, 127.23, 127.25, 127.84, 128.03, 128.31, 129.77, 131.78, 139.55, 145.33, 164.32 ppm.

Alkynylsilyl allylic alcohol 16d: Yellow liquid, GC yield 86%, isolated yield 82% (325 mg); ^{1}H NMR ($CDCl_3$, TMS): $\delta = -0.03$ (s, 6H), 1.01 (t, $J = 7.2$ Hz, 3H), 1.90–1.96 (br, 1H), 2.16 (q, $J = 7.2$ Hz, 2H), 6.31 (s, 1H), 6.72–7.44 ppm (m, 15H); ^{13}C NMR ($CDCl_3$): $\delta = -0.40$, −0.32, 7.96, 32.22, 80.28, 93.76, 105.31, 123.20, 123.52, 126.32, 126.81, 127.37, 127.41, 127.86, 128.14, 128.43, 129.83, 131.91, 139.59, 144.40, 163.32 ppm; HRMS: *m*/*z* calcd for $C_{27}H_{28}OSi$: 396.1909; found: 396.1909.

Alkynylsilyl allylic alcohol 16e: Yellow liquid, GC yield 83%, isolated yield 63% (250 mg); ^{1}H NMR ($CDCl_3$, TMS): $\delta = -0.10$ (s, 3H), −0.08 (s, 3H), 1.70 (s, 3H), 1.96–2.00 (br, 1H), 2.35 (s, 3H), 6.24 (s, 1H), 6.80–7.44 ppm (m, 14H); ^{13}C NMR ($CDCl_3$): $\delta = -0.38$, −0.33, 21.04, 28.70, 78.03, 93.77, 105.30, 122.82, 125.78, 127.38, 128.14, 128.49, 128.72, 129.90, 131.93, 136.60, 139.68, 142.54, 164.43 ppm; HRMS: *m*/*z* calcd for $C_{27}H_{28}OSi$: 396.1909; found: 396.1897.

Alkynylsilyl allylic alcohol 16f: Colorless liquid, GC yield 72%, isolated yield 63% (262 mg); ^{1}H NMR ($CDCl_3$, TMS): $\delta = -0.10$ (s, 3H), −0.07 (s, 3H), 1.70 (s, 3H), 2.00–2.04 (br, 1H), 6.23 (s, 1H), 6.78–7.44 ppm (m, 14H); ^{13}C NMR ($CDCl_3$): $\delta = -0.45$, −0.37, 28.80, 77.84, 93.46, 105.48, 123.09, 123.62, 127.39, 127.54, 127.59, 128.08, 128.16, 128.49, 129.85, 131.90, 132.79, 139.17, 144.15, 163.74 ppm.

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Alkynylsilyl allylic alcohol 16g: Yellow liquid, GC yield 71%, isolated yield 69% (298 mg); ^{1}H NMR ($CDCl_3$, TMS): $\delta = -0.08$ (s, 3H), -0.05 (s, 3H), 1.81 (s, 3H), 1.96–2.04 (br, 1H), 6.32 (s, 1H), 6.80–7.83 ppm (m, 17H); ^{13}C NMR ($CDCl_3$): $\delta = -0.39$, -0.32, 28.76, 78.34, 93.66, 105.44, 123.16, 123.77, 124.22, 124.66, 125.84, 125.96, 127.45, 127.73, 128.13, 128.25, 128.44, 129.85, 131.91, 132.47, 132.98, 139.44, 142.88, 163.95 ppm; HRMS: *m*/*z* calcd for $C_{30}H_{28}OSi$: 432.1909; found: 432.1900.

