Intramolecular Coupling of Alkynyl Groups of Bis(alkynyl)silane Mediated by Zirconocene Compounds: Formation of Silacyclobutene Derivatives[†]

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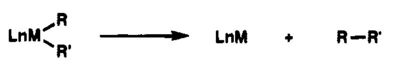
Carbon–carbon bond-forming reaction from diorganometal compounds has been well known for transition metals (eq 1).[2]

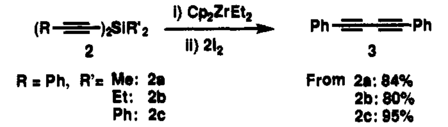


$$L_nM{<}^{R}_{R'} \longrightarrow L_nM + R{-}R' \qquad (1)$$

However, this type of reaction has been very rare for diorganosilicon compounds, to the best of our knowledge.[3]

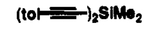
Recently we investigated the selective stoichiometric or catalytic reactions of the zirconocene–ethylene complex $Cp_2Zr(CH_2{=}CH_2)$ (**1**) formed in situ from Cp_2ZrEt_2.[4,5] During the course of our study on the reaction of **1** with silylacetylenes, we found an interesting coupling reaction of alkynyl groups of bis(alkynyl)silanes. In this paper we report a novel intramolecular coupling reaction of bis(alkynyl)silane and a formation of silacyclobutene derivatives.

Treatment of bis(alkynyl)silane **2** (R = Ph, R′ = Me (**2a**), Et (**2b**), Ph (**2c**)) with Cp_2ZrEt_2 and iodine in this order gave diphenyldiyne **3** in high yields (eq 2). We recently reported that



(2)

the reaction of **1** with a silylacetylene such as 1–(trimethylsilyl)–1–propyne produced a coupling product of the acetylene with an ethylene as a zirconacyclopentene derivative.[5f] However, no incorporation of ethylene was observed in the reaction product of **1** with **2a–c** as shown in eq 2. When a mixture of a phenyl-substituted bis(alkynyl)silane **2a** and a tolyl-substituted **4** was used, only *intra*molecular coupling diynes **3** and **5** were observed. Formation of an *inter*molecular coupling product **6** was not detected.



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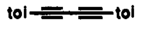

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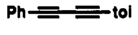

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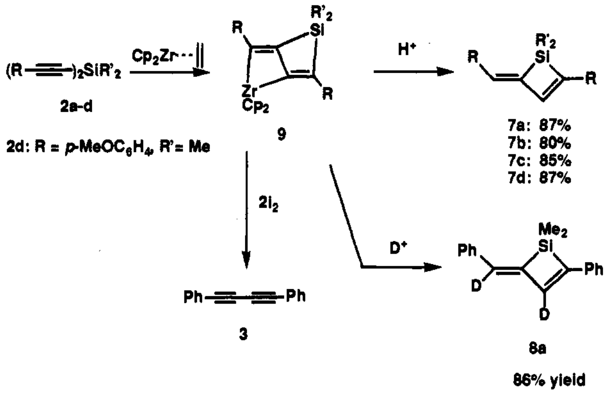
In order to understand the mechanism, we investigated the reaction mixture of **2a–c** with Cp_2ZrEt_2. Very interestingly, silacyclobutene derivatives **7** were formed in high yields after hydrolysis (Scheme 1). The ^1H NMR spectrum of **7a** indicated two singlets at 6.70 and 7.70 ppm assignable to PhC*H*=C and –C*H*=C(Ph)Si, respectively. Its ^{13}C NMR spectrum showed two trisubstituted olefinic carbons at 146.15 and 158.51 ppm assignable to two ring carbons, Ph*C*Si and =*C*Si, respectively, and two methine carbons at 128.86 and 149.02 ppm assignable to PhCH= and a ring carbon –*C*H=C, respectively. The two trisubstituted olefinic carbons had a satellite due to ^{29}Si. Long-range coupling study also indicated the coupling of the two trisubstituted olefinic carbons with methyl protons on silicon. These data were reasonable compared with those of silacyclobutenes reported so far, which showed a proton –C*H*=CSi in the ring system at 7.12–7.16 ppm in their ^1H NMR spectra, an olefin carbon attached to Si at 132–142 ppm, and a signal for –*C*H= at 152–157 ppm in their ^{13}C NMR spectra.[6]

