

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

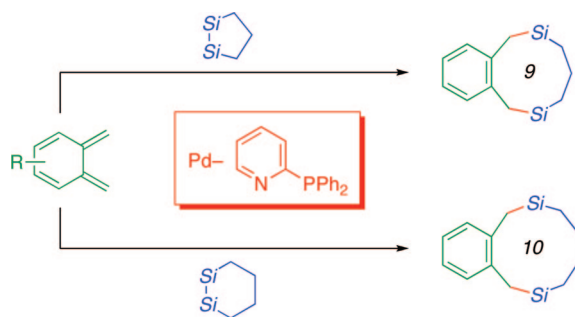
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Received August 1, 2008

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, benzodisilone and benzodisilene.

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 fullerenes⁵ 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-

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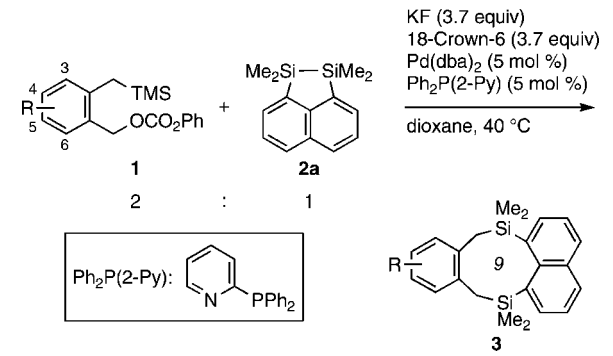
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Table 1. Palladium-Catalyzed Disilylation of *o*-Quinodimethanes with **2a**^a



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 Ph₂P(2-Py) (0.010 mmol).
^b Isolated yield based on **2a**. ^c 60 °C.

carbon unit in constructing 9- and 10-membered disilacarbycles, that is, benzodisilonine and benzodisilecine, through palladium-catalyzed disilylation of 5- and 6-membered cyclic disilanes.^{9,10}

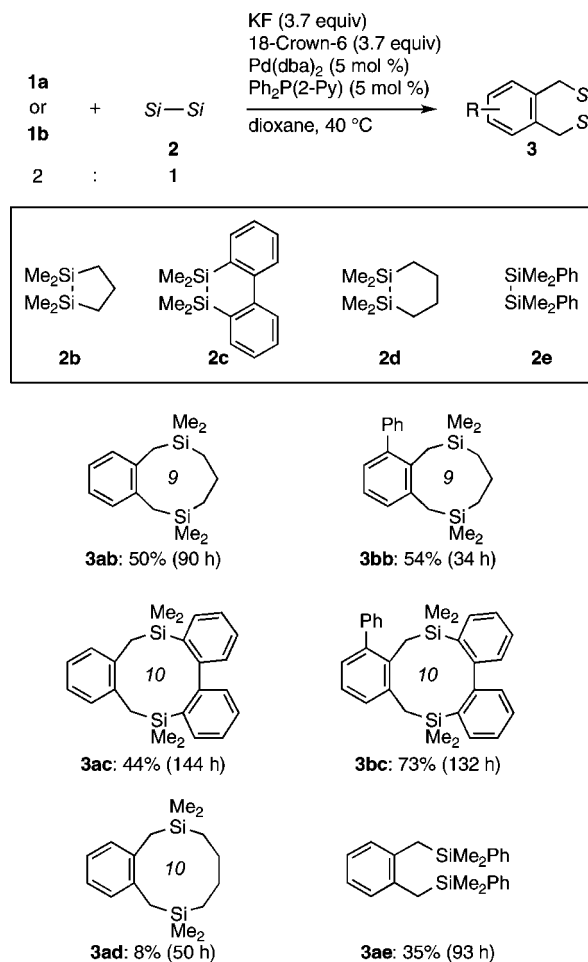
Disilylation of *o*-quinodimethanes, generated in situ from 2-[(trimethylsilyl)methyl]benzyl phenyl carbonates (**1**) and a fluoride ion,^{11,12} with naphthalene-fused disilacyclopentane **2a** could be achieved by the use of a catalytic amount of bis(dibenzylideneacetone)palladium–diphenyl-2-pyridylphosphine complex, which is also effective for the above distannylation. As depicted in Table 1, a 9-membered disilacarbycle, 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

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(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) Sugimoto, M.; Ito, Y. *Chem. Rev.* **2000**, *100*, 3221. (c) Beletskaya, I.; Moberg, C. *Chem. Rev.* **2006**, *106*, 2320.

