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Palladium-Catalyzed Additions of Silyl-Element Bonds to Bicyclopropylidene—A New Access to Bicyclopropyl and Functionally Substituted Cyclopropylidenepropane Derivatives[†]

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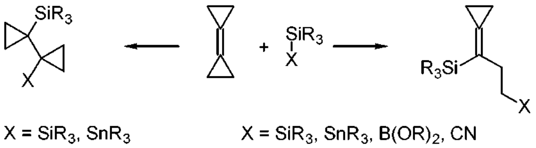
ABSTRACT



Palladium-catalyzed additions of disilanes, silylboranes, silylstannanes, and silyl cyanides across the double bond of bicyclopropylidene proceed with remarkable ease by two modes yielding either bicyclopropyl or cyclopropylidenepropane derivatives.

Much attention in recent years has been focused on the introduction of silicon into organic molecules. The addition of disilanes,[1] silylboranes,[2] and silylstannanes[3] to C−C multiple bonds opens the possibility to introduce two functional groups in one step. Palladium-catalyzed additions of disilanes, silylboranes, and silylstannanes to alkynes are well documented, while such intermolecular additions to alkenes are very rare.[1c] Bicyclopropylidene, however, is a particularly reactive, though tetrasubstituted, alkene[4] and thus should offer itself for palladium-catalyzed bissilylations, silylborations, and silylstannations. According to the generally accepted notion that a cyclopropane to a certain extent resembles an alkene,[5] the double bond in bicyclopropylidene must have features of the central double bond in butatriene.[4] In fact, disilanes have been reported to add to both 1,3-dienes and cumulenes.[6] Therefore, we have tested a number of inter- and intramolecular palladium-catalyzed additions of disilanes, silylboranes, and silylstannanes to the double-bond of bicyclopropylidene (**1**),[7] and we here wish to report the results.

With the palladium(II) acetate *tert*-isooctyl isocyanide complex[1] as a catalyst, hexamethyldisilane (**2a**) in a toluene

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[†] Part 63 in the series “Cyclopropyl Building Blocks for Organic Synthesis”. For Part 62 see: Brandl, M.; Kozhushkov, S. I.; Loscha, K.; Kokoreva, O. V.; Yufit, D. S.; Howard, J. A. K.; de Meijere, A. *Synlett* **2000**, in press.

[1] (a) Ito, Y.; Suginome, M.; Murakami, M. *J. Org. Chem.* **1991**, *56*, 1948. (b) Murakami, M.; Suginome, M.; Fujimoto, K.; Nakamura, H.; Andersson, P. G.; Ito, Y. *J. Am. Chem. Soc.* **1993**, *115*, 6487. (c) Suginome, M.; Ito, Y. *Chem. Rev.* **2000**, *100*, 3221.

[2] (a) Suginome, M.; Nakamura, H.; Ito, Y. *Angew. Chem.* **1997**, *109*, 2626; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2516. (b) Suginome, M.; Nakamura, H.; Ito, Y. *J. Chem. Soc., Chem. Commun.* **1996**, 2777.

[3] Chenard, B. L.; Zyl, C. M. Van. *J. Org. Chem.* **1986**, *51*, 3561.

[4] For reviews see: (a) de Meijere, A.; Kozhushkov, S. I.; Khlebnikov, A. F. *Topics Curr. Chem.* **1999**, *207*, 89. (b) de Meijere, A.; Kozhushkov, S. I. *Eur. J. Org. Chem.* **2000**, in press. (c) Traetteberg, M.; Simon, A.; Peters, E.-M.; de Meijere, A. *J. Mol. Struct.* **1984**, *118*, 333.

[5] (a) de Meijere, A. *Angew. Chem.* **1979**, *91*, 867; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 809. (b) Wiberg, K. B. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: Chichester, 1987; p 1.

[6] Horn, K. A. *Chem. Rev.* **1995**, *95*, 1317.

