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Synthesis of Multiply Substituted Alkylidene Silacyclohexadiene Derivatives via Palladium-Catalyzed Insertion of Alkynes into Alkylidene Silacyclobutenes

Junhui Liu,[†] Xiaohua Sun,[‡] Mikihiro Miyazaki,[||] Lantao Liu,[‡]
Congyang Wang,[†] and Zhenfeng Xi*[,†,§]

*Beijing National Laboratory for Molecular Sciences (BNLMS),
Key Laboratory of Bioorganic Chemistry and Molecular
Engineering of Ministry of Education, College of Chemistry,
Peking University, Beijing 100871, China,
Institute of Chemistry, Chinese Academy of Sciences,
Beijing 100080, China, and State Key Laboratory of
Organometallic Chemistry, Shanghai Institute of
Organic Chemistry, Chinese Academy of Sciences,
Shanghai 200032, China*

zfxi@pku.edu.cn

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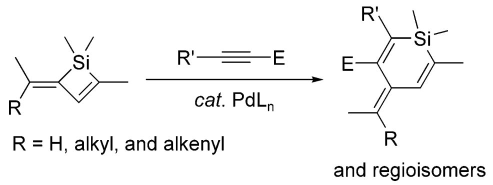

Palladium-catalyzed insertion of activated alkynes into silacyclobutene derivatives proceeded smoothly to afford *exo*-alkylidenesilacyclohexadiene derivatives of unique structure with diversified conjugation systems in high isolated yields. Interesting regioselectivity of insertion, which afforded only one regioisomer or a mixture of two or more regioisomers, was also observed.

Development of synthetically useful methods for preparation of various functionalized sila-heterocycles has become ever more attractive.[1−5] These types of compounds have continuously been the subject of extensive studies, with recent focus on their practical applications, including as new π-system organic materials of electronic and optoelectronic devices.[1] However, most of the related work has been focused on the synthesis, reaction, and property of silacyclopentadienes (siloles).[1−3] Although interesting and useful chemical and physical properties can be expected from other silacycles,[4−13] such as silacyclobutenes,[5−9] and silacyclohexadienes,[9−12] research on these types of silacycles has been relatively rare.[9,11,12] One of the main reasons is the lack of general synthetic methods for the preparation of these silacycles with a variety of functional groups and structures.

[†] Peking University.

[‡] Institute of Chemistry.

[§] State Key Laboratory of Organometallic Chemistry.

[||] Visiting research student from Okayama University, Japan (2006).

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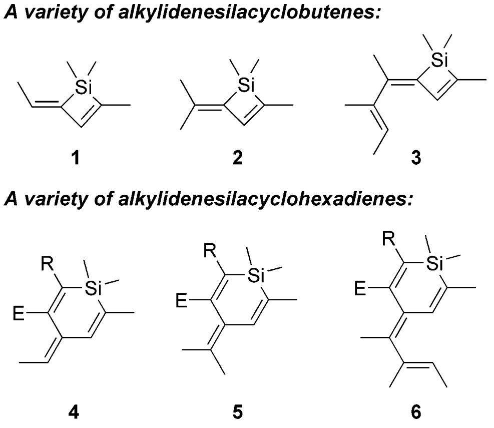
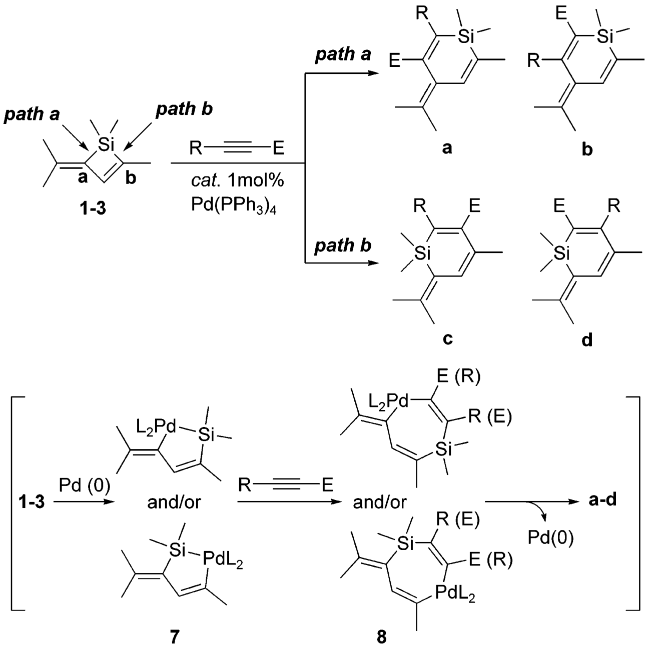


FIGURE 1. Expected silacyclohexadienes **4**−**6** from silacyclobutenes **1**−**3**.

