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Palladium-Catalyzed Dimerization Disilylation of 1,3-Butadiene with Chlorosilanes

Jun Terao, Akihiro Oda, and Nobuaki Kambe*

Department of Molecular Chemistry & Science and Technology Center for Atoms, Molecules and Ions Control, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

kambe@chem.eng.osaka-u.ac.jp

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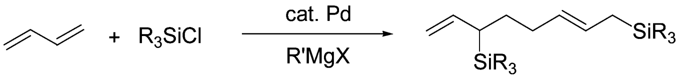
ABSTRACT



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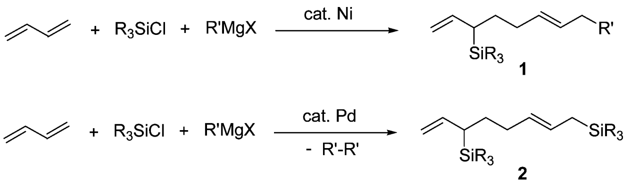
1,3-Butadiene reacted with chlorosilanes and Grignard reagents at 20 °C in the presence of a catalytic amount of Pd(acac)$_2$ to give disilylated dimers 2 regioselectively, which have two silyl groups (R$_3$Si) at the 3- and 8-positions of a 1,6-octadiene skeleton. When phenyl- or allyl-substituted chlorosilanes were used, coupling product was obtained stereo- as well as regioselectively, giving rise to only (*E*)-olefins. It is proposed that Pd-ate complexes play important roles in both C–Si bond-forming processes.

The carbon−silicon bond-forming reaction is of great importance and widely used for the synthesis of organosilanes. Among a variety of methods having been developed for such transformations, transition metal-catalyzed silylation provides useful routes to organosilanes from carbon−carbon unsaturated compounds. In these reactions various silylating reagents possessing silicon−hydrogen,[1] silicon−silicon,[2] or silicon−heteroatom bonds[2b] have been employed; however, chlorosilanes (R$_3$SiCl) have rarely been employed in transition metal-catalyzed C−Si bond-forming reactions probably due to the difficulty of the oxidative addition of the Si−Cl bond to low-valent metal complexes.[3] During the course of our project on the synthetic use of chlorosilanes in transition metal-catalyzed reactions, we have reported unique silylation reactions of olefins and dienes with chlorosilanes by the combined use of Grignard reagents and early transition metal catalysts such as Cp$_2$ZrCl$_2$[4] or Cp$_2$TiCl$_2$.[5] As the first example of late transition metal-catalyzed C−Si bond formation using chlorosilanes, we have recently developed dimerization carbosilylation of 1,3-butadienes with chlorosilanes and Grignard reagents in the presence of a Ni catalyst (Scheme 1).[6] When we carried out a similar reaction using Pd, we happened to find that dimerization disilylation of 1,3-butadiene proceeds regioselectively under mild conditions to give bis(allylsilane)s (**2**) (Scheme 1).

Scheme 1



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(1) (a) Makabe, H.; Negishi, E. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; John Wiley & Sons: New York, 2002; Vol. II, VII.4, pp 2789−2823. (b) Ojima, I.; Li, Z.; Zhu, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1998; Vol. 2, Part 2, pp 1687−1792. (c) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Li, Z., Zhu, J., Eds.; John Wiley & Sons: 1989; Vol. 1, Part 2, pp 1479−1526.

(2) (a) Oshima, K. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; John Wiley & Sons: 2002; Vol. II, VII.5, pp 2825−2839. (b) Suginome, M.; Ito, Y. *Chem. Rev.* **2000**, *100*, 3221−3256. (c) Horn, K. A. *Chem. Rev.* **1995**, *95*, 1317−1350.

(3) Yamashita, H.; Tanaka, M.; Goto, M. *Organometallics* **1997**, *16*, 4696−4704 and references therein.