Alkynylsilyl allylic alcohol 16h: Yellow liquid, GC yield 81%, isolated yield 81% (298 mg); ^{1}H NMR ($CDCl_3$, TMS): $\delta = -0.01$ (s, 6H), 2.16 (br, 1H), 5.42 (s, 1H), 6.23 (s, 1H), 6.99–7.43 ppm (m, 15H); ^{13}C NMR ($CDCl_3$): $\delta = -0.26$, -0.15, 79.48, 93.63, 105.52, 123.16, 127.01, 127.54, 127.69, 127.71, 128.12, 128.28, 128.44, 129.11, 131.93, 140.02, 141.22, 161.17 ppm; HRMS: *m*/*z* calcd for $C_{25}H_{24}OSi$: 368.1596; found: 368.1600.

Alkynylsilyl allylic alcohol 16i: Colorless liquid, GC yield 93%, isolated yield 79% (315 mg); ^{1}H NMR ($CDCl_3$, TMS): $\delta = -0.01$ (s, 6H), 2.08 (br, 1H), 3.77 (s, 3H), 5.37 (s, 1H), 6.21 (s, 1H), 6.78–7.43 ppm (m, 14H); ^{13}C NMR ($CDCl_3$): $\delta = -0.22$, -0.13, 55.20, 78.98, 93.74, 105.51, 113.73, 122.69, 123.21, 127.49, 127.69, 128.14, 128.36, 128.44, 129.10, 131.95, 133.43, 140.27, 159.20, 161.43 ppm; HRMS: *m*/*z* calcd for $C_{26}H_{26}O_2Si$: 398.1702; found: 398.1709.

Alkynylsilyl allylic alcohol 16j: Yellow liquid, isolated yield 79% (351 mg); ^{1}H NMR ($CDCl_3$, TMS): $\delta = -0.02$ (s, 3H), -0.03 (s, 3H), 5.27(s, 1H), 5.59 (br, 1H), 6.09 (s, 1H), 6.86–7.45 ppm (m, 19H); ^{13}C NMR ($CDCl_3$): $\delta = -0.25$, -0.14, 0.56, 0.64, 78.16, 79.10, 93.44, 93.64, 105.53, 107.21, 123.13, 126.88, 126.92, 126.98, 127.19, 127.40, 127.52, 127.67, 127.91, 127.95, 128.09, 128.15, 128.40, 128.62, 128.66, 128.83, 129.08, 131.81, 131.87, 139.19, 140.00, 140.22, 140.28, 140.33, 140.59, 140.72, 141.76, 142.78, 143.08, 166.11 ppm; HRMS: *m*/*z* calcd for $C_{31}H_{28}OSi$: 444.1909; found: 444.1892.

General procedure for the reaction of compounds 2 with isocyanates leading to alkynylsilyl amides (17a–d, 18a–d): After an isocyanate (1.0 mmol) was added to **2**, the reaction mixture was stirred at 30°C for 6 h. Quench of the reaction mixture with aqueous HCl (1N) followed by normal workup afforded products **17**; treatment of the reaction mixture with I_2 (1 mmol) or NBS (1 mmol) followed by normal workup afforded halogenated products **18**.

Alkynylsilyl amide 17a: Colorless solid, isolated yield 62% (245 mg); ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.06$ (s, 6H), 2.26 (s, 3H), 7.04–7.41 ppm (m, 16H); ^{13}C NMR ($CDCl_3$): $\delta = -0.88$, 20.76, 91.87, 106.32, 119.80, 122.76, 128.08, 128.57, 128.72, 128.82, 129.30, 129.63, 131.85, 134.07, 135.07, 137.20, 137.93, 151.01, 163.72 ppm; HRMS: *m*/*z* calcd for $C_{26}H_{25}NOSi$: 395.1705; found: 395.1671.

Alkynylsilyl amide 17b: Yellow liquid, isolated yield 55% (228 mg); ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.06$ (s, 6H), 7.22–7.45 ppm (m, 16H); ^{13}C NMR ($CDCl_3$): $\delta = -0.85$, 91.73, 106.49, 121.07, 122.79, 128.17, 128.69, 128.92, 128.94, 129.07, 129.50, 129.71, 131.94, 136.26, 136.99, 138.96, 150.54, 163.86 ppm; HRMS: *m*/*z* calcd for $C_{25}H_{22}ClNOSi$: 415.1159; found: 415.1171.

