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Rhodium-Catalyzed Synthesis of Germoles via the Activation of Carbon−Germanium Bonds

Mamoru Tobisu,[*,‡] Katsuaki Baba,[†] and Naoto Chatani[*,†]

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan, and Center for Atomic and Molecular Technologies, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

tobisu@chem.eng.osaka-u.ac.jp; chatani@chem.eng.osaka-u.ac.jp

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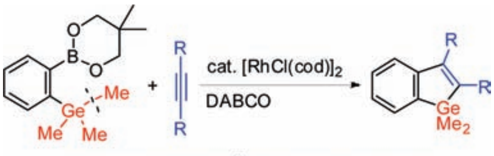
ABSTRACT



germoles via C(sp^3)-Ge bond activation

The rhodium-catalyzed reaction of 2-germylphenylboronic esters with alkynes in the presence of a rhodium(I) catalyst is established as a modular method for the synthesis of an array of benzogermole derivatives. The reaction proceeds through the activation of C(sp^3)−Ge bonds. The mechanism of this new bond activation process is discussed based on the activation aptitude of alkyl and aryl substituents on germanium.

The activation of C−E bonds (E = Si, Ge, Sn, Pb) by transition metal complexes is a fundamental process in organometallic chemistry and is involved, for instance, in a transmetalation step of cross-coupling reactions.[1−4] The activation of C−E bonds, especially where E = Si and Ge, normally requires the addition of an internal or external Lewis base to convert the tetracoordinated group 14 elements into a more reactive hypervalent state.[1a,c,2,5] By contrast, this group recently reported a catalytic reaction that involved the activation of C−Si bonds without forming a discrete hypervalent silicate species.[6] In this catalytic reaction, C(sp^3)−Si and C(sp^2)−Si bonds are activated comparably, which is an eminent feature that differs from the activation process via silicates.[7] Motivated by the desire to verify the generality of rhodium-mediated C−Si bond activation, comparable studies have been conducted using germanium, a heavier congener. However, the development of such catalytic reactions involving C−Ge bond activation poses a daunting challenge, when recognizing the fact that organogermanes are less effective transmetalating agents than silanes and stannanes even in the presence of Lewis basic activators.[2b] The present paper describes the activation of C(sp^3)−Ge bonds in the rhodium-catalyzed annulation of 2-germylphenylboronic esters and alkynes. Although several catalytic reactions

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[‡] Center for Atomic and Molecular Technologies.

[†] Department of Applied Chemistry.

(1) For leading references on the C−Si bond cleavage in coupling reactions, see: (a) Hiyama, T.; Shirakawa, E. *Top. Curr. Chem.* **2002**, *219*, 61. (b) Denmark, S. E.; Regens, C. S. *Acc. Chem. Res.* **2008**, *41*, 1486. (c) Chen, J.; Tanaka, M.; Sahoo, A. K.; Takeda, M.; Yada, A.; Nakao, Y.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **2010**, *83*, 554.

(2) For selected catalytic reactions involving the cleavage of C−Ge bonds, see: (a) Kosugi, M.; Tanji, T.; Tanaka, Y.; Yoshida, A.; Fugami, K.; Kameyama, M.; Migita, T. *J. Organomet. Chem.* **1996**, *508*, 255. (b) Spivey, A. C.; Gripton, C. J. G.; Hannah, J. P.; Tseng, C.-C.; de Fraine, P.; Parr, N. J.; Scicinski, J. J. *Appl. Organomet. Chem.* **2007**, *21*, 572. (c) Pitteloud, J.-P.; Zhang, Z.-T.; Liang, Y.; Cabrera, L.; Wnuk, S. F. *J. Org. Chem.* **2010**, *75*, 8199.

(3) For a leading review on the mechanism of C−Sn bond cleavage in the Migita−Kosugi−Stille coupling reaction, see: Espinet, P.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 4704.

(4) For selected catalytic reactions involving the cleavage of C−Pb bonds, see: (a) Kang, S.-K.; Choi, S.-C.; Ryu, H.-C.; Yamaguchi, T. *J. Org. Chem.* **1998**, *63*, 5748. (b) Ding, R.; Chen, Y.-J.; Wang, D.; Li, C.-J. *Synlett* **2001**, 1470.

(5) For a notable exception, in which C−Si bond activation in metal silanolates has been proposed to proceed without forming pentacoordinated silicate species, see ref 1b.