[7] Bicyclopropylidene (**1**) is easily prepared in three simple steps from commercially available methyl cyclopropanecarboxylate: (a) de Meijere, A.; Kozhushkov, S. I.; Spaeth, T.; Zefirov, N. S. *J. Org. Chem.* **1993**, *58*, 502. (b) de Meijere, A.; Kozhushkov, S. I.; Spaeth, T. *Org. Synth.* **2000**, *78*, in press.

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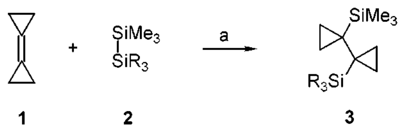
solution at 70 °C added to **1** to give 1,1′-bis(trimethylsilyl)bicyclopropyl (**3a**) with retention of both rings isolated in 77% yield. Under the same reaction conditions, 1,1,1-trimethyl-2,2,2-triphenyldisilane (**2b**) added to **1** to yield 87% of 1′-(trimethylsilyl)-1-(triphenylsilyl)bicyclopropyl (**3b**).

Scheme 1[a]



	R	%
a	Me	77
b	Ph	87

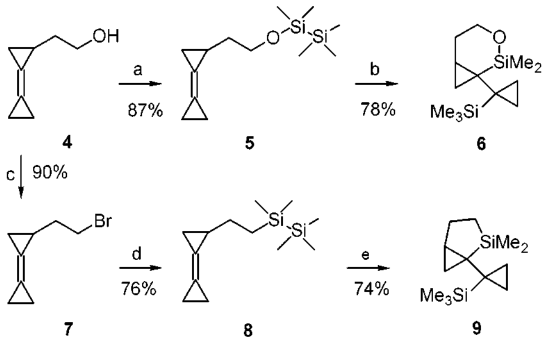
[a] (a) Pd(OAc)$_2$, 1,1,3,3-tetramethylbutylisonitrile, PhMe, 70 °C, 3 d.

The same reaction mode was also observed intramolecularly for bicyclopropylidene derivatives tethered to a disilane moiety. Two model compounds, [2-(pentamethyldisilanoxy)ethyl]bicyclopropylidene (**5**) and [2-(pentamethyldisilyl)ethyl]bicyclopropylidene (**8**), were prepared from (2-hydroxyethyl)bicyclopropylidene (**4**) either by direct silylation with chloropentamethyldisilane or by transformation to the bromide **7**[8] and subsequent silylation of the Grignard reagent derived from **7**.

When treated with palladium(II) acetate in the presence of *tert*-isooctyl isocyanide, both disilane derivatives **5** and **8** underwent intramolecular additions across the double bond of their bicyclopropylidene moieties to form 2,2-dimethyl-1-(1-trimethylsilylcyclopropyl)-3-oxa-2-silabicyclo[4.1.0]heptane (**6**) (78%) and 2,2-dimethyl-1-(1-trimethylsilylcyclopropyl)-2-silabicyclo[3.1.0]hexane (**9**) (74% yield), respectively.

In contrast to all of these additions occurring with retention of both cyclopropyl groups in **1**, the reaction of 1,2-difluoro-1,1,2,2-tetramethyldisilane (**12a**) with **1** in the presence of Pd(PPh$_3$)$_2$Cl$_2$ as a catalyst gave 1,3-bis(fluorodimethylsilyl)-1-cyclopropylidenepropane (**13a**)[9] in 75% yield.[10] Apparently, the intermediate of type **10** with a fluorodimethylsilyl group attached to one of the cyclopropane rings, formed by silylpalladation of the double bond in **1**, does not undergo reductive elimination to form a product of type **3**. Instead, it experiences a cyclopropylmethyl to homoallyl rearrangement to yield the σ-homoallylpalladium intermediate **11**, which then undergoes reductive elimination to give **13a**. 1,2-Dichloro-1,1,2,2-tetramethyldisilane (**12b**) and 1,1,2,2-tetramethyl-1,2-diphenyldisilane (**12c**) did not react with **1** under various conditions. On one hand, the additions of **2a,b** to **1** and intramolecular reactions of **5** and **8** could not be brought about with Pd(PPh$_3$)$_2$Cl$_2$; on the other hand, the palladium-*tert*-isooctyl isocyanide catalyst did not achieve the addition of **12a** to **1**. Tetrakis(triphenylphosphine)palladium and palladium(II) chloride did not catalyze any of these reactions.