(4) (a) Terao, J.; Torii, K.; Saito, K.; Kambe, N.; Baba, A.; Sonoda, N. *Angew. Chem., Int. Ed.* **1998**, *37*, 2653−2656. (b) Terao, J.; Jin, Y.; Torii, K.; Kambe, N. *Tetrahedron* **2004**, *60*, 1301−1308.

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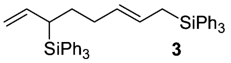
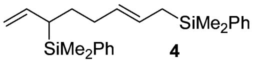
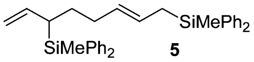
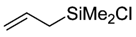
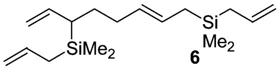
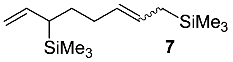
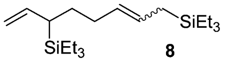
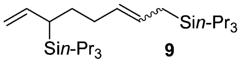
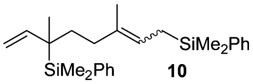
Table 1. Pd-Catalyzed Dimerization Disilylation of 1,3-Butadienes

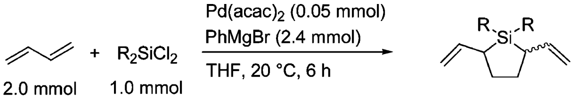
Entry[a]	Chlorosilane	Product	Isolated yield [*E*/*Z*][b]
1	Ph_3SiCl	 **3**	93% [100/0]
2[c]			83% [100/0]
3[d]			88% [100/0]
4	$PhMe_2SiCl$	 **4**	88% [100/0]
5	$Ph_2MeSiCl$	 **5**	74% [100/0]
6		 **6**	81% [100/0]
7	Me_3SiCl	 **7**	57% [88/12]
8	Et_3SiCl	 **8**	79% [78/22]
9	*n*-Pr_3SiCl	 **9**	91% [80/20]
10[e]	$PhMe_2SiCl$	 **10**	18% [77/23]

[a] 1,3-Butadiene and PhMgBr were used unless otherwise stated. [b] By NMR and GC. [c] Reaction was carried out on a 20 mmol scale. [d] Isopropenylmagnesium bromide was employed. [e] Isoprene was used.

For example, a reaction of 1,3-butadiene (2 mmol) with Ph_3SiCl (2 mmol) in the presence of PhMgBr (1 M in THF, 2.4 mL, 2.4 mmol) and a catalytic amount of $Pd(acac)_2$ (0.05 mmol) at 20 °C for 6 h gave a 1,6-octadiene **3** possessing two triphenylsilyl groups at the 3- and 8-positions[7] with perfect regio- and stereoselectivity in 98% NMR yield. The product was obtained in pure form in 93% yield by HPLC (Table 1, entry 1). In this reaction, 1.05 mmol of biphenyl was formed as a byproduct; however, NMR, GC, and GC-MS analyses of the resulting mixture showed no evidence for the presence of the regioisomers of **3**, dimerization carbosilylation products (**1**),[6] or any other monosilylated products.[8]

Results obtained using various chlorosilanes are shown in Table 1. Entry 2 shows an example of large-scale preparation (20 mmol of 1,3-butadiene) under the identical conditions, where 5.2 g (83%) of **3** was synthesized in pure form by recrystallization from a 1:2 solution of ether and *n*-hexane. Isopropenylmagnesium bromide could be employed instead of PhMgBr to give **3** in 88% isolated yield (entry 3). Phenyl- or allyl-substituted chlorosilanes also afforded the corresponding coupling products **4**−**6** regio- and stereoselectively. The corresponding products **7**−**9** were obtained in good yields using chlorotrialkylsilanes; however, stereoisomers were obtained concomitantly (entries 7−9). When $PdCl_2$ and $PdCl_2(PPh_3)_2$ were used instead of $Pd(acac)_2$ as catalysts under conditions identical to those of entry 8 in Table 1, **8** was obtained in 76 and 64% yields, respectively, whereas no reaction took place with $PdCl_2$(dppe). Under the same conditions, isoprene gave **10** in only 18% yield. 2,3-Dimethyl-1,3-butadiene did not react, resulting in the formation of a substantial amount of $PhMe_2SiPh$ by direct reaction of $PhMe_2SiCl$ with PhMgBr.