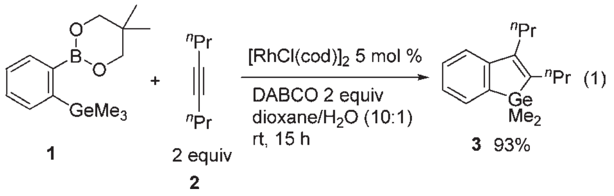
(6) (a) Tobisu, M.; Onoe, M.; Kita, Y.; Chatani, N. *J. Am. Chem. Soc.* **2009**, *131*, 7506. For related processes, see:(b) Ojima, I.; Fracchiolla, D. A.; Donovan, R. J.; Banerji, P. *J. Org. Chem.* **1994**, *59*, 7594. (c) Matsuda, T.; Suda, Y.; Fujisaki, Y. *Synlett* **2011**, 813. (d) Liang, Y.; Zhang, S.; Xi, Z. *J. Am. Chem. Soc.* **2011**, in press; doi: 10.1021/ja2024959.

(7) (a) Wang, Z.; Fang, H.; Xi, Z. *Tetrahedron Lett.* **2005**, *46*, 499. (b) Hudrlik, P. F.; Dai, D.; Hudrlik, A. M. *J. Organomet. Chem.* **2006**, *691*, 1257.

10.1021/ol201251e

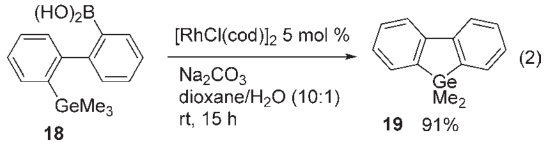
involving the activation of C(sp^2)−Ge bonds exist,[2] the corresponding activation of unactivated C(sp^3)−Ge bonds has never been attained with the exception of one specific reaction using trimethylgermyl cyanide.[8,9]

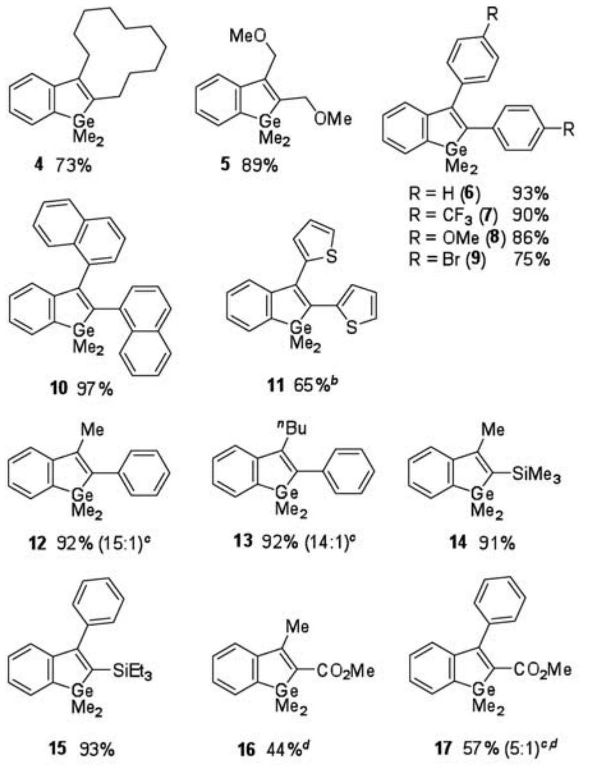
The reaction of 2-trimethylgermylphenylboronic ester **1** with alkyne **2** in the presence of a rhodium catalyst under the conditions typical for the generation of arylrhodium species from arylboron derivatives[10,11] furnished benzogermole **3** in excellent yield (eq 1).[12] The cleavage of a Me−Ge bond proceeded at ambient temperature, which contrasts with the requirement of an elevated temperature for the activation of even weaker C(sp^2)−Ge bonds in pentacoordinated germanates.[2]



The rhodium-catalyzed C−Ge bond activation reaction proved to be applicable to the synthesis of a diverse array of benzogermoles, all of which were previously unknown compounds and were otherwise difficult to prepare (Figure 1).[13] In addition to simple aliphatic alkynes, such as **2**, cyclic and oxygenated aliphatic alkynes also participated in this rhodium-catalyzed cyclization to form germoles **4** and **5**, respectively. Aromatic alkynes successfully underwent the reaction irrespective of the electronic and steric nature of the substituents (**6**, **7**, **8**, **9**, and **10**). Notably, bromide remained intact, as in **9**, which allows for further structural modification through, for example, cross-coupling reactions. Germoles bearing heteroaromatics (**11**) can be synthesized by this rhodium catalysis. Several sets of unsymmetrical internal alkynes delivered the corresponding germoles in a regioselective fashion. In the case of alkynes bearing phenyl and alkyl groups, a phenyl group was selectively incorporated at the 2-position of the germole ring (**12** and **13**). Silyl (**14** and **15**) and ester (**16** and **17**) groups are also suitable directors to deliver 2,3-disubstituted germoles bearing these groups at the 2-position irrespective of the C-3 substituents. The regioselectivity observed in the present study is consistent with that obtained in the reported catalytic reactions involving the addition of arylrhodium to alkynes.[10]

The rhodium-catalyzed C−Ge bond activation can be exploited for the construction of a dibenzogermole skeleton by using boronic acid **18** (eq 2).