Scheme 2[a]



[a] (a) ClMe$_2$SiSiMe$_3$, NEt$_3$, DMAP, THF, 25 °C, 24 h; (b) Pd(OAc)$_2$, 1,1,3,3-tetramethylbutylisonitrile, PhH, 70 °C, 3 d; (c) PPh$_3$·Br$_2$, CH$_2$Cl$_2$, 25 °C, 2 h; (d) 1, Mg, THF, 25 °C, 90 min; 2, ClMe$_2$SiSiMe$_3$, THF, 25 °C, 16 h; (e) Pd(OAc)$_2$, 1,1,3,3-tetramethylbutylisonitrile, PhH, 70 °C, 3 d.

(Dimethylphenylsilyl)pinacolborane (**12d**)[2b] could be added to **1** in the presence of palladium(II) acetate and *tert*-isooctyl isocyanide. This reaction also proceeded with a concomitant cyclopropylmethyl to homoallyl rearrangement, yet with remarkable regioselectivity to yield only the [3-cyclopropylidene-3-(dimethylphenylsilyl)propyl]boronate **13d** (56%).[10]

The same regioselective reaction mode was observed with (trimethylsilyl)tributylstannane (**12e**) and (trimethylsilyl)trimethylstannane (**12f**) in the presence of tetrakis(triphenylphosphine)palladium to give 1-cyclopropylidene-3-(tributylstannyl)-1-(trimethylsilyl)propane (**13e**)[10] (61% yield) and 1-cyclopropylidene-1-(trimethylsilyl)-3-(trimethylstannyl)-

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(8) Becker, H., Dissertation, Georg-August-Universität Göttingen, 1997.

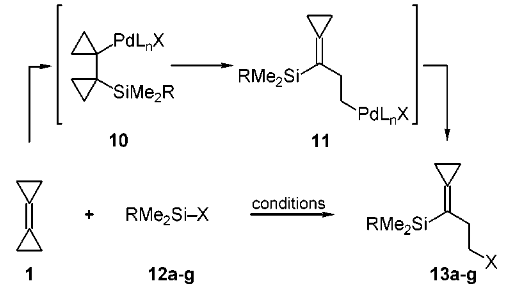
(9) **Preparation of 1,3-bis(fluorodimethylsilyl)-1-cyclopropylidenepropane (13a).** A solution of 1.73 g (11.2 mmol) of 1,2-difluoro-1,1,2,2-tetramethyldisilane (**12a**), 900 mg (11.2 mmol) of bicyclopropylidene (**1**), and 158 mg (0.23 mmol) of bis(triphenylphosphine)palladium(II) chloride in 10 mL of benzene was heated under an argon atmosphere in a screw-capped Pyrex bottle at 70 °C for 12 h. Kugelrohr distillation (145 °C, 100 Torr) gave 1.97 g (8.42 mmol, 75%) of **13a** as a colorless liquid. IR (film): ν 3045 cm^{-1} (C−H), 3017 (C−H), 2963 (C−H), 2922 (C−H), 1728, 1407, 1258 (Si−CH$_3$), 1046, 915, 868. ^{1}H NMR (250 MHz, CDCl$_3$): δ 0.20 [d, $^3J_{HF} = 7.5$ Hz, 6 H, Si(CH_3)$_2$], 0.33 [d, $^3J_{HF} = 7.4$ Hz, 6 H, Si(CH_3)$_2$], 0.91 (dt, $^3J_{HF} = 11.3$ Hz, $^3J_{HH} = 6.4$ Hz, 2 H, 3-H), 1.05 (s, 4 H, *c*Pr-H), 2.36−2.43 (m, 2 H, 2-H). ^{13}C NMR (62.9 MHz, CDCl$_3$, plus DEPT): δ −1.53 [+, d, $^2J_{CF} = 14.9$ Hz, 2 C, Si(CH_3)$_2$], −0.87 [+, d, $^2J_{CF} = 15.7$ Hz, 2 C, Si(CH_3)$_2$], 1.45 (−, *c*Pr-CH_2), 2.85 (−, *c*Pr-CH_2), 16.58 (−, d, $^2J_{CF} = 13.6$ Hz, C-3), 26.52 (−, C-2), 127.50 (C$_{quat}$, d, $^2J_{CF} = 16.2$ Hz, C-1), 134.82 (C$_{quat}$, d, $^4J_{CF} = 4.8$ Hz, *c*Pr-C$_{quat}$). MS (CI, NH$_3$) *m/z* (%): 271/270/269 (5/16/72) [M + NH$_3$ + NH$_4^+$], 254/253/252 (7/19/100) [M + NH$_4^+$]. Anal. Calcd for C$_{10}$H$_{20}$F$_2$Si$_2$ (234.4): C, 51.23; H, 8.60. Found: C, 51.51; H, 8.85.

