

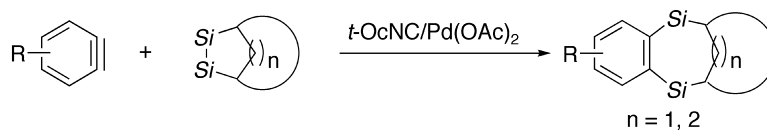
Communication

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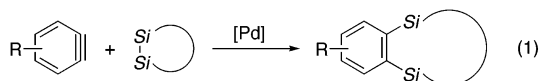
Palladium-Catalyzed Bissilylation of Arynes with Cyclic Disilanes: Synthesis of Benzo-Annulated Disilacarbocycles

Hiroto Yoshida,* Junnai Ikadai, Miwa Shudo, Joji Ohshita,[†] and Atsutaka Kunai*

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

Received February 8, 2003; E-mail: yhiroto@hiroshima-u.ac.jp; akunai@hiroshima-u.ac.jp

Arynes have been recognized as useful reactive intermediates in organic synthesis, undergoing a wide variety of reactions such as electrophilic coupling, cycloaddition, and the ene reaction.¹ These transient molecules have been known to be stabilized by coordination to transition metals, and their reactivities are thereby altered remarkably.² Consequently, considerable attention has been paid to the synthetic applications of transition metal–aryne complexes. Although stoichiometric reactions of zirconium–^{2a,b} and nickel–aryne^{2d} complexes were extensively studied, there have been a limited number of reports on catalytic transformations of arynes. Recently, Peña reported palladium-catalyzed trimerization of arynes³ and cocyclization of arynes with alkynes.⁴ Catalytic reactions of arynes with alkynes and/or allyl chlorides in the presence of a palladium complex were found also by Yamamoto,⁵ while Murai and co-workers developed catalytic carbonylation of arynes.⁶ On the other hand, no report has been published on the transition metal-catalyzed addition of an element–element σ -bond to arynes,⁷ except for the carbostannylation of arynes.⁸ We report herein the first demonstration of metal–metal σ -bond addition to arynes, that is, palladium-catalyzed bissilylation of arynes (eq 1).⁹



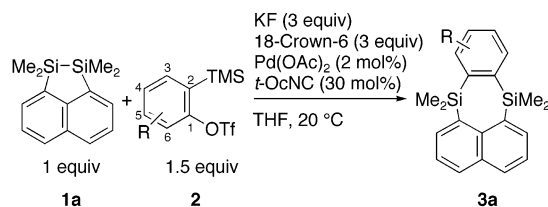
First, we investigated the reaction of 1,1,2,2-tetramethyl-1,2-(1,8-naphthylene)disilane (**1a**) and an aryne, generated in situ from 2-(trimethylsilyl)aryl triflate (**2**) and a fluoride ion (KF/18-crown-6),¹⁰ in the presence of a palladium–*t*-OcNC (1,1,3,3-tetramethylbutyl isocyanide) complex (Scheme 1), which is an excellent catalyst for bissilylations of alkynes and alkenes as reported by Ito and co-workers.^{7b,9e–g} As described in Table 1, the silicon–silicon bond of **1a** was found to readily add to the triple bond of benzyne (from **2a**) to afford the seven-membered disilacarbocycle, 7,7,12,12-tetramethyl-7,12-dihydro-7,12-disilapleiadene (**3aa**), in 66% yield (entry 1). The use of cesium fluoride in acetonitrile in lieu of KF/18-crown-6 in THF resulted in the formation of **3aa** in 78% yield, although the reaction required 2 days to be completed. The catalysis of the palladium complex is apparently crucial in the present reaction, because no trace of the insertion product was observed in the absence of the palladium complex.¹¹ Besides simple benzyne, 4-substituted benzyne (from **2b–2d**) and 4,5-disubstituted benzyne (from **2e** or **2f**) also gave good to high yields of the corresponding bissilylation products (entries 2–6). On the other hand, the reaction of 3-substituted benzyne (from **2g–2i**) and 1,2-naphthalene (from **2j**) was rather sluggish to provide the products in 30–40% yields, probably due to the steric hindrance around the triple bond of the arynes (entries 7–10). It should be noted that

Table 1. Palladium-Catalyzed Bissilylation of Arynes with **1a**^a

entry	R in 2	precursor	time (h)	yield (%) ^b	product
1	H	2a	1.5	66	3aa
2	5-Me	2b	1.5	72	3ab
3	4-MeO	2c	1.5	75	3ac
4	4-Ph	2d	3	54	3ad
5	4,5-Me ₂	2e	1.5	77	3ae
6	4,5-(CH ₂) ₃ –	2f	1.5	76	3af
7	6-Me	2g	3	40	3ag
8	3-MeO	2h	3	37	3ah
9	6-Ph	2i	3	30	3ai
10	3,4-(CH) ₄ –	2j	3	33	3aj
11	3,4-(MeO) ₂	2k	24	63	3ak
12	3,6-(MeO) ₂	2l	3	72	3al

^a The reaction was carried out in THF (1.0 mL) at 20 °C using **1a** (0.40 mmol), an aryne precursor (0.60 mmol), KF (1.2 mmol), and 18-crown-6 (1.2 mmol) in the presence of Pd(OAc)₂ (8.0 μ mol) and *t*-OcNC (0.12 mmol). ^b Isolated yield based on **1a**.

