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Palladium-Catalyzed Distannylation of *ortho*-Quinodimethanes

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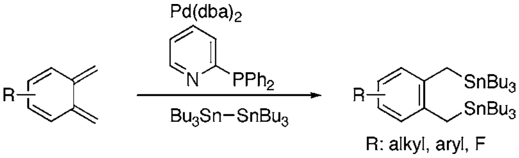
ABSTRACT

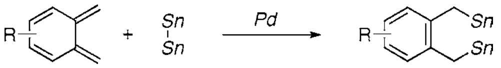


An *exo*-diene moiety of various *ortho*-quinodimethanes, regardless of its transient character, was inserted into a Sn–Sn σ-bond of hexabutyldistannane in the presence of a palladium catalyst, giving α,α′-bis(tributylstannyl)-*o*-xylenes straightforwardly.

o-Quinodimethanes are recognized as potent reactive intermediates in organic synthesis,[1] which have been utilized for preparing steroids,[1d] alkaloids,[2] polyacenes,[3] modified fullerenes,[4] etc. These transformations are based on [4+2] cycloadditions (Diels−Alder reaction),[1f] in which *o*-quinodimethanes act as dienes, and thus, little attention has been focused on their utilization for other types of reactions, despite their great synthetic potential.[5,6]

We have already reported on palladium-catalyzed carbostannylation,[7] disilylation,[8] and distannylation[9] of arynes, demonstrating that the transient carbon−carbon triple bond species can be applied to the catalytic insertion reaction into an element−element σ-bond.[10] Taking into account that *o*-quinodimethanes also hold a transient carbon−carbon unsaturated bond like arynes, we envisioned that *o*-quinodimethanes would be inserted into an element−element σ-bond with the aid of a transition-metal catalyst. Herein, we disclose the first demonstration of element−element σ-bond addition to *o*-quinodimethanes, that is, palladium-catalyzed distannylation (Scheme 1).[11]

Scheme 1



We first examined the reaction of simple *o*-quinodimethane, generated in situ from 2-[(trimethylsilyl)methyl]benzyl phenyl carbonate (**1a**) and a fluoride ion,[12−14] with hexabutylditin (**2**) in the presence of bis(dibenzylidene-

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(2) (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.

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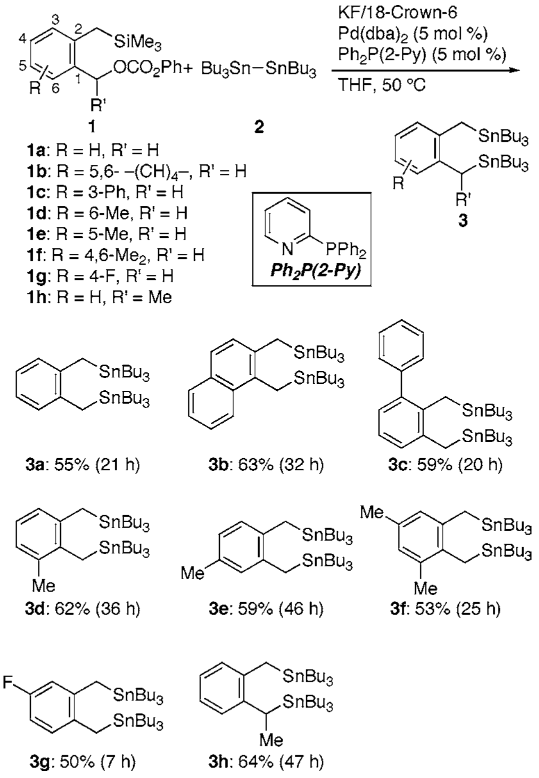
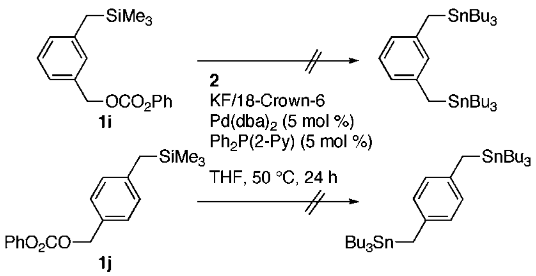
acetone)palladium-diphenyl-2-pyridylphosphine (Ph_2P(2-Py)) and observed that the *exo*-diene moiety was inserted into the Sn−Sn σ-bond to produce the distannylation product, α,α'-bis(tributylstannyl)-*o*-xylene (**3a**) in 55% yield (Scheme 2). The reactions using other *o*-quinodimethane precursors or ligands also gave **3a**, although the yields were rather low.[15] The distannylation product was not formed at all in the absence of the palladium catalyst or the fluoride ion, which confirms that both of them are essential for the reaction to proceed. Similarly to the case of simple *o*-quinodimethane, the reaction of *o*-quinodimethane bearing a naphthalene backbone (from **1b**) or 3-phenyl-*o*-quinodimethane (from **1c**) proceeded smoothly to give the distannylation product (**3b** or **3c**) in 63% or 59% yield. Methyl-substituted *o*-quinodimethanes (from **1d**−**1f**) or 4-fluoro-*o*-quinodimethane (from **1g**) also underwent the addition of **2**, affording moderate yields of the respective products (**3d**−**3g**). Furthermore, a methyl group of α-methyl-*o*-quinodimethane (from **1h**) did not inhibit the course of the distannylation to furnish **3h** in 64% yield.[16]