Alkynylsilyl amide 17c: Yellow liquid, isolated yield 43% (197 mg); ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.06$ (s, 6H), 7.29–7.45 ppm (m, 16H); ^{13}C NMR ($CDCl_3$): $\delta = -0.86$, 91.71, 106.49, 117.12, 121.37, 122.77, 128.16, 128.69, 128.93, 129.07, 129.70, 131.86, 131.93, 136.74, 136.94, 139.00, 150.52, 163.85 ppm; HRMS: *m*/*z* calcd for $C_{25}H_{22}BrNOSi$: 459.0654; found: 459.0640.

Alkynylsilyl amide 17d: Yellow liquid, isolated yield 64% (253 mg); ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.03$ (s, 6H), 4.49 (d, $J = 5.7$ Hz, 2H), 7.21–7.39 ppm (m, 17H); ^{13}C NMR ($CDCl_3$): $\delta = -0.83$, 44.05, 92.04, 106.24, 122.87, 127.36, 127.41, 128.15, 128.63, 129.61, 131.94, 137.49, 137.58, 138.10, 150.47, 166.04 ppm; HRMS: *m*/*z* calcd for $C_{26}H_{25}NOSi$: 395.1705; found: 395.1690.

Alkynylsilyl amide 18a: Colorless solid, isolated yield 53% (276 mg); ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.22$ (s, 6H), 2.30 (s, 3H), 7.11–7.48 ppm (m, 15H); ^{13}C NMR ($CDCl_3$): $\delta = 1.05$, 20.87, 91.34, 106.04, 107.54, 120.25, 122.57, 128.14, 128.51, 128.85, 129.24, 129.51, 131.97, 134.51, 134.54, 137.47, 158.76, 167.88 ppm; HRMS: *m*/*z* calcd for $C_{26}H_{24}INOSi$: 521.0672; found: 521.0666.

Alkynylsilyl amide 18b: Colorless solid, isolated yield 67% (317 mg); ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.23$ (s, 6H), 2.30 (s, 3H), 7.13–7.50 ppm (m, 15H); ^{13}C NMR ($CDCl_3$): $\delta = 0.19$, 20.87, 90.56, 107.45, 120.17, 122.47, 125.61, 128.16, 128.52, 128.82, 128.91, 129.28, 129.51, 132.04, 134.47, 134.63, 136.46, 152.96, 166.06 ppm; HRMS: *m*/*z* calcd for $C_{26}H_{24}BrNOSi$: 473.0811; found: 473.0788.

Alkynylsilyl amide 18c: Yellow liquid, isolated yield 60% (313 mg); ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.18$ (s, 6H), 4.52 (d, $J = 5.7$ Hz, 2H), 7.26–7.41 ppm (m, 16H); ^{13}C NMR ($CDCl_3$): $\delta = -0.83$, 43.82, 91.36, 105.60, 107.43, 122.63, 127.64, 128.09, 128.28, 128.38, 128.45, 128.63, 129.10, 131.95, 137.34, 137.58, 137.71, 158.86, 170.03 ppm; HRMS: *m*/*z* calcd for $C_{26}H_{24}INOSi$: 521.0672; found: 521.0666.

Alkynylsilyl amide 18d: Yellow liquid, isolated yield 55% (260 mg); ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.19$ (s, 6H), 4.52 (d, $J = 5.7$ Hz, 2H), 7.26–7.44 ppm (m, 16H); ^{13}C NMR ($CDCl_3$): $\delta = 0.17$, 43.78, 90.59, 107.34, 122.52, 125.21, 127.64, 128.11, 128.16, 128.47, 128.67, 128.70, 128.85, 129.16, 132.03, 136.71, 137.49, 153.03, 168.23 ppm.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (20172003, 20232010, 20328201), the Major State Basic Research Development Program (G2000077502-D), and Dow Corning Corporation. Cheung Kong Scholars Program, Qiu Shi Science & Technologies Foundation, and BASF are gratefully acknowledged.