In recent years, a variety of silacyclobutenes (**1**−**3**) have become readily available from the zirconocene- or titanocene-mediated novel skeletal rearrangement of bis(alkynyl)silanes.[6,7] As our continuous interest in the preparation and reaction of four- and six-membered silacycles,[3e,6a−c] we envisioned that six-membered silacycles, silacyclohexadiene derivatives **4**−**6**, might be prepared from the readily available silacyclobutenes **1**−**3** via transition metal catalyzed or mediated insertion reaction of alkynes (Figure 1). These types of alkylidenesilacyclohexadiene derivatives (**4**−**6**) are particularly interesting because of their diversified π-conjugated systems. To the best of our knowledge, the only precedented example was transformation of four-membered silacyclobutanes to their corresponding six-membered silacyclohexenes employing the Pd-catalyzed insertion of alkynes.[9] In this paper, we report the first example of preparation of six-membered silacyclohexadiene derivatives **4**−**6** from Pd-catalyzed alkyne insertion into the four-membered silacyclobutenes **1**−**3**.

Although the silacyclobutene ring in **1**−**3** has a relatively higher ring tension than that of a silacyclobutane,[2e,6e,14] it shows surprisingly high thermal and kinetic stability toward heating and low-valent transition metals, probably due to the conjugation of the *exo*-alkylidene moiety. Thus, after screening of transition metal catalysts and reaction conditions, we found that 1 mol % of $Pd(PPh_3)_4$ could effectively catalyze the insertion of activated alkynes at reflux of toluene (Scheme 1). $PdCl_2(PPh_3)_2$ (1 mol %) could also catalyze the insertion of DMAD at reflux of toluene, but with a longer reaction time (3 h); with $Pd(PPh_3)_4$ the above reaction completed within 1 h. Other palladium complexes such as $Pd_2(dba)_3$, $(PhCN)_2PdCl_2$, and $(CH_3CN)_2PdCl_2$ were much less effective as catalysts for the above-mentioned reaction, affording the product in 10−20% yields. No reaction proceeded when $(PPh_3)_2NiCl_2$ was used as the catalyst. The two Si−C bonds (Si−C_a and Si−C_b) in **1**−**3**, as demonstrated by their X-ray single-crystal structural analysis, have similar lengths, with the length of allylic Si−C_a slightly longer than that of vinyl Si−C_b.[6e−g] Similar to the reaction mechanism proposed by Oshima[9b] and others[10] for the Pd-catalyzed insertion of alkynes into silacyclobutanes,[9b,10] we assumed that oxidative insertion of Pd(0) into either the Si−C_a bond or the Si−C_b bond of silacyclobutenes **1**−**3** must be the first step for this catalytic cycle. Thus the in situ generated five-membered cyclic intermediates **7** react with alkynes via silyl palladation to provide seven-membered intermediates **8**, which undergo reductive elimination of Pd(0) to afford the final silacyclohexadiene derivatives **a**−**d** (Scheme 1).[9b] As illustrated in Scheme 1, two regioisomers of products can be expected from the insertion reaction (via both path a and path b) of symmetrical alkynes. For unsymmetrical alkynes, up to four isomers can be expected. Interestingly, regioselectivity of insertion was obtained for the formation of silacyclohexadienes. Only one isomer was obtained in several cases. In some cases the insertion reaction proceeded smoothly and completed within 1 h, whereas a longer reaction time was required in other cases, depending on the nature of the substrates used.[9]

SCHEME 1. Insertion Paths of Alkynes into Silacyclobutenes



Listed in Table 1 are representative results of silacyclohexadienes **4** obtained from the reaction of silacyclobutenes of type **1** and activated alkynes catalyzed by 1 mol % of $Pd(PPh_3)_4$ in reflux of toluene. The reactions generally afforded silacyclohexadiene derivatives **4** in good to excellent isolated yields. When DMAD was used, the reaction of **1a** and **1b** afforded a mixture of two products of type **a** (via path a) and type **c** (via path b), with the isomer of type **a** (via path a) as the major product, which is consistent with the allylic character of the Si−C_a bond. In the cases of $HC\equiv CCO_2Me$ and $HC\equiv CCOPh$, surprisingly only one isomer was obtained in excellent isolated yields from both **1a** and **1b**. Unsymmetrical alkynes $MeC\equiv CCO_2Me$ and $PhC\equiv CCO_2Me$ could be also applied in this insertion reaction, but these reactions were very slow and afforded relatively less selective results. Three products were obtained in the case of $PhC\equiv CCO_2Me$ and they could not be properly assigned.