Scheme 1



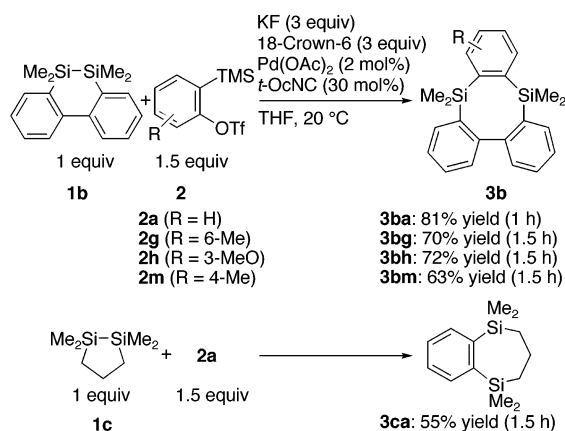
3,4-dimethoxybenzyne (from **2k**) and 3,6-dimethoxybenzyne (from **2l**) reacted smoothly with **1a** to give the insertion products in 63% and 72% yields, despite their steric congestion (entries 11 and 12), which may be attributed to the enhanced kinetic stability of the aryne induced by the two electron-withdrawing methoxy groups ($-I$ effect),¹² although examples to support this stabilizing effect remain to be found.

Furthermore, the present reaction was also applicable to a six-membered cyclic disilane (1,1,2,2-tetramethyl-1,2-(2,2'-biphenylene)disilane, **1b**) and 1,1,2,2-tetramethyl-1,2-disilacyclopentane (**1c**), giving an eight-membered disilacarbocycle, 1,6-dihydrotribenzo-[1,4]disilocene (**3b**), and benzodisilapine (**3ca**), respectively (Scheme 2). In the case of **1b**, the yields of the insertion products were relatively higher irrespective of the substitution patterns of the arynes employed. In marked contrast to the reaction of **1a–1c**, a four-membered cyclic disilane (1,1,2,2-tetraethyl-1,2-(1,2-phenylene)disilane) decomposed in the reaction with **2a** through the fluoride ion attack on the disilane. No insertion product was generated in the reaction of 1,1,2,2-tetramethyl-1,2-disilacyclohexane or an acyclic disilane (hexamethyldisilane or 1,2-diphenyltetramethyldisilane) with **2a**, where the starting disilane was recovered intact.

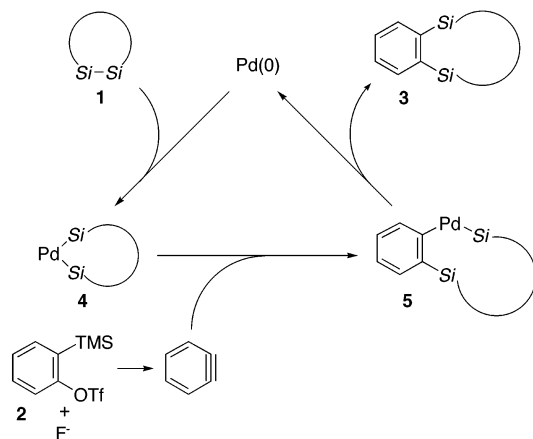
Although details of the reaction mechanism remain unclear at present, a plausible catalytic cycle is depicted in Scheme 3. First, complex **4** is formed through oxidative addition of the silicon–

[†] Present address: Institute for Fundamental Research of Organic Chemistry, Kyushu University, Fukuoka 812-8581, Japan.

Scheme 2



Scheme 3



silicon bond of **1** to the palladium(0) complex, which is widely accepted as the initiation step of catalytic bissylations of unsaturated organic compounds.¹³ Subsequent insertion of an in situ-generated aryne into the silicon–palladium bond of **4** produces arylpalladium complex **5**, which then undergoes reductive elimination to provide bissilylation product **3** with regeneration of the palladium(0) complex.

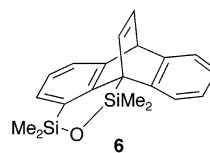
In conclusion, we have disclosed that the palladium-catalyzed bissilylation of arynes with cyclic disilanes offered diverse benzoannulated disilacarbo-cycles, which would be potentially valuable as a new functionality molecule such as siloles.¹⁴ Further studies on synthetic applications to various organodisilanes and other interelement linkages¹⁵ as well as on the reaction mechanism are in progress.