Scheme 2



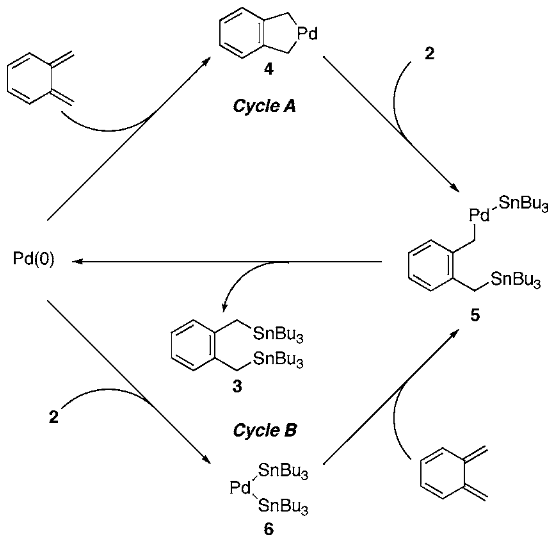
Scheme 3



Because **1** has electrophilic (C−OCO_2Ph) and nucleophilic (C−$SiMe_3$) sites at each benzylic position, the distannylation might proceed through a pathway which does not involve an *o*-quinodimethane intermediate: cross-coupling of **1** at a C−OCO_2Ph moiety with **2**[17] followed by fluoride ion-induced tin−silicon exchange between the resulting 2-[(tributylstannyl)methyl]benzylsilane and Bu_3SnOCO_2Ph (and/or Bu_3SnOPh).[18] Therefore, we examined the reaction of **1i** or **1j**, a regioisomer of **1a**, and observed that no trace of the respective product was formed, which eliminates the cross-coupling pathway in the distannylation (Scheme 3).[19]

On the basis of the above result, we propose cycle A, which includes the formation of palladacycle **4**[20] from a Pd-

Scheme 4



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(11) Palladium-catalyzed distannylations of other carbon−carbon multiple bonds have been reported. For alkynes, see: (a) Mitchel, T. N.; Amamria, A.; Killing, H.; Rutschow, D. *J. Organomet. Chem.* **1983**, *241*, C45. (b) Piers, E.; Skerlj, R. T. *J. Chem. Soc., Chem. Commun.* **1986**, 626. (c) Mancuso, J.; Lautens, M. *Org. Lett.* **2003**, *5*, 1653. For 1,3-dienes, see: (d) Tsuji, Y.; Kakehi, T. *J. Chem. Soc., Chem. Commun.* **1992**, 1000. For allenes, see: (e) Killing, H.; Mitchell, T. N. *Organometallics* **1984**, *3*, 1318.