Scheme 2

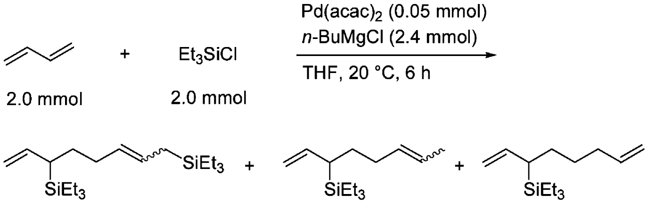


11a; R = Ph, 78 % [*syn*/*anti*=49/51]
11b; R = Et, 69 % [*syn*/*anti*=39/61]

It is worth noting that when dichlorosilanes (R_2SiCl_2) were used, cyclization took place exclusively to give 2,5-divinylsilolanes **11a** and **11b** in 78 and 69% yields, respectively (Scheme 2).

When *n*-BuMgCl was employed, a 47% yield of the desired product **8** was obtained along with hydrosilylation products **12** and **13** in 3 and 25% yields, respectively (vide infra) (Scheme 3).

Scheme 3



8, 47% [*E*/*Z*=87/13]　**12**, 3%　**13**, 25%

A plausible reaction pathway is depicted in Scheme 4. First, $Pd(acac)_2$ is reduced by R′MgX to afford Pd(0) **15** via **14** with the concomitant formation of R′−R′. Then, **15** reacts with 2 equiv of butadiene, giving rise to bis-π-allylpalladium complex **16**,[9] which is attacked by R′MgX to form η^1,η^3-octadienediylpalladate complex **17**.[10] The ate complex **17** reacts with a chlorosilane at the allylic γ-carbon[11] leading to π-allylpalladium complex **18**, which reacts again with R′MgX to form another ate complex **19**. Then, **19** reacts with chlorosilane at the γ-allyl carbon giving rise to disilyl coupling product **2** along with regeneration of **14** to complete the

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(5) (a) Terao, J.; Kambe, N.; Sonoda, N. *Tetrahedron Lett.* **1998**, *39*, 9697−9698. (b) Nii, S.; Terao, J.; Kambe, N. *J. Org. Chem.* **2000**, *65*, 5291−5297. (c) Watabe, H.; Terao, J.; Kambe, N. *Org. Lett.* **2001**, *3*, 1733−1735. (d) Nii, S.; Terao, J.; Kambe, N. *Tetrahedron Lett.* **2004**, *45*, 1699−1702.

(6) Terao, J.; Oda, A.; Ikumi, A.; Nakamura, A.; Kuniyasu, H.; Kambe, N. *Angew. Chem., Int. Ed.* **2003**, *42*, 3412−3414.

(7) It has been reported that the reaction of 1,3-butadienes with hexamethyldisilane gives rise to 1,8-bis(trimethylsilyl)-2,6-octadiene; see: Sakurai, H.; Eriyama, Y.; Kamiyama, Y.; Nakadaira, Y. *J. Organomet. Chem.* **1984**, *264*, 229−237.