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

References

- (1) For reviews, see: (a) Hoffmann, R. W. *Dehydrobenzene and Cycloalkynes*; Academic Press: New York, 1967. (b) Hart, H. In *The Chemistry of Triple-Bonded Functional Groups, Supplement C2*; Patai, S., Ed.; Wiley: Chichester, U.K., 1994; Chapter 18. (c) Gilchrist, T. L. In *The Chemistry of Functional Groups, Supplement C2*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1983; Chapter 11.
- (2) For reviews, see: (a) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047. (b) Buchwald, S. L.; Broene, R. D. In *Comprehensive Organometallic Chemistry II*; Able, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 12, pp 771–784. (c) Bennett, M. A.; Schwemlein, H. P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1296. (d) Bennett, M. A.; Wenger, E. *Chem. Ber.* **1997**, *130*, 1029.
- (3) (a) Peña, D.; Escudero, S.; Pérez, D.; Guitián, E.; Castedo, L. *Angew. Chem., Int. Ed.* **1998**, *37*, 2659. (b) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *Org. Lett.* **1999**, *1*, 1555. (c) Peña, D.; Cobas, A.; Pérez, D.; Guitián, E.; Castedo, L. *Org. Lett.* **2000**, *2*, 1629.
- (4) (a) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *J. Am. Chem. Soc.* **1999**, *121*, 5827. (b) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *Synlett* **2000**, 1061. (c) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *J. Org. Chem.* **2000**, *65*, 6944.
- (5) (a) Radhakrishnan, K. V.; Yoshikawa, E.; Yamamoto, Y. *Tetrahedron Lett.* **1999**, *40*, 7533. (b) Yoshikawa, E.; Radhakrishnan, K. V.; Yamamoto, Y. *Tetrahedron Lett.* **2000**, *41*, 729. (c) Yoshikawa, E.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2000**, *39*, 173. (d) Yoshikawa, E.; Radhakrishnan, K. V.; Yamamoto, Y. *J. Am. Chem. Soc.* **2000**, *122*, 7280.
- (6) Chatani, N.; Kamitani, A.; Oshita, M.; Fukumoto, Y.; Murai, S. *J. Am. Chem. Soc.* **2001**, *123*, 12686.
- (7) For reviews on the addition of element–element σ -bonds to unsaturated organic compounds, see: (a) Beletskaya, I.; Moberg, C. *Chem. Rev.* **1999**, *99*, 3435. (b) Sugimoto, M.; Ito, Y. *Chem. Rev.* **2000**, *100*, 3221.
- (8) Yoshida, H.; Honda, Y.; Shirakawa, E.; Hiyama, T. *Chem. Commun.* **2001**, 1880.
- (9) For pioneering works on the bissilylation of unsaturated organic compounds, see: (a) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 26. (b) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Organomet. Chem.* **1975**, *86*, C27. (c) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1975**, *97*, 932. (d) Tamao, K.; Hayashi, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *114*, C19. (e) Ito, Y.; Sugimoto, M.; Murakami, M. *J. Org. Chem.* **1991**, *56*, 1948. (f) Sugimoto, M.; Yamamoto, Y.; Fujii, K.; Ito, Y. *J. Am. Chem. Soc.* **1995**, *117*, 9608. (g) Sugimoto, M.; Matsumoto, A.; Ito, Y. *J. Am. Chem. Soc.* **1996**, *118*, 3061.
- (10) Himeshima, Y.; Sonoda, T.; Kobayashi, H. *Chem. Lett.* **1983**, 1211.
- (11) In this case, trace amounts of compound **6** were formed through the Diels–Alder reaction of **1a** with benzyne, followed by oxidation of the Si–Si bond.



- For the Diels–Alder reaction of naphthalene with benzyne, see: (a) Miller, R. G.; Stiles, M. *J. Am. Chem. Soc.* **1963**, *85*, 1798. (b) Serratos, J. F. F.; Vilarrasa, L. *Tetrahedron Lett.* **1969**, 4743.
- (12) (a) Gaviña, F.; Luis, S. V.; Costero, A. M.; Gil, P. *Tetrahedron* **1986**, *42*, 155. (b) Kessar, S. V. In *Comprehensive Organic Synthesis*, Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 4, pp 483–515.
 - (13) Sugimoto, M.; Oike, H.; Park, S.-S.; Ito, Y. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 289.
 - (14) (a) Yamaguchi, S.; Tamao, K. *J. Chem. Soc., Dalton Trans.* **1998**, 3693. (b) Adachi, A.; Ohshita, J.; Kunai, A.; Okita, K.; Kido, J. *Chem. Lett.* **1998**, 1233.
 - (15) The Chemistry of Interelement Linkage. *J. Organomet. Chem.* **2000**, *611*, 1.

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