ORGANIC LETTERS

2008
Vol. 10, No. 19
4319−4322

Palladium-Catalyzed Disilylation of *o*-Quinodimethanes: Synthesis of 9- and 10-Membered Disilacarbocycles

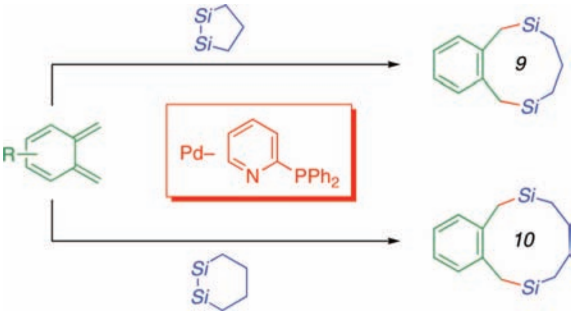
Hiroto Yoshida,* Saori Nakano, Masashi Mukae, and Joji Ohshita

Department of Applied Chemistry, Graduate School of Engineering,
Hiroshima University, Higashi-Hiroshima 739-8527, Japan

yhiroto@hiroshima-u.ac.jp

Received August 1, 2008

ABSTRACT



_o_-Quinodimethanes are efficiently inserted into a silicon−silicon bond of cyclic disilanes in the presence of a palladium−diphenyl-2-pyridylphosphine catalyst, giving 9- and 10-membered disilacarbocycles, that is, benzodisilonine and benzodisilecine.

Much attention has been directed to synthetic utilization of *o*-quinodimethanes as an efficient 4-carbon unit in constructing 6-membered carbocyclic frameworks via [4 + 2] cycloaddition (Diels−Alder reaction).[1] Although the wide applicability of the cycloaddition enables diverse functional molecules including steroids,[2] alkaloids,[3] polyacenes,[4] and fullerenes[5] to be synthesized in a straightforward manner, little has been known about a different type of transformation using *o*-quinodimethanes,[6,7] which would lead to production of cyclic structures of other sizes, despite the significant synthetic potential arising from their highly reactive character.

We have recently reported on the palladium-catalyzed distannylation of *o*-quinodimethanes, which provides α,α′-distannyl-*o*-xylenes of structural diversity, exemplifying that the transient carbon−carbon double bond can undergo a facile transition-metal-catalyzed insertion reaction into an element−element σ-bond.[8] In this context, we have been investigating the synthetic utility of this protocol and have found that a silicon−silicon bond of disilanes is likewise added across *o*-quinodimethanes smoothly. Herein we disclose that *o*-quinodimethanes serve as an efficacious four-

---

[1] For reviews, see: (a) Oppolzer, W. *Synthesis* **1978**, 793. (b) Charlton, J. L.; Alauddin, M. M. *Tetrahedron* **1987**, *43*, 2873. (c) Martin, N.; Seoane, C.; Hanack, M. *Org. Prep. Proc. Int.* **1991**, *23*, 237. (d) Segura, J. L.; Martin, N. *Chem. Rev.* **1999**, *99*, 3199. (e) Oppolzer, W. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: New York, 1991; Vol. 5,Chapter 4.1, pp 385−396.

[2] Nemoto, H.; Fukumoto, K. *Tetrahedron* **1998**, *54*, 5425.

[3] (a) Kametani, T.; Fukumoto, K. *Acc. Chem. Res.* **1976**, *9*, 319. (b) Magnus, P.; Gallagher, T.; Brown, P.; Pappalardo, P. *Acc. Chem. Res.* **1984**, *17*, 35.

[4] Morris, J. L.; Becker, C. L.; Fronczek, F. R.; Daly, W. H.; McLaughlin, M. L. *J. Org. Chem.* **1994**, *59*, 6484.