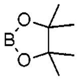
(10) The structural assignments of **13a**,**d**−**g** rest on their ^{13}C NMR data in comparison with those of **3** and of 1,3-bis(trimethylsilyl)-1-cyclopropylidenepropane, which was obtained in 78% yield by treatment of **13a** with methylmagnesium iodide in diethyl ether. The latter compound shows two ^{13}CH$_3$ signals at δ_{TMS} −1.79 and −0.77 ppm for two different SiMe$_3$ groups, while **3** shows only one at δ_{TMS} −0.77 ppm. The corresponding signals for the SiMe$_2$F groups in **13a** show up at δ_{TMS} −1.53 and − 0.87 ppm, respectively. The fact that the single ^{13}CH$_3$ signals for the SiMe$_3$ groups in **13e**,**f** and the SiMe$_2$Ph groups in **13d**,**e** occur at δ_{TMS} −0.70, −0.69, −2.87, −2.75 ppm, respectively, was taken to indicate that the silyl groups in these products were attached at the vinylic positions. For **13g** this assignment was corroborated by the fact that the aminomethyl group of the reduction product showed a triplet in the ^{1}H NMR spectrum.

propane (**13f**)[10] (92%), respectively. However, in the presence of the palladium(II) acetate *tert*-isooctyl isocyanide complex as a catalyst, the addition of **12e** to **1** occurred without ring opening to yield 45% of 1-(tributylstannyl)-1′-(trimethylsilyl)bicyclopropyl (**14**). In both reactions of **1** with **12e**, hexabutyldistannane was formed as a side product that could not be separated from either **13e** or **14**. Higher temperatures did not accelerate the reaction but promoted the formation of **15**. When (trimethylsilyl)trimethylstannane (**12f**) and $Pd(PPh_3)_4$ were employed, the addition to **1** proceeded very cleanly without formation of hexamethyldistannane to yield **13f**.

Eventually, (dimethylphenyl)silyl cyanide (**12g**) was treated with **1** in the presence of $PdCl_2 \cdot Py$ and was found to react regioselectively as well to yield **13g** (58%).[10,11]

