

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

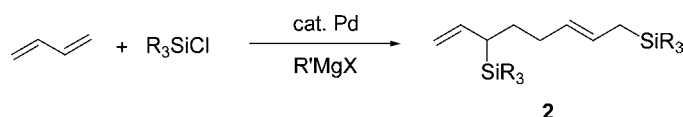
Jun Terao, Akihiro Oda, and Nobuaki Kambe*

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

Received July 1, 2004

ABSTRACT

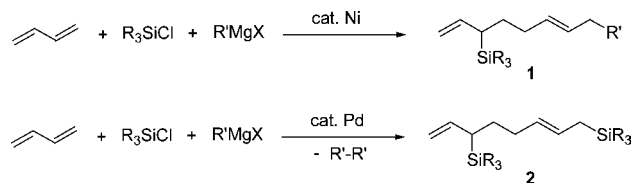


1,3-Butadiene reacted with chlorosilanes and Grignard reagents at 20 °C in the presence of a catalytic amount of $\text{Pd}(\text{acac})_2$ to give disilylated dimers **2** regioselectively, which have two silyl groups (R_3Si) at the 3- and 8-positions of a 1,6-octadiene skeleton. When phenyl- or allyl-substituted 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_3SiCl) 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_2ZrCl_2 ⁴ or Cp_2TiCl_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-butenes 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

Scheme 1



happened to find that dimerization disilylation of 1,3-butadiene proceeds regioselectively under mild conditions to give bis(allylsilane)s (**2**) (Scheme 1).

(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) Sugimoto, 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.

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

Entry ^a	Chlorosilane	Product	Isolated yield [E/Z] ^b
1	Ph ₃ SiCl		93% [100/0]
2 ^c	Ph ₃ SiCl		83% [100/0]
3 ^d	Ph ₃ SiCl		88% [100/0]
4	PhMe ₂ SiCl		88% [100/0]
5	Ph ₂ MeSiCl		74% [100/0]
6	CH ₂ =CHSiMe ₂ Cl		81% [100/0]
7	Me ₃ SiCl		57% [88/12]
8	Et ₃ SiCl		79% [78/22]
9	<i>n</i> -Pr ₃ SiCl		91% [80/20]
10 ^e	PhMe ₂ SiCl		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 Ph₃SiCl (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-positions⁷ 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

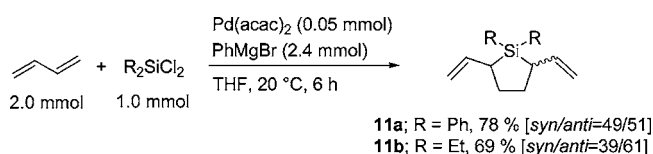
(5) (a) Terao, J.; Kambe, N.; Sonoda, N. *Tetrahedron Lett.* **1998**, 39, 9697–9698. (b) Nii, S.; Terao, J.; Kambe, N. *J. Org. Chem.* **2000**, 65, 5291–5297. (c) Watabe, H.; Terao, J.; Kambe, N. *Org. Lett.* **2001**, 3, 1733–1735. (d) Nii, S.; Terao, J.; Kambe, N. *Tetrahedron Lett.* **2004**, 45, 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 Ph₄Si (<2%) was formed by the direct reaction of Ph₃SiCl with PhMgBr.

Scheme 2

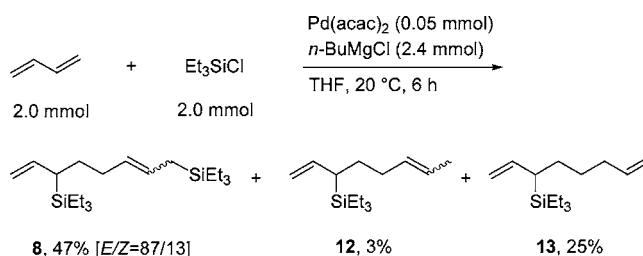


stereoselectively. The corresponding products **7–9** were obtained in good yields using chlorotrialkylsilanes; however, stereoisomers were obtained concomitantly (entries 7–9). When PdCl₂ and PdCl₂(PPh₃)₂ were used instead of Pd(acac)₂ as catalysts under conditions identical to those of entry 8 in Table 1, **8** was obtained in 76 and 64% yields, respectively, whereas no reaction took place with PdCl₂(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 PhMe₂SiPh by direct reaction of PhMe₂SiCl with PhMgBr.