Scheme 1



Deuterolysis of the reaction mixture afforded deuterated compounds **8a** in 86% yield with >99% of deuterium incorporation. This result strongly suggested that the zirconium-containing intermediate was the fused ring compounds **9**. In fact, the NMR spectra of the reaction mixtures of **2a** and **2c**

[†] Dedicated to Professor Ei-ichi Negishi on the occasion of his 60th birthday.

[1] Visiting research student from Gifu University (1993, IMS).

(2) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980.

(3) (a) Birkofer, L.; Haddad, H. *Chem. Ber.* **1969**, *102*, 432–434. (b) Barton, T. J.; Kippenhan, R. C., Jr.; Nelson, A. J. *J. Am. Chem. Soc.* **1974**, *96*, 2272–2273. (c) Puranik, D. B.; Fink, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 5951–5952. (d) It is known that some special silyl compounds containing a Si–Si bonds such as $(R_3Si){-}SiR'_2{-}X$ gave $R_3Si{-}X$ along with the formation of silylene compounds either under irradiation or by pyrolysis. See: Brook, A. G. In *The Chemistry of Organic Silicon Compounds. Part 2*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; p 965. For recent work on the formation of a double bond from silacyclopropane, see also: (e) Boudjouk, P.; Black, E.; Kumarathasan, R. *Organometallics* **1991**, *10*, 2095–2096. (f) Dickinson, A. P.; O'Neal, H. E.; Ring, M. A. *Organometallics* **1991**, *10*, 3513–3520.

(4) For preparation of zirconocene–ethylene complexes by the reaction of Cp_2ZrCl_2 with EtMgBr, see: (a) Takahashi, T.; Murakami, M.; Kunishige, M.; Saburi, M.; Uchida, Y.; Kozawa, K.; Uchida, T.; Swanson, D. R.; Negishi, E. *Chem. Lett.* **1989**, 761–764. (b) Takahashi, T.; Nitto, Y.; Seki, T.; Saburi, M.; Negishi, E. *Chem. Lett.* **1990**, 2259–2262. (c) Takahashi, T.; Suzuki, N.; Kageyama, M.; Nitto, Y.; Saburi, M.; Negishi, E. *Chem. Lett.* **1991**, 1579–1582. (d) Takahashi, T.; Kasai, K.; Suzuki, N.; Nakajima, K.; Negishi, E. *Organometallics* **1994**, *13*, 3413–3414. See also: (e) Binger, P.; Müller, P.; Berm, R.; Rufinska, A.; Gabor, B.; Krüger, C.; Betz, P. *Chem. Ber.* **1989**, *122*, 1035.