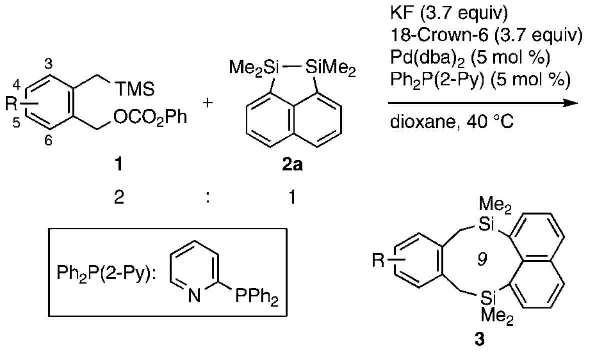
[5] (a) Belik, P.; Gügel, A.; Spickermann, J.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 78. (b) Diederich, F.; Jonas, U.; Gramlich, V.; Herrmann, A.; Ringsdorf, H.; Thilgen, C. *Helv. Chim. Acta* **1993**, *76*, 2445. (c) Zhang, X.; Foote, C. S. *J. Org. Chem.* **1994**, *59*, 5235. (d) Belik, P.; Gügel, A.; Kraus, A.; Walter, M.; Müllen, K. *J. Org. Chem.* **1995**, *60*, 3307.

[6] For polymerization of *o*-quinodimethanes, see: Chino, K.; Takata, T.; Endo, T. *Macromolecules* **1997**, *30*, 6715.

[7] For *o*-quinodimethanes as nitric oxide cheletropic traps, see: Korth, H. G. In *Free Radicals in Biology and Environment*; Springer: New York, 1997; NATO ASI Series 3, Vol. 27, pp 331−349.

10.1021/ol801788t CCC: $40.75

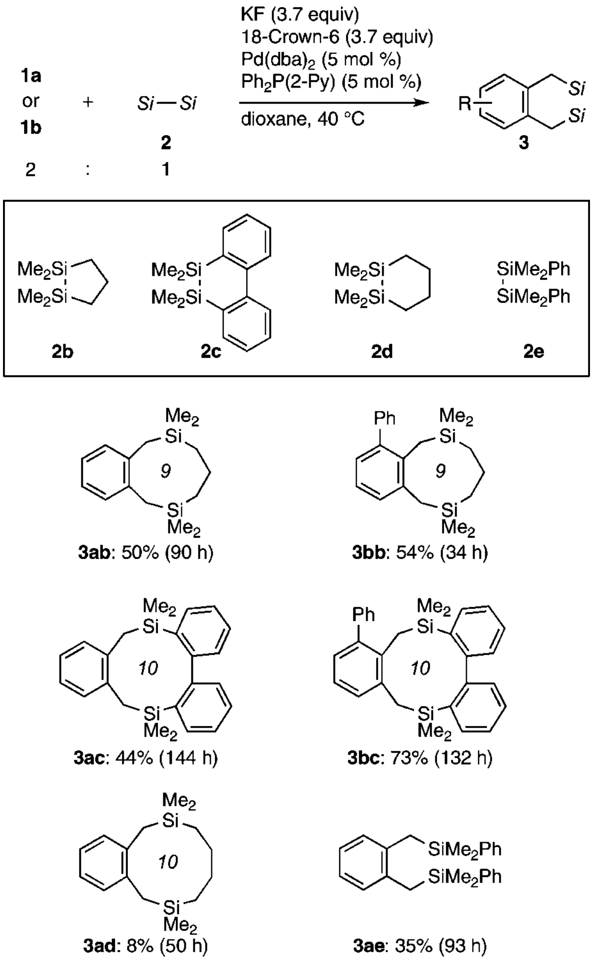
Table 1. Palladium-Catalyzed Disilylation of *o*-Quinodimethanes with **2a**[a]



entry	R	3	time (h)	yield (%)[b]
1	H (**1a**)	**3aa**	48	46
2	3-Ph (**1b**)	**3ba**	67	64
3	4-F (**1c**)	**3ca**	20	59
4	4-Cl (**1d**)	**3da**	21	57
5[c]	5-Me (**1e**)	**3ea**	70	43
6[c]	6-Me (**1f**)	**3fa**	47	36
7[c]	4,6-Me_2 (**1g**)	**3ga**	76	36

[a] The reaction was carried out in dioxane (1 mL) at 40 °C using **1** (0.40 mmol), **2a** (0.20 mmol), KF (0.74 mol), and 18-crown-6 (0.74 mmol) in the presence of $Pd(dba)_2$ (0.010 mmol) and $Ph_2P(2\text{-}Py)$ (0.010 mmol). [b] Isolated yield based on **2a**. [c] 60 °C.

