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Palladium-Catalyzed Silylene-1,3-Diene [4 + 1] Cycloaddition with Use of (Aminosilyl)boronic Esters as Synthetic Equivalents of Silylene

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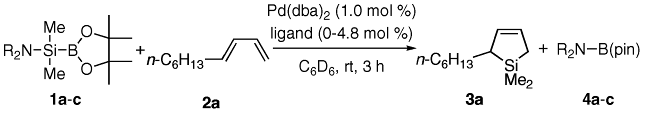
Carbon−silicon bond formations involving silylene and its equivalents have received increasing attention in the synthesis of organosilicon compounds.[1] Silylene species can be generated by dehalogenation of dihalosilanes as well as thermolysis or photolysis of oligosilanes, disilenes, and strained cyclic organosilanes and undergo cycloaddition with unsaturated hydrocarbons to give cyclic organosilanes.[2] Among the formation of silacarbocycles, cycloaddition with 1,3-dienes is attractive because the reaction provides silacyclopent-3-enes that serve as useful intermediates in organic synthesis.[3,4] However, control of the reaction is rather difficult, because the reaction proceeds via the transient formation of vinylsilacyclopropanes,[5] which then rearrange via biradical intermediates to lead to the formation of undesired side products[6] along with loss of stereospecificity.[7] As a result, synthesis of silacyclopent-3-enes via silylene transfer to 1,3-dienes has been limited to isoprene and 2,3-dimethyl-1,3-butadiene.[3,8]

Transition-metal-catalyzed silylene transfer would be an attractive method for overcoming the limitations of the thermal or photochemical reactions. However, no efficient silylene transfer to 1,3-dienes has been reported,[9] despite recent successes in catalytic silylene transfer from silacyclopropanes or other silylene precursors to alkynes,[10] alkenes,[11] and α,β-unsaturated carbonyl compounds.[12] We recently found that silylboronic esters bearing a dialkylamino group on the silicon atoms reacted as silylene equivalents in the presence of terminal alkynes and a palladium catalyst, giving 2,4-disubstituted siloles.[13] Our effort was then focused on application of the new silylene transfer system to 1,3-dienes. Herein, we describe palladium-catalyzed reaction of silylboronic esters with 1,3-dienes, leading to efficient access to silacyclopent-3-enes.[14]

Reactions of 1,3-decadiene (**2a**) with silylboronic esters **1a**−**c**[15] bearing dialkylamino groups on the silicon atoms were examined (Table 1). In the presence of Pd(dba)$_2$ (1.0 mol %) and PPh$_3$ (1.2 mol %), Et$_2$N-substituted **1a** reacted slowly with **2a** in C$_6$D$_6$ at room temperature to give silacyclopent-3-ene **3a** and aminoboronic ester **4a** in 17 and 36% yields, respectively (entry 1). It should be remarked that silylborane **1a** did not afford silaboration products[16] but served as a silylene equivalent under the reaction conditions. We found that the yields of **3a** and **4a** were greatly improved when the reaction was carried out with Pd/PMePh$_2$ catalyst (entry 2). A palladium complex bearing PMe$_2$Ph also showed high catalyst ability (entry 5), whereas almost no reaction took place with PMe$_3$ (entry 6). The reaction proceeded smoothly with Pd/P ratios of 1:1.2 to 1:2.4 (entries 2 and 3), while a slow reaction was observed with higher ligand/Pd ratios (entries 4 and 7). Reaction of Me$_2$N-substituted **1b** gave **3a** in much lower yield than did **1a**, while retaining the high yield of aminoborane **4b** (entry 8). This result may indicate that silylene extrusion, which forms **4b**, and trapping of the silylene by 1,3-dienes take place sequentially on the palladium. On the other hand, slower formation of both **3a** and **4c** was observed in the reaction with pyrrolidino-substituted **1c** (entry 9).