Although the mixture of products, such as **4aa** and **4ac**, could not be separated completely, some amount of pure isomer could be obtained. Thus, a small amount of pure **4aa** was separated and recrystallized. Its structure was determined by single-crystal X-ray structural analysis (CCDC 630403; see Supporting Information). Structures of **4da** and **6da** were further confirmed by their corresponding satellite peaks due to ^{29}Si.

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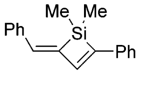
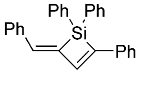
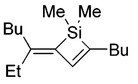
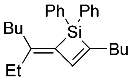
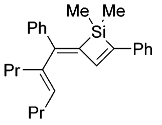
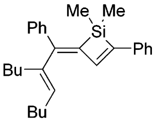
TABLE 1. Pd-Catalyzed Insertion of Alkynes into Silacycbutenes 1 Affording Silacyclohexadienes 4

silacyclobutene **1**	alkyne	t (h)	product **4**/%[a]	
 **1a**	$MeO_2C{-}{\equiv}{-}CO_2Me$	1	**4aa+4ac**	96 (3:1)[b]
 **1b**	$MeO_2C{-}{\equiv}{-}CO_2Me$	1	**4ba+4bc**	82 (10:1)[b]
1a	$EtO_2C{-}{\equiv}{-}CO_2Et$	1	**4ca+4cc**	95 (6:1)[b]
1a	$H{-}{\equiv}{-}CO_2Me$	3	**4da**	91[c]
1b	$H{-}{\equiv}{-}CO_2Me$	3	**4ea**	89[c]
1a	$H{-}{\equiv}{-}COPh$	3	**4fa**	70[c]
1a	$Me{-}{\equiv}{-}CO_2Me$	24	**4ga+4gc**	80 (7:1)[b]
1a	$Ph{-}{\equiv}{-}CO_2Me$	40	**4ha**	72 (2:1:1)[d]

[a] Isolated yields. Ratio was determined by ^1H NMR. [b] Combined isolated yield. These two products could not be completely separated. [c] Only one isomer. [d] Three isomers were obtained. They could not be assigned.

TABLE 2. Formation of Silacyclohexadienes 5 and 6 from Alkyne Insertion into Silacycbutenes 2 and 3 Catalyzed by Pd

silacyclobutene **2,3**	alkyne	t (h)	product **5,6**/%[a]	
 **2a**	$MeO_2C{-}{\equiv}{-}CO_2Me$	1	**5aa+5ac**	87 (10:1)[b]
 **2b**	$MeO_2C{-}{\equiv}{-}CO_2Me$	1	**5ba+5bc**	84 (2:1)[b]
2a	$H{-}{\equiv}{-}CO_2Me$	3	**5ca**	80[c]
2b	$H{-}{\equiv}{-}CO_2Me$	3	**5da**	79[c]
2b	$Me{-}{\equiv}{-}CO_2Me$	32	**5ea**	60 (6:2:1:1)[d]
 **3a**	$MeO_2C{-}{\equiv}{-}CO_2Me$	1	**6aa**	76[c]
 **3b**	$MeO_2C{-}{\equiv}{-}CO_2Me$	1	**6ba**	78[c]
3a	$H{-}{\equiv}{-}CO_2Me$	3	**6ca**: 70 + **6cc**: 12[e]	
3b	$H{-}{\equiv}{-}CO_2Me$	3	**6da**: 50 + **6dc**: 14[e]	

[a] Isolated yields. Ratio was determined by ^1H NMR. [b] Combined isolated yield. These two products could not be completely separated. [c] Only one isomer. [d] Four isomers were obtained. The major was **5ea,** others could not be assigned. [e] Two isomers could be separated.