Scheme 1. Palladium-Catalyzed Disilylation of *o*-Quinodimethanes with **2b**−**2e**



carbon unit in constructing 9- and 10-membered disilacarbocycles, that is, benzodisilonine and benzodisilecine, through palladium-catalyzed disilylation of 5- and 6-membered cyclic disilanes.[9,10]

Disilylation of *o*-quinodimethanes, generated in situ from 2-[(trimethylsilyl)methyl]benzyl phenyl carbonates (**1**) and a fluoride ion,[11,12] with naphthalene-fused disilacyclopentane **2a** could be achieved by the use of a catalytic amount of bis(dibenzylideneacetone)palladium−diphenyl-2-pyridylphosphine complex, which is also effective for the above distannylation. As depicted in Table 1, a 9-membered disilacarbocycle, benzodisilonine **3aa**, was formed straightforwardly via insertion of an *exo*-1,3-diene moiety of simple *o*-quinodimethane (from **1a**) into the silicon−silicon bond of **2a** (entry 1). Such substituted *o*-quinodimethanes as 3-phenyl- (from **1b**), 4-fluoro- (from **1c**), or 4-chloro-*o*-quinodimethane (from **1d**) took part in the disilylation efficiently to afford the respective products (**3ba**−**3da**) in 64%, 59%, or 57% yield (entries 2−4), whereas the reaction using methyl-substituted *o*-quinodimethanes (from **1e**−**1g**) became somewhat sluggish (entries 5−7).

The present insertion reaction was also applicable to disilacyclopentane **2b**, giving moderate yields of a benzodisilonine (**3ab** or **3bb**) (Scheme 1). Furthermore, a 10-membered disilacarbocycle, benzodisilecine (**3ac** or **3bc**), could be synthesized by treatment of biphenyl-fused disilacyclohexane **2c** with *o*-quinodimethanes, while the reaction of disilacyclohexane **2d** furnished **3ad** in only 8% yield. Although the yield was slightly lower than those observed with cyclic disilanes, an acyclic disilane (**2e**) participated in the reaction to provide a disilyl-*o*-xylene (**3ae**).

---

(8) Yoshida, H.; Nakano, S.; Yamaryo, Y.; Ohshita, J.; Kunai, A. *Org. Lett.* **2006**, *8*, 4157.

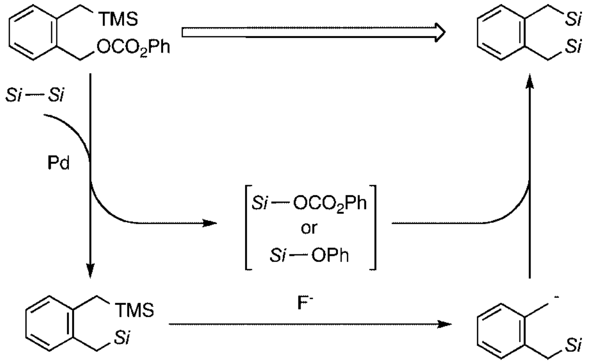
(9) We have also reported catalytic insertion reactions of arynes into an element−element σ-bond. (a) Yoshida, H.; Honda, Y.; Shirakawa, E.; Hiyama, T. *Chem. Commun.* **2001**, 1880. (b) Yoshida, H.; Ikadai, J.; Shudo, M.; Ohshita, J.; Kunai, A. *J. Am. Chem. Soc.* **2003**, *125*, 6638. (c) Yoshida, H.; Ikadai, J.; Shudo, M.; Ohshita, J.; Kunai, A. *Organometallics* **2005**, *24*, 156. (d) Ikadai, J.; Yoshida, H.; Ohshita, J.; Kunai, A. *Chem. Lett.* **2005**, *34*, 56. (e) Yoshida, H.; Tanino, K.; Ohshita, J.; Kunai, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 5052. (f) Yoshida, H.; Tanino, K.; Ohshita, J.; Kunai, A. *Chem. Commun.* **2005**, 5678.