[a] Reaction conditions: **1** (0.50 mmol), alkyne (1.0 mmol), $[RhCl(cod)]_2$ (0.025 mmol), and DABCO (1.0 mmol) in dioxane (1 mL) and H_2O (0.1 mL) at 80 °C for 15 h. Isolated yields based on **1** are shown. [b] Run at 100 °C for 72 h using $[RhCl(cod)]_2$ (0.050 mmol). [c] Ratio of regioisomers. [d] Run at 100 °C using alkyne (2.5 mmol), $[RhCl(cod)]_2$ (0.050 mmol), and Na_2CO_3 in place of DABCO.

Figure 1. Scope of the reaction.[a]

The scope of the present C−Ge bond activation with respect to the substituent on the germanium was next investigated (Table 1). A bulkier triethylgermyl group underwent rhodium-catalyzed annulation to afford the corresponding germole **21**. In the case where the germanium bears both methyl and benzyl groups, as in **22**, a Me−Ge bond was exclusively cleaved to form germole **23**. This observation indicates that the reactivity is largely determined by a steric factor.[14] Importantly, Ph−Ge and Me−Ge bonds were activated competitively, as exemplified by

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[8] Chatani, N.; Morimoto, T.; Muto, T.; Murai, S. *J. Organomet. Chem.* **1994**, *473*, 335.

[9] Activated C(sp^3)−Ge bonds in allylgermanium reagents can be cleaved in the presence of Lewis acids: Akiyama, T. In *Main Group Metals in Organic Synthesis*; Yamamoto, H., Oshima, K., Eds.; Wiley-VCH: Weinheim, 2004; pp 593−619.

[10] (a) Fagnou, K.; Lautens, M. *Chem. Rev.* **2003**, *103*, 169. (b) Hayashi, T.; Yamasaki, K. *Chem. Rev.* **2003**, *103*, 2829. (c) Miura, T.; Murakami, M. *Chem. Commun.* **2007**, 217.

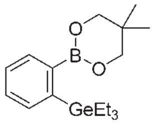
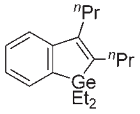
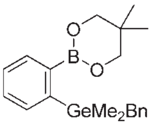
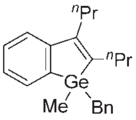
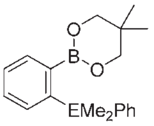
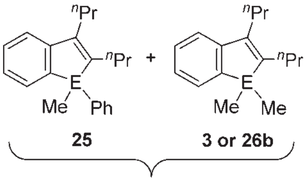
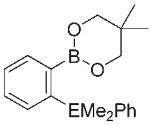
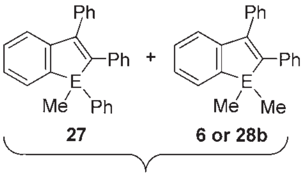
[11] DABCO serves as a base to generate a catalytically active Rh−OH species (see ref 10). The formation of hypervalent germanate species by the coordination of DABCO is unlikely under these conditions because (1) the boron atom in **1** is much more Lewis acidic to accept DABCO and (2) at least one halogen atom on the germanium center is reported to be required for the formation of pentacoordinated germanates using a fluoride activator (see ref 2c).

[12] For other catalytic synthesis of germoles, see: (a) Tsumuraya, T.; Ando, W. *Organometallics* **1990**, *9*, 869. (b) Brauer, H.; Neumann, W. P. *Synlett* **1991**, 431. (c) Matsuda, T.; Kadowaki, S.; Yamaguchi, Y.; Murakami, M. *Org. Lett.* **2010**, *12*, 1056. (d) Lesbani, A.; Kondo, H.; Yabusaki, Y.; Nakai, M.; Yamanoi, Y.; Nishihara, H. *Chem.—Eur. J.* **2010**, *16*, 13519.