[1] a) N. E. Schore, *Chem. Rev.* **1988**, *88*, 1081–1119; b) M. Lautens, W. Klute, W. Tam, *Chem. Rev.* **1996**, *96*, 49–92; c) I. Ojima, M. Tzamarioudaki, Z. Li, R. J. Donovan, *Chem. Rev.* **1996**, *96*, 635–662; d) H.-W. Fruhauf, *Chem. Rev.* **1997**, *97*, 523–596; e) R. H. Grubbs, S. Chang, *Tetrahedron* **1998**, *54*, 4413–4450.

[2] a) T. Takahashi, Z. Xi, R. Hara, *Trends Organomet. Chem.* **1997**, *2*, 117–133; b) M. Kotora, Z. Xi, T. Takahashi, *J. Synth. Org. Chem. Jpn.* **1997**, *55*, 958–969; c) T. Takahashi, M. Kotora, R. Hara, Z. Xi, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2591–2602.

[3] a) E. Negishi, *Acc. Chem. Res.* **1987**, *20*, 65–72; b) S. L. Buchwald, R. B. Nielsen, *Chem. Rev.* **1988**, *88*, 1047–1058; c) E. Negishi, T. Takahashi, *Acc. Chem. Res.* **1994**, *27*, 124–130.

[4] a) A. Ohff, S. Pulst, C. Lefeber, N. Peulecke, P. Arndt, V. V. Burkalov, U. Rosenthal, *Synlett* **1996**, 111–118; b) T. L. Breen, D. W. Stephan, *J. Am. Chem. Soc.* **1996**, *118*, 4204–4205; c) T. L. Breen, D. W. Stephan, *Organometallics* **1996**, *15*, 5729–5737; d) U. Rosenthal, P. M. Pellny, F. G. Kirchbauer, V. V. Burlakov, *Acc. Chem. Res.* **2000**, *33*, 119–129; e) D. W. Stephan, *Angew. Chem.* **2000**, *112*, 322–338; *Angew. Chem. Int. Ed.* **2000**, *39*, 314–329 and references therein; f) S. A. Blum, K. L. Tan, R. G. Bergman, *J. Org. Chem.* **2003**, *68*, 4127–4137 and references therein.

[5] a) H. Yamazaki, K. Aoki, *J. Organomet. Chem.* **1976**, *122*, C54-C58; b) R. H. Grubbs, A. Miyashita, *J. Am. Chem. Soc.* **1978**, *100*, 7418–7420; c) N. A. Grabowski, R. P. Hughes, B. S. Jaynes, A. L. Rheingold, *J. Chem. Soc. Chem. Commun.* **1986**, 1694–1695; d) J. R. Bleeke, W. Peng, *Organometallics* **1987**, *6*, 1576–1578; e) C. A. Mike, T. Nelson, J. Graham, A. W. Cordes, N. T. Allison, *Organometallics* **1988**, *7*, 2573–2575; f) N. W. Alcock, K. H. Bryars, P. G. Pringle, *J. Chem. Soc. Dalton Trans.* **1990**, 1433–1439; g) J. R. Bleeke, T. Haile, P. R. New, M. Y. Chiang, *Organometallics* **1993**, *12*, 517–528.