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



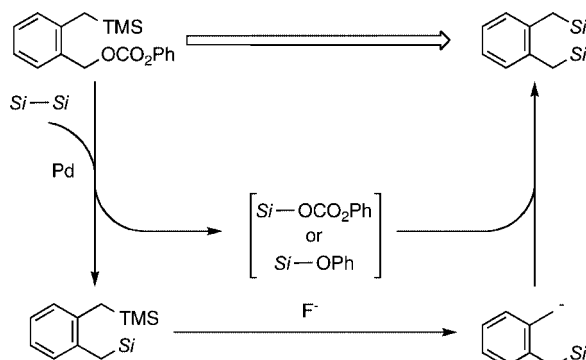
(**3ba–3da**) in 64%, 59%, or 57% yield (entries 2–4), whereas the reaction using methyl-substituted *o*-quinodimethanes (from **1e–1g**) became somewhat sluggish (entries 5–7).

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 disilacarbycle, 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**).

(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.

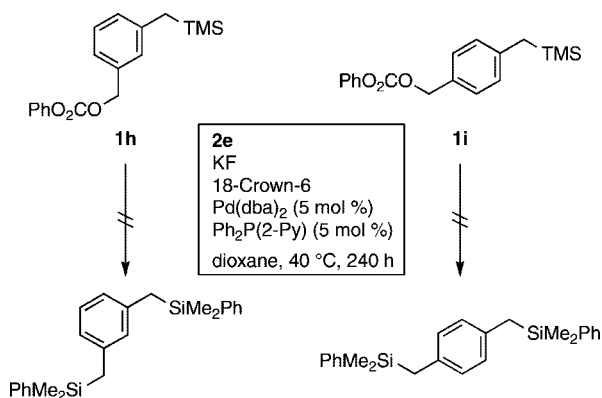
(12) Diels–Alder reaction of *o*-quinodimethanes using 2-[(trimethylsilyl)methyl]benzyl acetate has been reported; see: (a) Askari, S.; Lee, S.; Perkins, R. R.; Scheffer, J. R. *Can. J. Chem.* **1985**, *63*, 3526. (b) Kuwano, R.; Shige, T. *Chem. Lett.* **2005**, 34, 728.

Scheme 2. Disilylation via Cross-Coupling



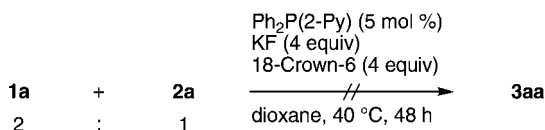
Because a benzylic carbonate moiety in **1** should be prone to undergo a cross-coupling reaction with **2** in the presence of a fluoride ion and a palladium catalyst,^{13,14} an *o*-quinodimethane intermediate might not be involved in the present disilylation: cross-coupling of **1** at a C-OCO₂Ph moiety with **2** followed by fluoride-ion-induced silicon-silicon exchange between the resulting 2-[(trimethylsilyl)methyl]benzylsilane and SiOCO₂Ph (and/or SiOPh) (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 3. Reaction Using **1h** or **1i**

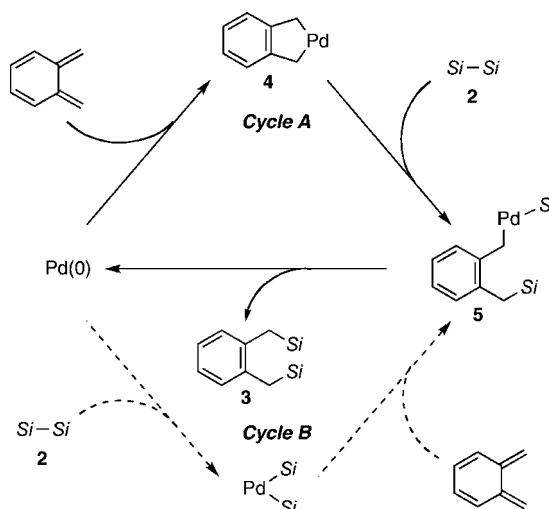


Scheme 4 describes the indispensability of the palladium catalysis for the disilylation. Thus, disilylation product **3aa** was not formed at all when the reaction of **1a** with **2a** was

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



Scheme 5. Plausible Catalytic Cycle



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

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)-Ph₂P(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-Ph₂P(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.

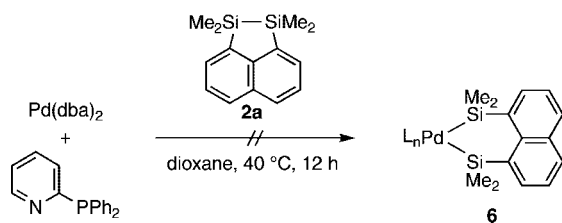
(14) For palladium-catalyzed cross-couplings of benzylic carbonates, see: (a) Kuwano, R.; Yokogi, M. *Org. Lett.* **2005**, *7*, 945. (b) Kuwano, R.; Yu, J.-Y. *Heterocycles* **2007**, *74*, 233. (c) Nakao, Y.; Ebata, S.; Chen, J.; Imanaka, H.; Hiyama, T. *Chem. Lett.* **2007**, *36*, 606. (d) Ohsumi, 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–Ph₂P(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