(10) For reviews on catalytic insertion reactions of carbon−carbon multiple bonds into an element−element σ-bond, see: (a) Beletskaya, I.; Moberg, C. *Chem. Rev.* **1999**, *99*, 3435. (b) Suginome, M.; Ito, Y. *Chem. Rev.* **2000**, *100*, 3221. (c) Beletskaya, I.; Moberg, C. *Chem. Rev.* **2006**, *106*, 2320.

(11) For pioneering works on the fluoride ion-induced generation of *o*-quinodimethanes, see: (a) Ito, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1980**, *102*, 863. (b) Ito, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1982**, *104*, 7609.

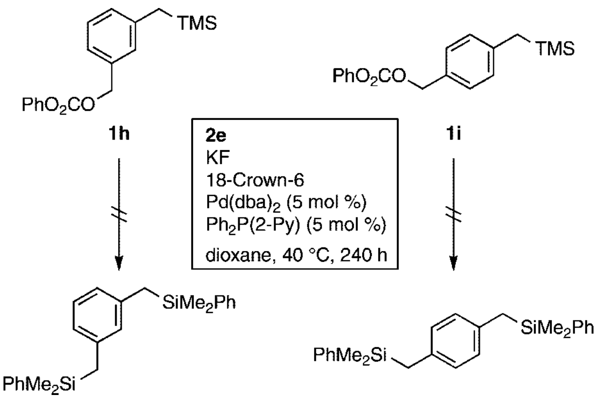
(12) Diels−Alder reaction of *o*-quinodimethanes using 2-[(trimethylsilyl)methyl]benzyl acetate has been reported; see: (a) Askari, S.; Lee, S.; Perkins, R. R.; Scheffer, J. R. *Can. J. Chem.* **1985**, *63*, 3526. (b) Kuwano, R.; Shige, T. *Chem. Lett.* **2005**, *34*, 728.

Scheme 2. Disilylation via Cross-Coupling



Because a benzylic carbonate moiety in **1** should be prone to undergo a cross-coupling reaction with **2** in the presence of a fluoride ion and a palladium catalyst,[13,14] an *o*-quinodimethane intermediate might not be involved in the present disilylation: cross-coupling of **1** at a $\mathrm{C{-}OCO_2Ph}$ moiety with **2** followed by fluoride-ion-induced silicon−silicon exchange between the resulting 2-[(trimethylsilyl)-methyl]benzylsilane and $Si\mathrm{OCO_2Ph}$ (and/or *Si*OPh) (Scheme 2). However, this pathway can be excluded since the reaction using **1h** or **1i**, a regioisomer of **1a**, did not afford the respective products (Scheme 3). In addition, Scheme 4 describes the indispensability of the palladium catalysis for the disilylation. Thus, disilylation product **3aa** was not formed at all when the reaction of **1a** with **2a** was carried out in the absence of the palladium catalyst. This result also rules out a pathway where a fluoride ion acts as a catalyst, as previously reported in the disilylation of 1,3-dienes.[15]

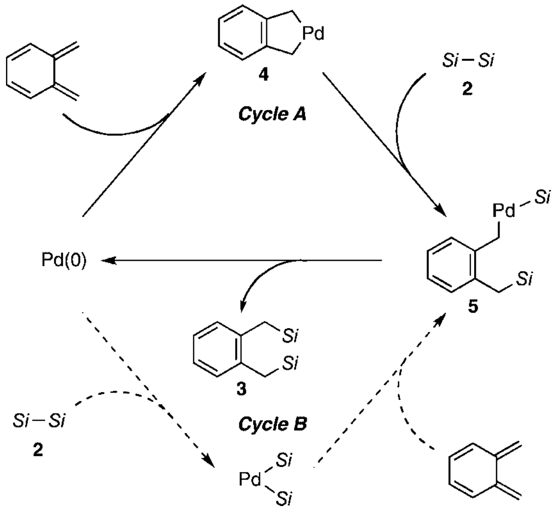
Scheme 3. Reaction Using **1h** or **1i**



Scheme 4. Reaction of **1a** with **2a** in the Absence of the Palladium Catalyst

$$\begin{array}{ccccc} \mathbf{1a} & + & \mathbf{2a} & \xrightarrow[\text{dioxane, 40 °C, 48 h}]{\substack{\text{Ph}_2\text{P(2-Py) (5 mol \%)}\\ \text{KF (4 equiv)}\\ \text{18-Crown-6 (4 equiv)}\\ /\!/}} & \mathbf{3aa} \\ 2 & : & 1 & & \end{array}$$