[6] a) J. M. Davis, R. J. Whitby, A. Jaxa-Chamiec, *Tetrahedron Lett.* **1992**, *33*, 5655–5658; b) J. M. Davis, R. J. Whitby, A. Jaxa-Chamiec, *Synlett* **1994**, 110–112; c) J. M. Davis, R. J. Whitby, A. Jaxa-Chamiec, *Tetrahedron Lett.* **1994**, *35*, 1445–1448; d) G. D. Probert, R. J. Whitby, S. J. Coote, *Tetrahedron Lett.* **1995**, *36*, 4113–4116; e) S. F. Fillery, G. J. Gordon, T. Licker, R. J. Whitby, *Pure. Appl. Chem.* **1997**, *69*, 633–638; f) N. Vicart, R. J. Whitby, *Chem. Commun.* **1999**, 1241–1242; g) A. N. Kasatkin, R. J. Whitby, *J. Am. Chem. Soc.* **1999**, *121*, 7039–7049; h) Z. Xi, S. Huo, Y. Noguchi, T. Takahashi, *Chem.*

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Lett. **2000**, 218–219; i) S. Dixon, S. M. Fillery, A. Kasatkin, D. Norton, E. Thomas, R. J. Whitby, *Tetrahedron* **2004**, *60*, 1401–1416 and references therein.

[7] a) J. Campora, S. L. Buchwald, *Organometallics* **1995**, *14*, 2039–2046; b) J. E. Hill, G. P. Balaich, E. I. Fannick, R. Rothwell, *Organometallics* **1993**, *12*, 2911–2924; c) K. Aoyagi, K. Kasai, D. Kondakov, R. Hara, N. Suzuki, T. Takahashi, *Inorg. Chim. Acta* **1994**, *220*, 319–326.

[8] a) L. Dupuis, N. Pirio, P. Meunier, A. Igau, B. Donnadieu, J. P. Majoral, *Angew. Chem.* **1997**, *109*, 1015–1017; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 987–989; b) N. Pirio, S. Bredeau, L. Dupuis, P. Schutz, B. Donnadieu, A. Igau, J. P. Majoral, J. C. Guillemin, P. Meunier, *Tetrahedron* **2004**, *60*, 1317–1327; see also: c) A. Gudima, A. Igau, B. Donnadieu, J. P. Majoral, *J. Org. Chem.* **1996**, *61*, 9585–9587; d) V. Cadierno, M. Zablocka, B. Donnadieu, A. Igau, J. P. Majoral, A. Skowronska, *Chem. Eur. J.* **2000**, *6*, 345–352.

[9] a) T. Takahashi, Z. Xi, Y. Obora, N. Suzuki, *J. Am. Chem. Soc.* **1995**, *117*, 2665–2666; b) Z. Xi, R. Fischer, R. Hara, W. Sun, Y. Obora, N. Suzuki, K. Nakajima, T. Takahashi, *J. Am. Chem. Soc.* **1997**, *119*, 12842–12848; see also ref .[8]

[10] X. Sun, C. Wang, Z. Li, S. Zhang, Z. Xi, *J. Am. Chem. Soc.* **2004**, *126*, 7172–7173.

[11] Preliminary results have been reported. T. Yu, L. Deng, C. Zhao, Z. Li, Z. Xi, *Tetrahedron Lett.* **2003**, *44*, 677–679.

[12] a) N. E. Schore, *Comprehensive Organic Synthesis*, *Vol. 5* (Eds.: B. M. Trost, I. Fleming, L. A. Paquette), Pergmon, Tokyo, **1991**, p. 1144; b) D. B. Grotjahn, *Comprehensive Organometallic Chemistry II*, *Vol. 12* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford, **1995**, p. 747; c) S. Saito, Y. Yamamoto, *Chem. Rev.* **2000**, *100*, 2901–2915.