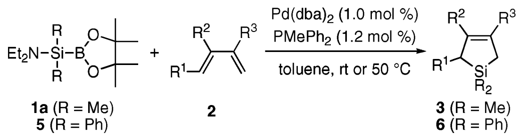
Table 1. Screening of Reaction Conditions[a]



entry	silylborane	ligand (Pd/P)	% yield of **3a**[b]	% yield of **4**[c]
1	**1a** (R$_2$N = Et$_2$N)	PPh$_3$ (1/1.2)	17	36 (**4a**)
2	**1a**	PMePh$_2$ (1/1.2)	62 (63)[d]	99 (**4a**)
3	**1a**	PMePh$_2$ (1/2.4)	61	81 (**4a**)
4	**1a**	PMePh$_2$ (1/4.8)	11	19 (**4a**)
5	**1a**	PMe$_2$Ph (1/1.2)	59	81 (**4a**)
6	**1a**	PMe$_3$ (1/1.2)	3	5 (**4a**)
7	**1a**	none	0	4 (**4a**)
8	**1b** (R$_2$N = Me$_2$N)	PMePh$_2$ (1/1.2)	15	92 (**4b**)
9	**1c** (R$_2$N = pyrrolidino)	PMePh$_2$ (1/1.2)	28	67 (**4c**)

[a] **1a**−**c** (0.30 mmol), **2a** (0.33 mmol), Pd(dba)$_2$ (3.0 μmol), and ligand (0−14.4 μmol) were stirred in C$_6$D$_6$ (0.15 mL) at room temperature unless otherwise noted. [b] GC yield based on silylborane. [c] ^{1}H NMR yield. [d] Isolated yield in the reaction of **1a** (0.43 mmol) with **2a** (0.38 mmol).

Table 2. Palladium-Catalyzed Reaction of Silylboronic Esters with Dienes[a]



entry	Si−B	R^1	R^2	R^3		yield (%)[b]
1[c]	**1a**	Ph	H	H	**2b**	93 (**3b**)
2	**5**	Ph	H	H	**2b**	77 (**6b**)
3	**5**	H	H	Me	**2c**	82 (**6c**)
4	**1a**	H	H	Ph	**2d**	84 (**3d**)
5	**1a**	H	H	(CH$_2$)$_2$CO$_2$Me	**2e**	77 (**3e**)
6	**1a**	H	H	(CH$_2$)$_2$CN	**2f**	71 (**3f**)
7	**1a**	H	H	(CH$_2$)$_2$CH=CMe$_2$	**2g**	71 (**3g**)
8[c]	**1a**	H	H	OSiMe$_2$Ph	**2h**	82 (**3h**)
9[c]	**1a**	Ph	H	Ph	**2i**	94 (**3i**)
10[c]	**1a**	*n*-Bu	H	OSiMe$_2$Ph	**2j**	92 (**3j**)
11	**5**	H	Me	Me	**2k**	79 (**6k**)
12	**1a**	H	*n*-C$_6$H$_{13}$	*n*-C$_6$H$_{13}$	**2l**	84 (**3l**)
13	**1a**	H		-(CH$_2$)$_4$-	**2m**	84 (**3m**)
14[c]	**1a**	Me	Me	Ph	**2n**	86 (**3n**)

[a] **1a** or **5** (0.40 mmol), **2** (0.44−0.68 mmol), Pd(dba)$_2$ (4.0 μmol), and PMePh$_2$ (4.8 μmol) were stirred in toluene (0.2 mL) at room temperature (for **1a**) or at 50 °C (for **5**) unless otherwise noted. [b] Isolated yield. [c] **1a** (0.44 mmol) and **2** (0.40 mmol) were employed.

