Organometallics **2001,** *20,* 5537−5541

Palladium-Catalyzed Double-Silylation Reactions of 3,4-Carboranylene-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene

Kyu Ho Song,[†] Il Jung,[†] Shim Sung Lee,[‡] Ki-Min Park,[‡] Mitsuo Ishikawa,[§]
Sang Ook Kang,*[,†] and Jaejung Ko*[,†]

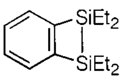
Department of Chemistry, Korea University, Chochiwon, Chungnam 339-700, Korea, Department of Chemistry, and Institute of Natural Sciences, Gyeongsang National University, Chinju 660-701, Korea, and Department of Chemical Technology, Kurashiki University of Science and the Arts, 2640 Nishinoura, Tsurajima-cho, Kurashiki, Okayama 712-8505, Japan

Received June 20, 2001

The reaction of the 1,2-dilithiated *o*-carborane with 1,2-dichlorotetraethyldisilane yielded the strained 3,4-carboranylene-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene (**2**), which was found to be a good reactant for the double-silylation reaction. Thus, the reaction of **2** with RC≡CR′ in the presence of a catalytic amount of Pd(PPh$_3$)$_4$ yielded the six-membered disilyl ring compounds $B_{10}H_{10}C_2(SiEt_2)_2(RC{=}CR')$ (R = Ph, R′ = H (**6**); R = Ph, R′ = CH$_3$ (**7**); R = R′ = COOCH$_3$ (**8**); R = C$_4$H$_9$, R′ = H (**9**)). The palladium-catalyzed reaction of **2** with 4-nitrobenzaldehyde afforded 5,6-carboranylene-2-oxa-1,4-disilacyclohex-5-ene (**10**). In contrast, the reaction of **2** with *trans*-cinnamaldehyde under the same reaction conditions yielded the insertion compound **11** formed via insertion of a carbonyl group into each of the C−Si bonds of **2**. The structures of compounds **2**, **6**, and **11** were determined by single-crystal X-ray crystallography.

Introduction

Recently, we found that 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene (**1**) displayed interesting chemical behavior with organic substrates such as aromatic compounds, carbonyl compounds, alkenes, and alkynes in the presence of a metal catalyst.[1] We have also described the double-silylation reaction of a variety of unsaturated organic substrates with cyclic bis(silyl)-metal complexes containing an *o*-carboranylene.[2] Accordingly, it seemed interesting to investigate the chemical behavior of the 3,4-carboranylene-1,1,2,2-tetraethyl-1,2-disilacyclo-but-3-ene (**2**) with a carboranyl unit toward unsaturated organic substrates in the presence of a transition metal catalyst because *o*-carborane has been described as “superaromatic” due to the delocalized nature of the bonding in the framework.[3] We now report the synthesis and reactivity of 3,4-carboranylene-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene (**2**).



1

2

Results and Discussion

Preparation of 2. The 3,4-carboranylene-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene (**2**) was readily prepared by a method similar to that reported by de Rege.[4] Thus, the 1,2-dilithiated carborane[5] generated by the reaction of *n*-BuLi with *o*-carborane reacted with 1,2-dichlorotetraethyldisilane to give **2** in 53% yield (eq 1). The colorless product **2** was a crystalline solid that was relatively stable in air and to brief heating to 110−120 °C. Compound **2** is readily soluble in hexane, toluene, and THF. The structure of **2**, unambiguously established by single-crystal X-ray analysis, is shown in Figure 1. The four C(1), C(2), Si(1), and Si(2) atoms

2

(1)

[†] Korea University.

[‡] Gyeongsang National University.

[§] Kurashiki University of Science and the Arts.

(1) (a) Naka, A.; Hayashi, M.; Okazaki, S.; Kunai, A.; Ishikawa, M. *Organometallics* **1996**, *15*, 1101. (b) Naka, A.; Okazaki, S.; Hayashi, M.; Ishikawa, M. *J. Organomet. Chem.* **1995**, *499*, 35. (c) Ishikawa, M.; Okazaki, S.; Naka, A.; Tachibana, A.; Kawauchi, S.; Yamabe, T. *Organometallics* **1995**, *14*, 114. (d) Naka, A.; Hayashi, M.; Okazaki, S.; Ishikawa, M. *Organometallics* **1994**, *13*, 4994. (e) Ishikawa, M.; Naka, A.; Oshita, J. *Organometallics* **1993**, *12*, 4987. (f) Ishikawa, M.; Naka, A.; Okazaki, S.; Sakamoto, H. *Organometallics* **1993**, *12*, 87. (g) Ishikawa, M.; Okazaki, S.; Naka, A.; Sakamoto, H. *Organometallics* **1992**, *11*, 4135. (h) Ishikawa, M.; Naka, A. *Synlett.* **1995**, 794.