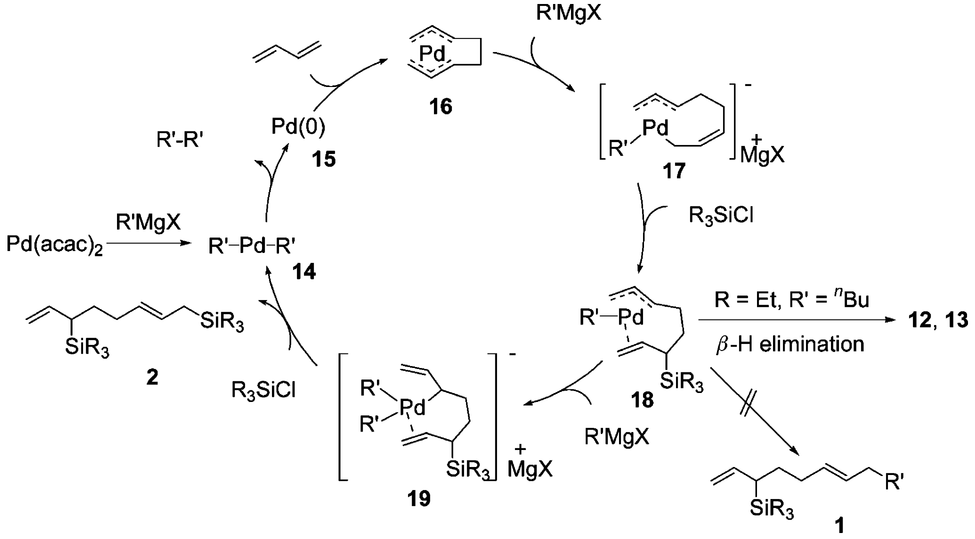
(8) Trace amount of Ph_4Si (<2%) was formed by the direct reaction of Ph_3SiCl with PhMgBr.

(9) Jolly, P. W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 283−295.

(10) π-Allylpalladate complex has been reported for Mg; see: Bogdanović, B.; Huckett, S. C.; Wilczok, U.; Rufińska, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1513−1516.

(11) η^1,η^3-Octadienediylpalladium complex reacts with Me_2HSiCl at the γ-allylic carbon; see: Jolly, P. W.; Mynott, R.; Raspel, B.; Schick, K.-P. *Organometallics* **1986**, *5*, 473−481.

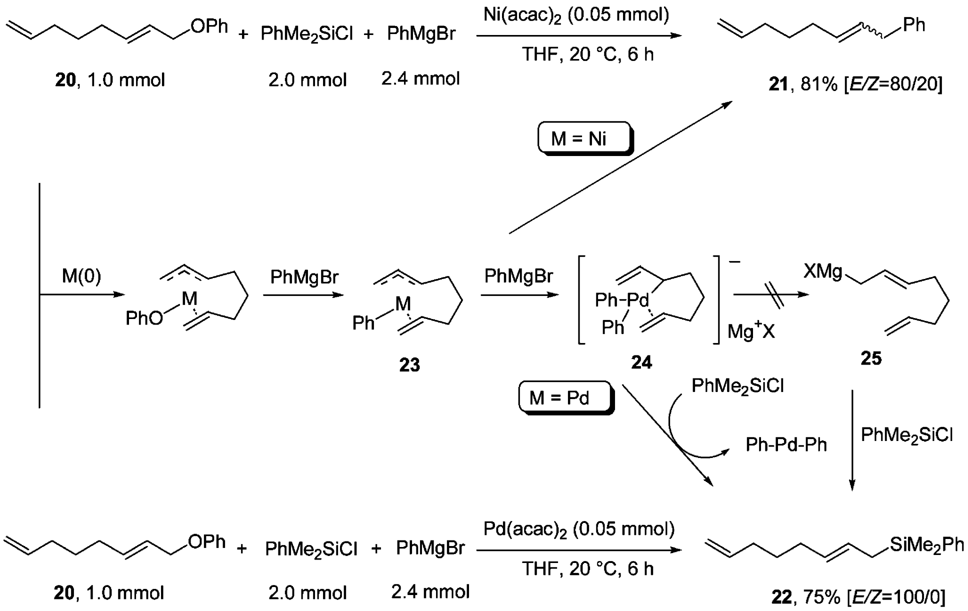
Scheme 4. Plausible Reaction Pathway



catalytic cycle. When *n*-BuMgCl is used, β-hydrogen elimination from **18** (R′ = *n*-Bu) might compete with ate complex formation leading to **19**, resulting in the formation of hydrosilylation products **12** and **13** as shown in Scheme 3.