Mono- and disubstituted 1,3-butadienes were then subjected to the reaction with Et$_2$N-substituted **1a** or diphenylsilyl analogue **5**

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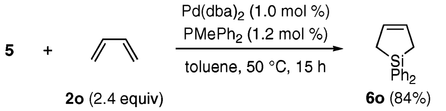
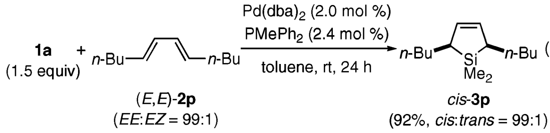
in the presence of the Pd/PMePh$_2$ catalyst (Table 2). Silylboronic esters **1a** and **5** reacted with 1-phenyl-1,3-butadiene (**2b**) at room temperature to give 2-phenyl-silacyclopent-3-enes **3b** and **6b**, respectively (entries 1 and 2). The reaction of diphenyl derivative required higher reaction temperature than the dimethylsilylene transfer. Reactions of **1a** or **5** with 1,3-butadienes **2c**−**h** bearing a substituent at C2 gave the corresponding silacyclopent-3-enes **3c**−**h** in 71−85% yields (entries 3−8). It should be noted that functional groups such as ester, nitrile, and isolated C−C double bonds did not affect the formation of silacyclopent-3-enes (entries 5−7). The reaction was applicable to dienol silyl ether **2h** (entry 8). Reactions of 1,3- and 2,3-disubstituted 1,3-butadienes **2i**−**m** and 1,2,3-trisubstituted **2n** also gave the corresponding products **3i**−**n** in good yields (entries 9−14).[17]

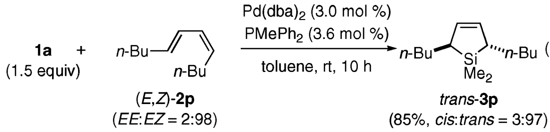
The catalytic silylene transfer using silylboronic esters was applicable to 1,3-dienes that had been reported to give undesired products under the thermal or photochemical conditions.[6,7] 1,3-Butadiene (**2o**) reacted with **5** to give **6o** in 84% yield without incorporation of a second 1,3-butadiene (eq 1).[6c] Stereospecific ring formation took place in the reaction of **1a** with either stereoisomer of 5,7-dodecadiene (**2p**): (*E*,*E*)-**2p** gave *cis*-**3p** (eq 2), whereas selective formation of *trans*-**3p** was observed in the reaction of (*E*,*Z*)-**2p** (eq 3).[7] Selective formation of 7-silanorbornene **6q** (88%) was achieved by reaction of 1,3-cyclohexadiene (**2q**) with **5**, in which no ring-opening products were formed (eq 4).[6a]



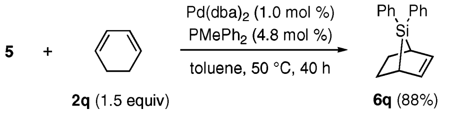
(1)



(2)



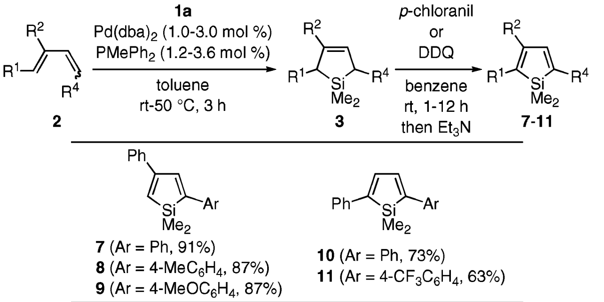
(3)



(4)

An application utilizing the silylene transfer is demonstrated by the synthesis of 2,4- and 2,5-diarylsiloles, for which no general synthetic methods have been established (Scheme 1).[18] We found that 2,4- and 2,5-diaryl-1-silacyclopent-3-enes were easily converted into the corresponding siloles by treatment with *p*-chloranil or DDQ.[19] Readily available dienes **2** (R^1 = H, R^2 = Ph, R^4 = Ar or R^1 = Ph, R^2 = H, R^4 = Ar) were converted into **3** and then oxidized with *p*-chloranil or DDQ to give **7**-**11** in high total yields.

Scheme 1. Synthesis of 2,4- and 2,5-Diarylsiloles from 1,3-Dienes[a]



[a] Total yields based on dienes **2** are shown.

In conclusion, we have established an efficient method to synthesize silacyclopent-3-enes via palladium-catalyzed silylene transfer to 1,3-dienes from silylboronic esters. The reaction was applicable to a wide variety of 1,3-dienes with high functional group tolerance and stereospecificity.

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

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