(2) (a) Kang, Y.; Lee, J.; Kong Y. K.; Kang, S. O.; Ko, J. *Chem. Commun.* **1998**, 2343. (b) Kang, Y.; Kang, S. O.; Ko, J. *Organometallics* **1999**, *18*, 1818. (c) Kang, Y.; Kang, S. O.; Ko, J. *Organometallics* **2000**, *19*, 1216. (d) Kang, Y.; Lee, J.; Kong, Y. K.; Kang, S. O.; Ko, J. *Organometallics* **2000**, *19*, 1722. (e) Kang, Y.; Kim, J.; Kong Y. K.; Lee, J.; Lee, S. W.; Kang, S. O.; Ko, J. *Organometallics* **2000**, *19*, 5026. (f) Kim, J.; Kang, Y.; Lee, J.; Kong Y. K.; Gong, M. S.; Kang, S. O.; Ko, J. *Organometallics* **2001**, *20*, 937.

(3) (a) Jemmis, E. D.; Kiran, B. *J. Am. Chem. Soc.* **1997**, *119*, 4076. (b) Ho, D. M.; Cunningham, R. J.; Brewer, J. A.; Bian, N.; Jones, M. *Inorg. Chem.* **1995**, *34*, 5274.

(4) de Rege, F. M.; Kassebaum, J. D.; Scott, B. L.; Abney, K. D.; Balaich, G. J. *Inorg. Chem.* **1999**, *38*, 486.

(5) Grimes, R. N. *Carboranes*; Academic Press: New York, 1975.

10.1021/om010535g CCC: $20.00
Publication on Web 11/20/2001

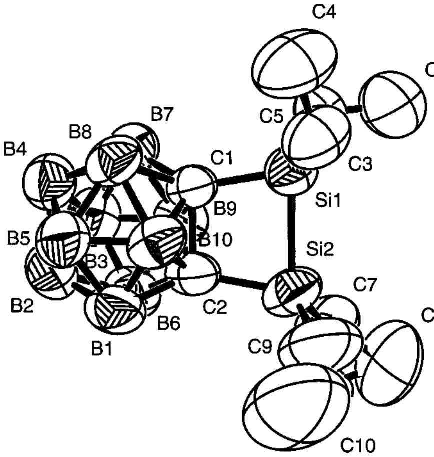
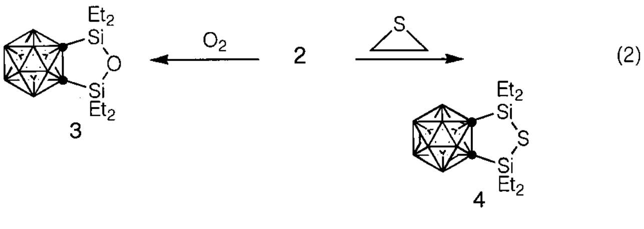


Figure 1. X-ray crystal structure of **2** with 50% probability thermal ellipsoids depicted. Selected bond lengths (Å) and angles (deg): C(1)−C(2) = 1.691(7), Si(1)−Si(2) = 2.344(2), Si(1)−C(1) = 1.931(6), Si(2)−C(2) = 1.934(6), Si(1)−C(3) = 1.847(7), Si(2)−C(7) = 1.857(7), Si(1)−C(5) = 1.889(6), Si(2)−C(9) = 1.924(13), C(1)−Si(1)−Si(2) = 80.3(2), C(2)−Si(2)−Si(1) = 99.7(3).

comprising the central skeleton of the molecule are nearly coplanar. The C(1)−Si(1) bond distance (1.931(6) Å) is slightly longer than the typical value for the carbon−silicon bond (1.88−1.91 Å)[6] and is comparable to that of the 1,2-(1′,1′,2′,2′-tetramethyldisilane-1′,2′)-carborane.[4] The Si(1)−Si(2) bond distance (2.344(2) Å) is within known values of the Si−Si bond lengths in analogous complexes.[7]

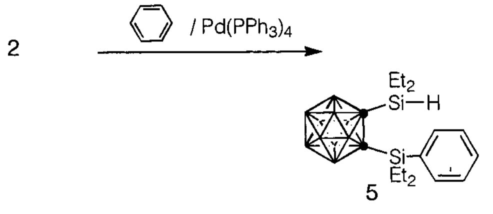
The ^{1}H, ^{13}C, and ^{29}Si NMR spectra and the mass spectrum of **2** were consistent with the structure determined by X-ray crystallography. The ^{29}Si NMR chemical shift of 21.68 ppm was downfield shifted from 8.05 ppm for **1**.