[13] a) K. P. C. Vollhardt, *Acc. Chem. Res.* **1977**, *10*, 1–8; b) K. P. C. Vollhardt, *Angew. Chem.* **1984**, *96*, 525–541; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 539–556; c) E. Negishi, L. S. Harring, Z. Owczarczyk, M. M. Mohamud, M. Ay, *Tetrahedron Lett.* **1992**, *33*, 3253–3256; d) Y. Yamamoto, A. Nagata, K. Itoh, *Tetrahedron Lett.* **1999**, *40*, 5035–5038; e) B. Witulski, T. Stengel, *Angew. Chem.* **1999**, *111*, 2521–2524; *Angew. Chem. Int. Ed.* **1999**, *38*, 2426–2430; f) Y. Yamamoto, R. Ogawa, K. Itoh, *Chem. Commun.* **2000**, 549–550; g) S. Kotha, K. Mohanraja, S. Durani, *Chem. Commun.* **2000**, 1909–1910; h) A. Jeevandam, R. P. Korivi, I. W. Huang, C. H. Cheng, *Org. Lett.* **2002**, *4*, 807–810.

[14] T. Takahashi, *Pure Appl. Chem.* **2001**, *73*, 271–274.

[15] M. Rubin, A. W. Sromek, V. Gevorgyan, *Synlett* **2003**, 2265–2291.

[16] a) T. Takahashi, M. Kotora, Z. Xi, *J. Chem. Soc. Chem. Commun.* **1995**, 361–362; b) T. Takahashi, Z. Xi, A. Yamazaki, Y. Liu, K. Nakajima, M. Kotora, *J. Am. Chem. Soc.* **1998**, *120*, 1672–1680; c) T. Takahashi, F. Tsai, Y. Li, K. Nakajima, M. Kotora, *J. Am. Chem. Soc.* **1999**, *121*, 11093–11100; d) T. Takahashi, F. Tsai, M. Kotora, *J. Am. Chem. Soc.* **2000**, *122*, 4994–4995; e) Z. Xi, T. Takahashi, *Acta Chim. Sin.* **2000**, *58*, 1177–1185.

[17] a) V. Gevorgyan, U. Radhakrishnan, A. Takeda, M. Rubina, M. Rubin, Y. Yamamoto, *J. Org. Chem.* **2001**, *66*, 2835–2841; b) N. Mori, S. Ikeda, K. Odashima, *Chem. Commun.* **2001**, 181–182; c) D. Suzuki, H. Urabe, F. Sato, *J. Am. Chem. Soc.* **2001**, *123*, 7925–7926; d) G. Chouraqui, M. Petit, C. Aubert, M. Malacria, *Org. Lett.* **2004**, *6*, 1519–1521; e) Y. Yamamoto, J. I. Ishii, H. Nishiyama, K. Itoh, *J. Am. Chem. Soc.* **2004**, *126*, 3712–3713; f) B. Traber, J. J. Wolff, F. Rominger, T. Oeser, R. Gleiter, M. Goebel, R. Wortmann, *Chem. Eur. J.* **2004**, *10*, 1227–1238; g) Y. R. Dumond, E. Negishi, *Tetrahedron* **2004**, *60*, 1345–1352.

[18] CCDC-242239 contains the supplementary crystallographic data for **14b**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[19] a) C. Coperet, E. Negishi, Z. Xi, T. Takahashi, *Tetrahedron Lett.* **1994**, *35*, 695–698; b) T. Takahashi, C. Xi, Z. Xi, M. Kageyama, R. Fischer, K. Nakajima, E. Negishi, *J. Org. Chem.* **1998**, *63*, 6802–6806; c) P. Li, Z. Xi, T. Takahashi, *Chin. J. Chem.* **2001**, *19*, 62–68.

[20] a) C. Zhao, T. Yu, Z. Xi, *Chem. Commun.* **2002**, 142–143; b) C. Zhao, J. Yan, Z. Xi, *J. Org. Chem.* **2003**, *68*, 4355–4360.

[21] CCDC-242240 contains the supplementary crystallographic data for **17a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[22] a) T. Takahashi, Y. Li, F. Y. Tsai, K. Nakajima, *Organometallics* **2001**, *20*, 595–597; b) Y. Li, H. Matsumura, M. Yamanaka, T. Takahashi, *Tetrahedron* **2004**, *60*, 1393–1400.

Received: July 8, 2004
Revised: October 2, 2004
Published online: January 26, 2005

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