(12) Generation of *o*-quinodimethane from **1a** has been confirmed by the Diels−Alder reaction with methyl acrylate; see Supporting Information for details.

(13) 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.

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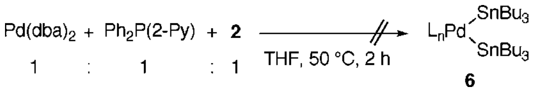
(15) See Supporting Information for details.

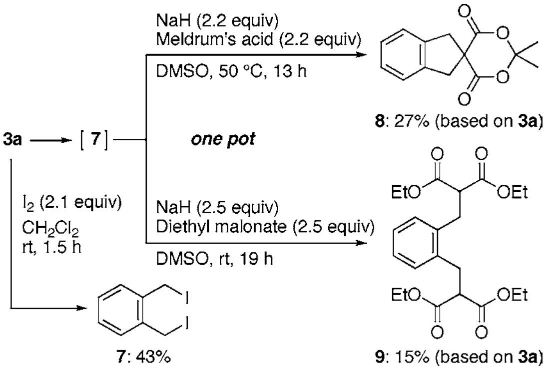
(0) complex and *o*-quinodimethane (Scheme 4). Subsequent reaction of **4** with **2** produces benzylpalladium complex **5**, followed by reductive elimination giving the product with regeneration of the Pd(0) complex.[21] Although the stoichiometric reaction of the Pd(0) complex with **2** did not afford an oxidative adduct (**6**) in contrast to the case with a Pd−isocyanide complex (Scheme 5),[9a] we cannot entirely rule out the possibility that the distannylation proceeds through oxidative addition of **2** to the Pd(0) complex (cycle B).

Scheme 5



Synthetic transformation of the distannylation product is briefly described in Scheme 6. Iododestannylation of **3a** gave α,α′-diiodo-*o*-xylene (**7**) in 43% yield. Moreover, the iododestannylation combined with the reaction using an active methylene compound furnished **8** or **9** in one pot, although the yields were rather low.[22]

Scheme 6



In conclusion, we have demonstrated that a variety of *o*-quinodimethanes, regardless of their transient character, can be applied for catalytic distannylation by use of the appropriate catalyst and precursor. Further studies on catalytic reactions of *o*-quinodimethanes involving unreactive σ-bond cleavage, on synthetic transformation of distannylation products, and on details of the reaction mechanism are in progress.

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

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(16) The major side product in the distannylation was tetrabutyltin.

(17) For the palladium-catalyzed cross-coupling of organic halides with distannanes, see: (a) Hitchcock, S. A.; Mayhugh, D. R.; Gregory, G. S. *Tetrahedron Lett.* **1995**, *36*, 9085. (b) Stork, G.; Isaacs, R. C. A. *J. Am. Chem. Soc.* **1990**, *112*, 7399.

(18) Warner, B. P.; Buchwald, S. L. *J. Org. Chem.* **1994**, *59*, 5822.

(19) Although the precursor (**1i** or **1j**) was totally consumed, most of **2** remained intact with some formation of tetrabutyltin.

(20) Transition-metal *o*-quinodimethane complexes: (a) Kündig, E. P.; Leresche, J. *Tetrahedron* **1993**, *49*, 5599. (b) Bennett, M. A.; Bown, M.; Hockless, D. C. R.; McGrady, J. E.; Schranz, H. W.; Stranger, R.; Willis, A. C. *Organometallics* **1998**, *17*, 3784. (c) Bennett, M. A.; Bown, M.; Byrnes, M. J. *J. Organomet. Chem.* **1998**, *571*, 139. (d) Cámpora, J.; Graiff, C.; Palma, P.; Carmona, E.; Tiripicchio, A. *Inorg. Chim. Acta* **1998**, *269*, 191.

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