Oxidation, Sulfurization, and C−H Activation of 2. From consideration of the reaction conditions, **2** seems to be less reactive than the strained disilanes.[8] However, **2** in toluene is rapidly oxidized in oxygen gas to give 4,5-carboranylene-1,3-disila-2-oxacyclopent-4-ene (**3**) in 92% yield (eq 2). It is well known that the 1,2-disilacyclobutenes are readily oxidized in air, giving 1,3-disila-2-oxacyclopentenes.[1h] Under similar conditions, sulfur is also inserted into the Si−Si bond of **2** to give 4,5-carboranylene-1,3-disila-2-thiacyclopent-4-ene (**4**) in 82% yield. A similar 4,5-carboranylene-1,1,3,3-tetramethyl-1,3-disila-2-oxacyclopent-4-ene has been prepared by reacting H_2O with 1,2-bis(chlorodimethylsilyl)carborane[9] or by reacting O_2 with the strained disilane.[8]



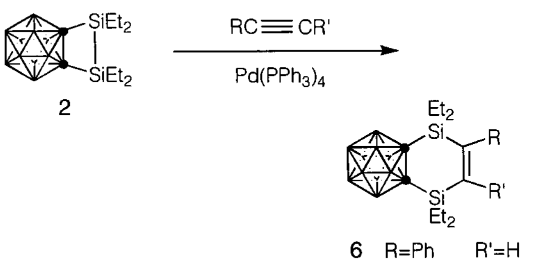
(2)

Since the C−H bond activation of benzene in the nickel-[1g] and platinum-catalyzed[1e] reaction of **1** took place at higher temperature, we carried out a similar reaction of **2** under the same reaction conditions. However, no products arising from C−H bond activation were formed. The starting compound **2** was recovered unchanged. In contrast to the above reactions, the palladium-catalyzed reaction of **2** in refluxing benzene for 72 h afforded 1-(diethylphenylsilyl)-2-(diethylsilyl)-carborane (**5**) in 38% yield (eq 3). The structure of **5** was confirmed by spectroscopic analysis as well as elemental analysis. The ^{13}C NMR spectrum of **5** reveals resonances at δ 7.62, 7.24, 5.76, and 4.85 ppm, assigned to the two kinds of ethyl carbons and six resonances in the aryl region. The ^{29}Si NMR spectrum shows two resonances at δ −2.74 and −6.46 ppm, arising from the two nonequivalent silicon atoms. The IR spectrum of **5** shows a strong absorption band at 2096 cm^{-1}, due to the Si−H stretching frequency.



(3)

Reactions of 2 with Alkynes. Previously, we reported the nickel-[1e], palladium-,[1d] and platinum-catalyzed[1b] reaction of **1** with alkynes to give 5,6-benzo-1,4-disilacyclohexa-2,5-dienes arising from insertion of a carbon−carbon triple bond into a silicon−silicon bond of the starting compound **1**. While a Pd complex readily catalyzed this type of double silylation with **2**, Pt and Ni complexes proved to be much less effective. For example, the Ni-catalyzed double silylation of **2** led predominantly to decomposition, and the Pt complex is not active in the double silylation of alkynes. Thus, the palladium-catalyzed reaction of **2** with phenylacetylene afforded 5,6-carboranylene-1,1,4,4-tetraethyl-2-phenyl-1,4-disilacyclohex-2-ene (**6**) as colorless crystals in 62% yield (eq 4). In a similar fashion, the reaction of **2** with other alkynes such as 1-phenylpropyne, dimethyl acetylenedicarboxylate, and 1-hexyne yielded the six-membered cyclic insertion products. However, compound **2** did not react with the disubstituted acetylenes such as diphenylacetylene and 3-hexyne under the same conditions. The formation of **6**−**9** can best be explained by



(4)

6 R=Ph R'=H
7 R=Ph R'=CH_3
8 R=R'=$COOCH_3$
9 R=C_4H_9 R'=H

---

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

(7) (a) Sita, L. R.; Lyon, S. R. *J. Am. Chem. Soc.* **1993**, *115*, 10374. (b) Carrell, H. L.; Donohue, J. *Acta Crystallogr., Sect. B* **1972**, *28*, 1566.