(5) For selective reactions using **1**, see: (a) Takahashi, T.; Seki, T.; Nitto, Y.; Saburi, M.; Rousset, C. J.; Negishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 6266–6268. (b) Takahashi, T.; Hasegawa, M.; Suzuki, N.; Saburi, M.; Rousset, C. J.; Negishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 8564–8566. (c) Takahashi, T.; Suzuki, N.; Hasegawa, M.; Nitto, Y.; Aoyagi, K.; Saburi, M. *Chem. Lett.* **1992**, 331–334. (d) Takahashi, T.; Aoyagi, K.; Hara, R.; Suzuki, N. *Chem. Lett.* **1992**, 1693–1696. (e) Takahashi, T.; Xi, Z.; Rousset, C. J.; Suzuki, N. *Chem. Lett.* **1993**, 1001–1004. (f) Takahashi, T.; Kageyama, M.; Denisov, V.; Hara, R.; Negishi, E. *Tetrahedron Lett.* **1993**, *34*, 687–690. (g) Suzuki, N.; Kondakov, D.; Takahashi, T. *J. Am. Chem. Soc.* **1993**, *115*, 8485–8486. (h) Takahashi, T.; Aoyagi, K.; Denisov, V.; Suzuki, N.; Choueiry, D.; Negishi, E. *Tetrahedron Lett.* **1993**, *51*, 8301–8304. (i) Takahashi, T.; Kondakov, D. Y.; Suzuki, N. *Chem. Lett.* **1994**, 259–262. (j) Suzuki, N.; Aoyagi, K.; Kotora, M.; Hasegawa, M.; Nitto, Y.; Saburi, M.; Takahashi, T. *J. Organomet. Chem.* **1994**, *473*, 117–128.

(6) (a) Block, E.; Revelle, L. K. *J. Am. Chem. Soc.* **1978**, *100*, 1630–1631. (b) Valkovich, P. B.; Weber, W. P. *Tetrahedron Lett.* **1975**, 2153–2154. (c) Gilman, H.; Atwell, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 2678–2683. For a review of silacyclobutenes, see: (d) George, M. V.; Balasubramanian, R. *J. Organomet. Chem. Libr.* **1976**, 2, 103–275. A similar type of silacyclobutene derivative, 1-mesityl-3-phenyl-2-[phenyl(trimethylsilyl)methylene]-1,4-bis(trimethylsilyl)-1-silacyclobut-3-ene, was prepared by a reaction of a 1-silapropadiene–nickel complex with phenyl(trimethyl)acetylene, see: Ishikawa M.; Ohshita, J.; Ito, Y. *Organometallics* **1986**, *5*, 1518–1519.

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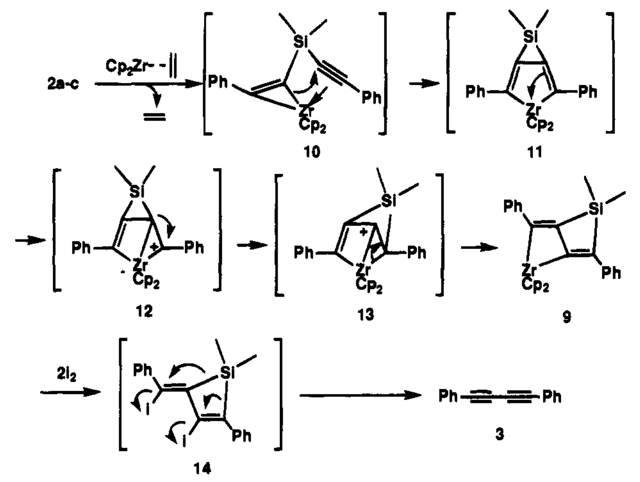
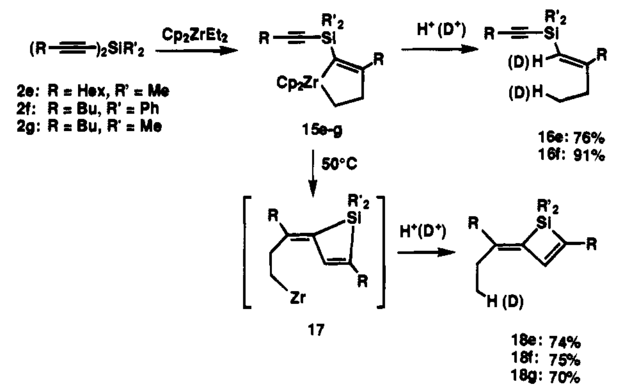
Scheme 2