Similar reaction was found for alkylidenesilacyclobutene derivatives **2** and **3**. However, a different regioselectivity was observed. As given in Table 2, the regioselectivity of **2a,b** with DMAD afforded products similar to those of **1a,b** (Table 1). However, in contrasty, the regioselectivity of **3a,b** gave opposite results. The reaction of **3a,b** with DMAD, unlike reactions with **1a,b** and **2a,b**, gave only one isomer, **6aa** and **6ba**, in 76% and 78% isolated yields, respectively, whereas the reaction of **3a,b** with $HC{\equiv}CCO_2Me$, which afforded only one isomer selectively when reacted with **1a,b** and **2a,b**, gave a mixture of two isomers. Fortunately, these isomers could be readily separated by using column chromatography to give **6ca** in 70% isolated yield and **6cc** in 12% isolated yield for the reaction with **3a**, and **6da** in 50% isolated yield and **6dc** in 14% isolated yield for the reaction with **3b**.

Both steric and electronic effects should be considered for this insertion reaction. Electronic effect is considered to be the major reason for the order of reactivity, e.g., DMAD > $HC{\equiv}CCO_2R$ > $R'C{\equiv}CCO_2R$. This is also the reason why alkynes such as $PrC{\equiv}CPr$ without electron-withdrawing substituents did not undergo this insertion reaction. For the regioselectivity of this insertion reaction with the activated alkynes used here, the steric effect is considered to have a more significant influence than the electronic effect. The bulky SiR_2 groups of **7** repulse the bigger substituent of the approaching alkyne.[10] This regioselectivity has been reported in the literature and has been rationalized by using steric effects.[9,10]

In summary, we have reported the first example of a metal-catalyzed alkyne insertion reaction into silacyclobutenes affording a variety of silacyclohexadiene derivatives. These *exo*-alkylidenesilacyclohexadiene derivatives, which are not available by other methods, possess very unique structures, especially the diversified conjugation systems. For examples, silacyclobutenes **1a** and **1b** were found to have an absorption maximum around 345 nm. The maximum absorption for **3a** was 347 nm with a shoulder peak at 354 nm. UV−vis spectra of **4da** and **4ea**, which are derived from **1a** and **1b**, showed their absorption maxima at 325 and 327 nm, respectively, with remarkable shifts. The maximum absorption for **6ca** at 334 nm, compared with that for **3a**, also shifted obviously.

Experimental Section

Typical Procedure for the Preparation of Silacyclohexadienes 4−6 from Their Corresponding Silacyclobutenes 1−3 and Alkynes. To a toluene (5 mL) solution of a silacyclobutene (1.0 mmol) and an alkyne (1.2 mmol) at room temperature was added $(PPh_3)_4Pd$ (0.01 mmol). The above mixture was then heated to reflux, stirred, and monitored by TLC. Once the silacyclobutene disappeared, the reaction mixture was cooled down and filtered through a thin pad of silica gel, and solvent was evaporated in vacuo. The titled product, silacyclohexadiene, was obtained after flash chromatography on silica gel (hexane/ether = 10:1).

4aa: partially separated from **4ac**; colorless crystal, mp 108−110 °C. ^1H NMR ($CDCl_3$, Me_4Si): δ 0.41 (s, 6H, CH_3), 3.06 (s, 3H, CH_3), 3.74 (s, 3H, CH_3), 7.12−7.38 (m, 12H, CH). ^{13}C NMR ($CDCl_3$): δ −2.2 (2 CH_3), 51.6 (1 CH_3), 52.0 (1 CH_3), 126.5 (2 CH), 126.9 (1 CH), 128.0 (2 CH), 128.4 (1 CH), 128.7 (2 CH), 129.4 (2 CH), 132.8 (1 quart C), 136.4 (1 quart C), 138.4 (1 quart C), 141.6 (1 quart C), 142.4 (1 quart C), 142.6 (1 CH), 143.4 (1 quart C), 144.8 (1 CH), 166.9 (1 quart C), 170.1 (1 quart C). IR (neat): ν (C═O) 1721 cm^{-1}; HRMS calcd for $C_{24}H_{24}O_4Si$ 404.1444, found 404.1424. Anal. Calcd for $C_{24}H_{24}O_4Si$: C, 71.26; H, 5.98. Found: C, 71.15; H, 5.86; CCDC: 630403. **4aa + 4ac:** a mixture of two isomers in 3:1 molar ratio, combined isolated yield 96% (388 mg). ^1H NMR ($CDCl_3$, Me_4Si): δ 0.41 (s, CH_3), 3.06 (s, CH_3), 3.74 (s, CH_3), 3.81 (s, CH_3), 3.97 (s, CH_3), 6.97−7.44 (m, CH). ^{13}C NMR ($CDCl_3$): δ −1.2, −2.2, 51.6, 52.0, 52.0, 52.6, 126.5, 126.7, 126.9, 127.0, 128.0, 128.3, 128.5, 128.6, 128.7, 129.3, 129.4, 130.2, 132.4, 132.8, 135.8, 135.9, 136.4, 138.4, 141.6, 141.6, 142.4, 142.6, 143.0, 143.2, 143.4, 144.8, 154.9, 166.9, 168.6, 170.1, 170.2. HRMS calcd for $C_{24}H_{24}O_4Si$ 404.1444, found 404.1431.