Scheme 5. Plausible Catalytic Cycle



These results prompt us to propose a catalytic cycle that is triggered by formation of palladacycle **4**[16] from an *o*-quinodimethane and a Pd(0) complex (Scheme 5, Cycle A). The resulting palladacycle then reacts with **2** to produce benzylpalladium complex **5**, which undergoes reductive elimination of **3** with regenerating the Pd(0) complex.[17] Although metal-catalyzed disilylation of such unsaturated carbon−carbon compounds as alkynes and alkenes generally involves oxidative addition of **2** to a Pd(0) complex as a key step,[10b] we are now in position that Cycle A would be more plausible than Cycle B, since a stoichiometric reaction of **2a** with the Pd(0)−$\mathrm{Ph_2P}$(2-Py) complex did not give oxidative adduct **6** (Scheme 6).

In conclusion, disilylation of *o*-quinodimethane has been accomplished by use of a palladium−$\mathrm{Ph_2P}$(2-Py) complex,

---

(13) (a) Matsumoto, H.; Nagashima, S.; Yoshihiro, K.; Nagai, Y. *J. Organomet. Chem.* **1975**, *85*, C1. (b) Azarian, D.; Dua, S. S.; Eabornand, C.; Walton, D. R. M. *J. Organomet. Chem.* **1976**, *117*, C55. (c) Matsumoto, H.; Yoshihiro, K.; Nagashima, S.; Watanabe, H.; Nagai, Y. *J. Organomet. Chem.* **1977**, *128*, 409. (d) Hatanaka, Y.; Hiyama, T. *Tetrahedron Lett.* **1987**, *28*, 4715. (e) Shirakawa, E.; Kurahashi, T.; Yoshida, H.; Hiyama, T. *Chem. Commun.* **2000**, 1895.

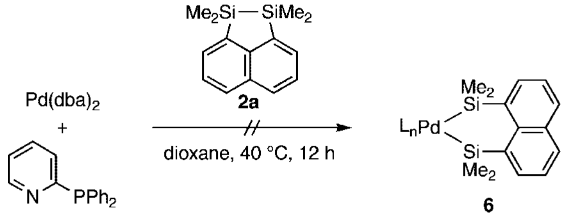
(14) For palladium-catalyzed cross-couplings of benzylic carbonates, see: (a) Kuwano, R.; Yokogi, M. *Org. Lett.* **2005**, *7*, 945. (b) Kuwano, R.; Yu, J.-Y. *Heterocycles* **2007**, *74*, 233. (c) Nakao, Y.; Ebata, S.; Chen, J.; Imanaka, H.; Hiyama, T. *Chem. Lett.* **2007**, *36*, 606. (d) Ohsumi, M.; Kuwano, R. *Chem. Lett.* **2008**, *37*, 796.

(15) Hiyama, T.; Obayashi, M.; Mori, I.; Nozaki, H. *J. Org. Chem.* **1983**, *48*, 912.

(16) Palladacycle **4** has been reported to be a key intermediate in palladium-catalyzed formal [4 + 2] cycloaddition of *o*-quinodimethanes with olefins. Kuwano, R.; Shige, T. *J. Am. Chem. Soc.* **2007**, *129*, 3802.

(17) For palladium-catalyzed carbostannylation of alkynes or arynes, which proceeds through a palladacycle, see: (a) Shirakawa, E.; Yoshida, H.; Nakao, Y.; Hiyama, T. *J. Am. Chem. Soc.* **1999**, *121*, 4290. (b) Yoshida, H.; Shirakawa, E.; Nakao, Y.; Honda, Y.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 637. (c) Matsubara, T. *Organometallics* **2003**, *22*, 4297.

Scheme 6. Stoichiometric Reaction of **2a** with Pd−Ph$_2$P(2-Py)



and various 9- and 10-membered disilacarbocycles, which would be otherwise difficult to be synthesized, are accessible directly. Further studies on catalytic insertion reactions of *o*-quinodimethanes into other element−element *σ*-bonds are in progress in our laboratory.

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

OL801788T