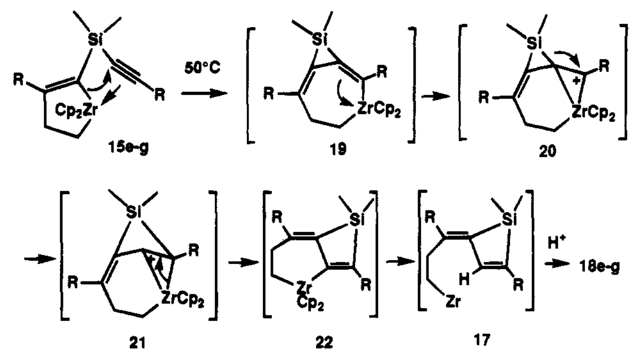
with Cp$_2$ZrEt$_2$ indicated a clean formation of **9a** and **9c**, respectively. Their ^{1}H NMR showed one Cp signal at 5.74 ppm for **9a** and at 5.81 ppm for **9c**. The ^{13}C NMR spectra revealed four trisubstituted olefinic carbons at 203.46, 162.41, 143.00, and 141.26 ppm for **9a** and at 204.00, 160.70, 145.00, and 142.52 ppm for **9c**. Iodination of these complexes gave diphenyldiyne **3** in a high yield. A 4,4 fused bicyclic complex with two Ti metal atoms similar to **9** has been prepared by the reaction of $(MeC_5H_4)_2TiCl$ with sodium phenylacetylide or the reaction of $(MeC_5H_4)_2Ti$ with 1,4-diphenylbutadiyne.[7]

A plausible mechanism is shown in Scheme 2 which involves (i) a replacement of an ethylene ligand of **1** by an alkynyl group of **2a–c** to form a zirconacyclopropene compound, (ii) an insertion of the second alkynyl group of **2a–c** into a Zr–C bond of the zirconacyclopropene to form **11**,[8] and (iii) 1,2-migration of a silyl group from **12** to **13** leading to **9**. Finally, (iv) iodination of **9** affords a diiodide species as an intermediate followed by an elimination of silyl and iodine groups to give diphenyldiyne **3**.

Scheme 3



Scheme 4



For alkyl-substituted bis(alkynyl)silanes **2e–g**, the reaction with Cp$_2$ZrEt$_2$ at room temperature afforded zirconacyclopentenes **15e–g** as expected (Scheme 3). Hydrolysis or deuterolysis of **15e–g** afforded **16e–g** in high yields. In this reaction, only one of two alkynyl groups of **2e–g** reacted with high regioselectivity (>98%) as usual. Interestingly, after the treatment of **15e–g** in the reaction mixture at 50 °C for 3 h, hydrolysis of the mixture gave silacyclobutene derivatives **18e–g** in 74%, 75%, and 70% yields, respectively. ^{1}H NMR spectrum of **18e** showed one singlet at 7.22 ppm assignable to $-CH{=}CSiR'$ in the ring. Its ^{13}C NMR spectrum showed three trisubstituted olefinic carbons at 160.10, 138.17, and 137.27 ppm assignable to $={C}Si$, Et(Hex)$C{=}C$, and Hex$C$Si, respectively. First and third trisubstituted olefinic carbons had a satellite due to ^{29}Si. One signal assigned to a methine carbon in a ring appeared at 147.37 ppm in its ^{13}C NMR spectrum. These data were consistent with those of silacyclobutene derivatives described above. Deuterolysis of the reaction mixture afforded only a monodeuterated compound at the methyl carbon of the ethyl group in 74% yield with >99% deuterium incorporation. Dideuterated compounds were not obtained. The zirconium-containing intermediate **17** might have one zirconium–carbon bond. Iodination of **17** did not give diynes. Unfortunately, NMR spectra of the mixture after heating were not clean; however, a similar insertion reaction of an alkynyl group of **15** into a Zr–C bond of a zirconacyclopentene moiety might proceed along with 1,2-migration of the silyl group, as shown in Scheme 4.

Further investigation in this area is in progress to elucidate the reaction mechanism.

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Supplementary Material Available: Experimental details for the coupling reactions (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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