5ca: colorless liquid, isolated yield 80% (267 mg). ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.14 (s, 6H, CH_3), 0.85−0.94 (m, 6H, CH_3), 1.03 (t, $J = 7.2$ Hz, 3H, CH_3), 1.23−1.42 (m, 8H, CH_2), 1.98 (t, $J = 7.5$ Hz, 2H, CH_2), 2.23−2.29 (m, 4H, CH_2), 3.43 (s, 3H, CH_3), 6.70 (s, 1H, CH), 7.12 (s, 1H, CH). ^{13}C NMR ($CDCl_3$): δ −2.9 (2 CH_3), 13.2 (1 CH_3), 13.9 (1 CH_3), 14.0 (1 CH_3), 22.5 (1 CH_2), 23.0 (1 CH_2), 25.2 (1 CH_2), 29.8 (1 CH_2), 32.1 (1 CH_2), 35.1 (1 CH_2), 36.2 (1 CH_2), 52.0 (1 CH_3), 128.1 (1 quart C), 137.0 (1 CH), 138.8 (1 quart C), 139.1 (1 CH), 147.1 (1 quart C), 148.7 (1 quart C), 170.1 (1 quart C). IR (neat): υ (C=O) 1723 cm^{-1}. HRMS calcd for $C_{20}H_{34}O_2Si$ 334.2328, found 334.2322.

6aa: yellow liquid, isolated yield 76% (390 mg). ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.39 (s, 6H, CH_3), 0.73 (t, $J = 7.5$ Hz, 3H, CH_3), 0.97 (t, $J = 7.5$ Hz, 3H, CH_3), 1.19 (m, 2H, CH_2), 1.51 (m, 2H, CH_2), 1.91 (t, $J = 7.5$ Hz, 2H, CH_2), 2.18 (t, $J = 7.5$ Hz, 2H, CH_2), 3.03 (s, 3H, CH_3), 3.69 (s, 3H, CH_3), 5.73 (t, $J = 7.5$ Hz, 1H, CH), 7.20−7.36 (m, 11H, CH), 7.86(s, 1H, CH). ^{13}C NMR ($CDCl_3$): δ −2.1 (2 CH_3), 14.0 (1 CH_3), 14.3 (1 CH_3), 21.3 (1 CH_2), 22.7 (1 CH_2), 30.2 (1 CH_2), 32.6 (1 CH_2), 51.5 (1 CH_3), 51.8 (1 CH_3), 126.4 (1 CH), 126.6 (2 CH), 127.7 (2 CH), 128.5 (2 CH), 128.6 (1 CH), 130.9 (1 quart C), 131.1 (2 CH), 132.5 (1 CH), 137.2 (1 quart C), 137.8 (1 quart C), 139.6 (1 quart C), 140.5 (1 quart C), 143.2 (1 quart C), 143.9 (1 CH), 147.0 (1 quart C), 158.7 (1 quart C), 167.7 (1 quart C), 170.2 (1 quart C). IR (neat): υ (C=O) 1720 cm^{-1}. HRMS calcd for $C_{32}H_{38}O_4Si$ 514.2539, found 514.2522.

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Supporting Information Available: General experimental condition and characterization data for all products except illustrative examples, copies of ^{1}H and ^{13}C NMR spectra for all isolated compounds, copies of ^{13}C NMR spectra showing satellite peaks due to ^{29}Si for products **4da** and **6da**, X-ray structure and crystallographic data for **4aa** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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