It is worth noting that when dichlorosilanes (R₂SiCl₂) 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



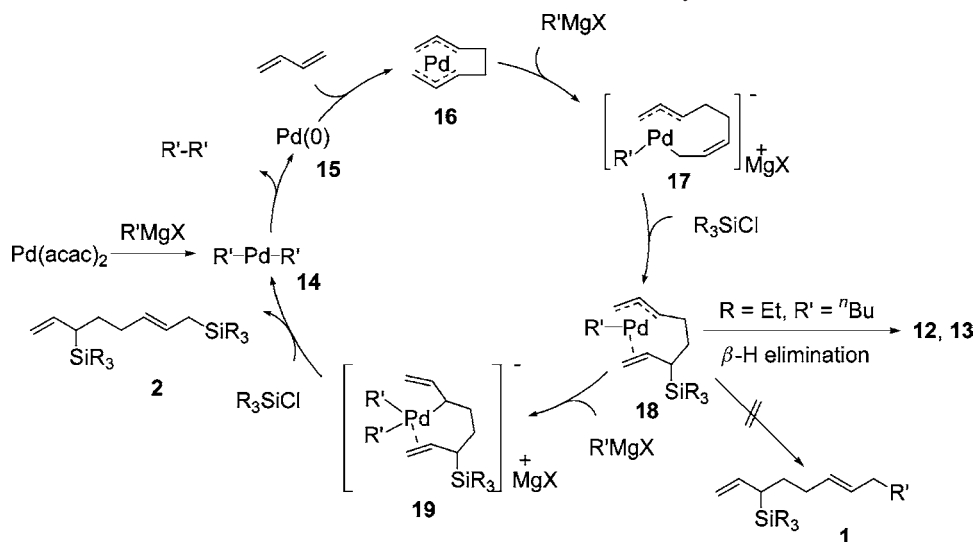
A plausible reaction pathway is depicted in Scheme 4. First, Pd(acac)₂ is reduced by R'MgX to afford Pd(0) **15** via **14** with the concomitant formation of R'–R'. Then, **15** reacts with 2 equiv of butadiene, giving rise to bis- π -allylpalladium complex **16**,⁹ which is attacked by R'MgX to form η^1, η^3 -octadienediylpalladate complex **17**.¹⁰ The ate complex **17** reacts with a chlorosilane at the allylic γ -carbon¹¹ 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

(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.; Hockett, S. C.; Wilczok, U.; Ruffinška, A. *Angew. Chem., Int. Ed. Engl.* **1988**, 27, 1513–1516.

(11) η^1, η^3 -Octadienediylpalladium complex reacts with Me₂HSiCl at the γ -allylic carbon; see: Jolly, P. W.; Mynott, R.; Raspe, B.; Schick, K.-P. *Organometallics* **1986**, 5, 473–481.

Scheme 4. Plausible Reaction Pathway

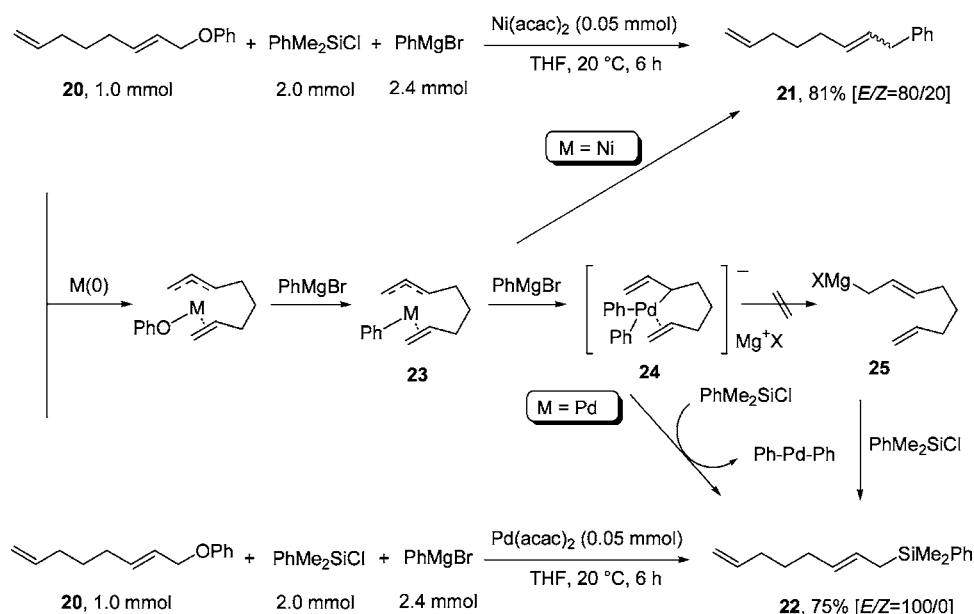


catalytic cycle. When *n*-BuMgCl is used, β -hydrogen elimination from **18** ($R' = n\text{-Bu}$) might compete with ate complex formation leading to **19**, resulting in the formation of hydrosilylation products **12** and **13** as shown in Scheme 3.

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 PhMe₂SiCl 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 Ni¹² or Pd¹³ 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 transmetalation¹⁷ 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.

(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.

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Acknowledgment. This research was financially supported in part by a grant from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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>.

OL048751J

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(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., Rappaport, Z., Eds.; John Wiley & Sons: New York, 1998; Vol. 2, Part 3, pp 1793–1868.