Under similar conditions, Ni and Pd follow different reaction courses leading to different products, i.e., Ni affords dimerization carbosilylation products **1**,[6] whereas dimerization disilylation products **2** are obtained by using Pd catalyst. To confirm these unique catalytic features of these metals, we examined the reaction of allyl ether **20** with 2 equiv of PhMgBr and $PhMe_2SiCl$ in the presence of $Ni(acac)_2$ or $Pd(acac)_2$ as catalysts (Scheme 5). In the case of the Ni-catalyzed reaction, allylbenzene derivative **21** was formed in 81% yield without formation of allylsilane **22**. On the other hand, $Pd(acac)_2$ gave allylsilane **22** in 75% yield along with 79% yield of biphenyl. These results can be rationally understood by assuming a π-allyl(aryl)metal complex **23** as a common intermediate that is formed by oxidative addition of allyl ether to zero-valent Ni[12] or Pd[13] followed by the reaction with PhMgBr. The π-allyl(aryl)nickel complex (**23a**, M = Ni) readily undergoes reductive elimination to give **21**.[14] On the other hand, π-allyl(aryl)palladium complex (**23b**, M = Pd) reacts with another PhMgBr molecule to form palladate complex **24**. This is in accordance with the evidence that reductive elimination of π-allyl(aryl)nickel complex proceeds ca. 26 times faster than that of the corresponding Pd complex.[15] Nucleophilic attack of a chlorosilane at the terminal γ-allylic carbon of **24** gives **22**. Since it is known

Scheme 5



that the reaction of crotyl Grignard reagent with trimethylchlorosilane gives a mixture of regioisomers of allylsilanes via both S_E2 and S_E2' mechanisms,[16] it might not be likely that a free allyl Grignard reagent **25** is generated by transmetalation[17] of **23** with PhMgBr and reacts with chlorosilanes.

In conclusion, we have developed a new, simple method for the synthesis of bis(allylsilanes)[18] from dienes and chlorosilanes, where two C−Si bonds and one C−C bond can be formed regioselectively using Pd catalyst in the presence of PhMgBr. This reaction also proceeds stereoselectively by the use of aryl- or allyl-substituted chlorosilanes. Two allylpalladate complexes **17** and **19** play important roles for regioselective C−Si bond-forming steps.

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

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(12) Yamamoto, T.; Ishizu, J.; Yamamoto, A. *J. Am. Chem. Soc.* **1981**, *103*, 6863−6869.

(13) Yamamoto, T.; Akimoto, M.; Yamamoto, A. *Chem. Lett.* **1983**, 1725−1726. For a recent review, see: Tsuji, J. *Palladium Reagents and Catalysts*, John Wiley & Sons: Chichester, 1995; pp 345−356.

(14) Hayashi, T.; Konishi, M.; Yokota, K.; Kumada, M. *Chem. Commun.* **1981**, 313−314.

(15) (a) Kurosawa, H.; Ohnishi, H.; Emoto, M.; Chatani, N.; Kawasaki, Y.; Murai, S.; Ikeda, I. *Organometallics* **1990**, *9*, 3038−3042. (b) Kurosawa, H.; Ogoshi, S. *Bull. Chem. Soc. Jpn.* **1998**, 973−984.

(16) Hosomi, A.; Iguchi, H.; Sakurai, H. *Chem. Lett.* **1982**, 223−226.

(17) For a review of an umpolung of π-allylpalladium intermediate by transmetalation with organometals, see: Tamaru, Y. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; John Wiley & Sons: New York, 2002; Vol. II, V.2.3.4, pp 1917−1943.

(18) Allylsilanes play important roles in organic synthesis as useful intermediates in a number of synthetic transformations; see: Luh, T.-Y.; Liu S.-T. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1998; Vol. 2, Part 3, pp 1793−1868.