[13] In the present study, reactions were routinely conducted at 80 °C, since several alkynes produced germoles in lower yields at room temperature.

the reaction using **24a**. These results are in sharp contrast to the palladium-catalyzed reaction of pentacoordinated $PhMe_2GeF_2^-$ species, wherein a Ph–Ge bond is exclusively activated.[2b] The relative reactivity of Ph–Ge/Me–Ge bonds in this rhodium catalysis was dependent on the structure of the alkyne coupled: the larger alkyne substituent increased the ratio of Me–Ge cleavage (entry 3 vs 5). Interestingly, the corresponding silicon derivatives exhibited a greater tendency to Me–Si cleavage over Ph–Si (entry 3 vs 4, entry 5 vs 6).

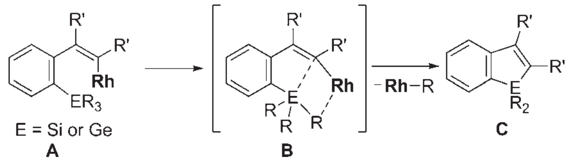
Table 1. Effect of the Substituents on Germanium[a]

entry	starting material	products
1	 **20**	 **21** 68%
2	 **22**	 **23** 83%
3 4	 **24**	 **25** + **3 or 26b** E = Ge (**a**) 88% (**25a**:**3** = 1:2.6) E = Si (**b**) 62% (**25b**:**26b** =1:1.5)[b]
5 6	 **24**	 **27** + **6 or 28b** E = Ge (**a**) 98% (**27a**:**6** = 1:1.6)[b] E = Si (**b**) 93% (**27b**:**28b** =1.5:1)[b]

[a] Reaction conditions: boronic ester (0.50 mmol), alkyne (1.0 mmol), $[RhCl(cod)]_2$ (0.025 mmol), and DABCO (1.0 mmol) in dioxane (1 mL) and H_2O (0.1 mL) at 80 °C for 15 h. Isolated yields based on boronic esters are shown. [b] NMR yield based on a boronic ester.

On the basis of the reactivity profile of a $PhMe_2Ge$ group, C–Ge bond activation is likely to proceed via a σ-bond metathesis-like concerted pathway (**B** in Scheme 1, E = Ge), rather than through a hypervalent germanate intermediate. A larger alkyne substituent R′ imposes an increased steric demand around a rhodium center in **A**, which may lead to the greater preference to interact with smaller substituent R in **B**.[15] The difference in Me/Ph cleavage ratio between germanium and silicon can be attributed to the difference in the bond length ($Me-SiMe_3$, 1.875 Å;[16] $Me-GeMe_3$, 1.945 Å[17]). Due to the slightly shorter C–Si bond length, silicon derivatives are more susceptible to the steric bulk, compared to germanium; therefore a smaller methyl group is activated more favorably.

Scheme 1. A Possible Mechanistic Pathway



In conclusion, the rhodium-catalyzed annulation reaction of 2-germylphenylboronic esters with alkynes is described. The method provides a rapid access to a diverse range of germoles simply by changing the alkyne structure. Given the fact that germoles are known to exhibit unique photophysical properties,[12c,d,18] the protocol described herein should facilitate the identification of potent organic materials.[19] More importantly, the reaction involves the activation of $C(sp^3)$–Ge bonds, a process which remained unexplored to date. Fundamental insight into this intriguing bond activation has been gained from the investigation into the activation aptitude of the substituents on germanium and from the comparable reactivity study of the silicon counterparts. Efforts to develop additional catalytic reactions involving C–Ge and C–Si bond activations are in progress.

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Supporting Information Available. Experimental procedures and full spectroscopic data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) A benzyl group is expected to be cleaved more facilely if a pentacoordinate germanate intermediate is involved based on the reactivity of corresponding silanes. See refs 2b and 7b.

(15) Electronic factors of alkynes may also affect the Me/Ph cleavage ratio.

(16) Beagley, B.; Monaghan, J. J.; Hewitt, T. G. *J. Mol. Struct.* **1971**, *8*, 401.

(17) Hencher, J. L.; Mustol, F. J. *Can. J. Chem.* **1975**, *53*, 3542.

(18) A review: (a) Dubac, J.; Laporterie, A.; Manuel, G. *Chem. Rev.* **1990**, *90*, 215. Selected examples:(b) Yamaguchi, S.; Itami, Y.; Tamao, K. *Organometallics* **1998**, *17*, 4910. (c) Tracy, H. J.; Mullin, J. L.; Klooster, W. T.; Martin, J. A.; Haug, J.; Wallace, S.; Rudloe, I.; Watts, K. *Inorg. Chem.* **2005**, *44*, 2003.

(19) A preliminary study revealed that some of the benzogermoles synthesized exhibited intense photoluminescence in the solid state. See Supporting Information for details.