Scheme 3



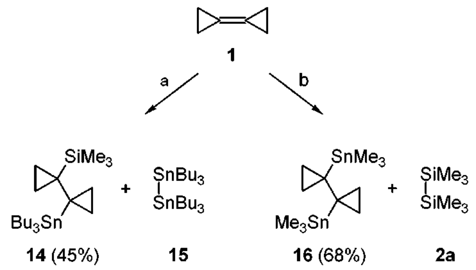
	R	conditions	X	13 (%)
a	F	$Pd(PPh_3)_2Cl_2$, PhH, 70 °C, 12 h	$SiMe_2F$	75
b	Cl	$Pd(PPh_3)_2Cl_2$, PhH, 70 °C, 3 d	$SiMe_2Cl$	–[a]
c	Ph	$Pd(OAc)_2$, NC, PhMe, 70 °C, 4 d	$SiMe_2Ph$	–[a]
d	Ph	$Pd(OAc)_2$, NC, PhMe, 130 °C, 3 d		56
e	Me	$Pd(PPh_3)_4$, Et_2O, 50 °C, 3 d	$SnBu_3$	41[b]
f	Me	$Pd(PPh_3)_4$, Et_2O, 50 °C, 4 d	$SnMe_3$	92
g	Ph	$PdCl_2 \cdot Py_n$, PhMe, 100 °C, 14 d	CN	58

[a] No conversion was observed, neither under these nor under various other conditions. [b] Hexabutyldistannane was formed as byproduct.

The reaction of 2 equiv of **12f** with bicyclopropylidene (**1**) under the catalysis of the palladium(II) acetate *tert*-isooctyl isocyanide complex gave 1,1′-bis(trimethylstannyl)bicyclopropyl (**16**) in 68% yield. It is well-known that silylstannanes can undergo a palladium-catalyzed disproportionation to form disilanes and distannanes.[3] In the case of bicyclopropylidene (**1**), apparently the addition of the thus formed hexamethyldistannane occurred more rapidly than that of the silylstannane **12f** and of hexamethyldisilane **2a**.

These reactions represent the first palladium-catalyzed intra- and intermolecular additions of disilanes, silylboranes, and silylstannanes to a tetrasubstituted double bond. The differentiation between the two reaction modes, i.e., addition without ring opening and addition accompanied by a cyclopropylmethyl to homoallyl rearrangement, must arise from the difference in the electrophility of the organopalladium residue in the first formed intermediate of type **10**, which is influenced both by the ligand additive and the residue stemming from the silane reagent. The cyclopropylmethyl to homoallyl rearrangement can be viewed as an intramolecular silylpalladation across one of the two vicinal cyclopropyl σ-bonds, and this reaction rate should be enhanced for a more electrophilic palladium moiety.

Scheme 4[a]



[a] (a) $Me_3SiSnBu_3$, $Pd(OAc)_2$, 1,1,3,3-tetramethylbutylisonitrile, pentane, 50 °C, 7 d; (b) $Me_3SiSnMe_3$, $Pd(OAc)_2$, 1,1,3,3-tetramethylbutylisonitrile, pentane, 50 °C, 7 d.

In conclusion, the reported palladium-catalyzed additions of disilanes, silylstannanes, silylboranes, and (dimethylphenyl)silyl cyanide to bicyclopropylidene (**1**) not only are interesting from a theoretical viewpoint but also open routes from a readily available starting material[7] to a number of functionally substituted methylenecyclopropane derivatives that may be useful as reactive building blocks for organic synthesis.[12]

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Supporting Information Available: Experimental procedures and full characterization for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] The Pd-catalyzed addition of trimethylsilyl cyanide to 2-phenylmethylenecyclopropane has been reported to yield a mixture of ring-opening and ring-retention products: cf. Chatani, N.; Takeyusa, T.; Hanafusa, T. *Tetrahedron Lett.* **1988**, *29*, 3979.

[12] For example, cross-coupling reactions should be possible with compound **13a** according to a recently developed protocol, cf. Denmark, S. E.; Wehrli, D.; Choi, J. Y. *Org. Lett.* **2000**, 2491 and references therein. The nitrile group in **13g** can easily be transformed to a carboxylic acid, an aldehyde, or an aminomethyl functionality, and these derivatives lend themselves to further elaborations.