(8) (a) Barton, T. J.; Kilgour, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 7746. (b) Sakurai, H.; Kobayashi, T.; Nakadaira, Y. *J. Organomet. Chem.* **1978**, *162*, C43. (c) Atwell, W. H.; Uhlmann, J. G. *J. Organomet. Chem.* **1973**, 521. (d) Seyferth, D.; Annarelli, D. C.; Vick, S. C. *J. Organomet. Chem.* **1984**, *272*, 123.

(9) Papetti, S.; Heying, T. L. *Inorg. Chem.* **1963**, *2*, 1105.

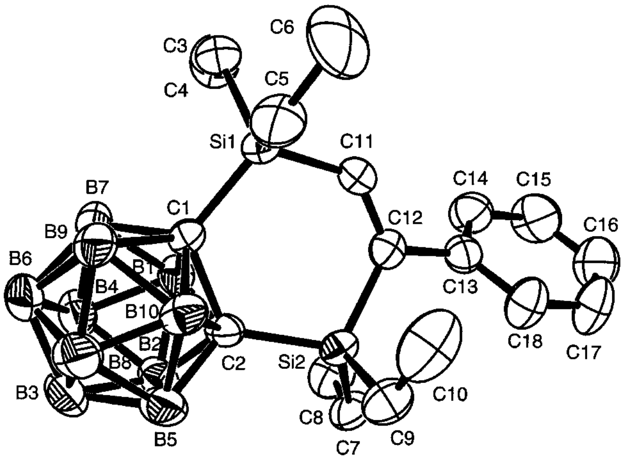


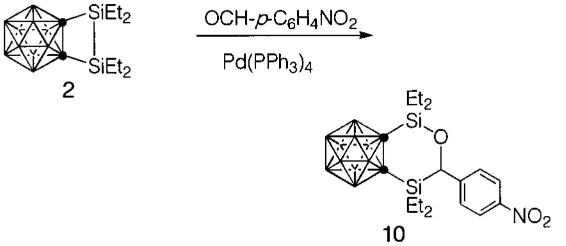
Figure 2. X-ray crystal structure of **6** with 50% probability thermal ellipsoids depicted. Selected bond lengths (Å) and angles (deg): Si(1)–C(11) = 1.859(3), Si(1)–C(1) = 1.905(3), Si(2)–C(12) = 1.873(3), Si(2)–C(2) = 1.920(3), C(1)–C(2) = 1.691(4), C(11)–C(12) = 1.355(4), C(12)–C(13) = 1.500(4), C(11)–Si(1)–C(1) = 108.0(1), C(12)–Si(2)–C(2) = 108.6(1), C(12)–C(11)–Si(1) = 130.4(2), C(11)–C(12)–C(13) = 119.5(3), C(11)–C(12)–Si(2) = 124.6(2), C(13)–C(12)–Si(2) = 115.9(2).

the reaction of the intermediate 4,5-carboranylene-1,1,3,3-tetraethyl-1-pallada-2,3-disilacyclopent-4-ene with alkynes.[10] Such alkyne insertion reactions have been effected using palladium and platinum complexes as catalysts with *o*-(dimethylsilyl)benzene[11] and 1,2-bis(dimethylsilyl)carborane.[2b–d]

To provide the structural information for one of the newly prepared compounds, a single-crystal X-ray diffaction study of the phenylacetylene insertion product **6** was undertaken. The molecular structure of **6** is shown in Figure 2. The X-ray crystal structure of **6** confirmed the presence of a six-memberd ring comprised of an *o*-carboranylene, two silicon atoms, and an unsaturated hydrocarbon fragment containing a C=C bond. The C=C bond length (1.355(4) Å) is slightly longer than the typical value for the carbon–carbon double bond (1.317 Å)[12] and is comparable to that of the tricyclic product formed in the reaction between diphenylacetylene and tetrakis(dimethylsilyl)benzene[13] and 5,6-carboranylene-1,1,4,4-tetramethyl-2,3-diphenyl-1,4-disilacyclohex-2-ene[1c] (1.33(2) Å).

The ^{1}H, ^{13}C, and ^{29}Si NMR spectra, the mass spectrum, and elemental analyses of compounds **6**–**9** were consistent with the structure determined for **6**. The ^{1}H NMR spectrum of **6** showed a low-field resonance at 6.61 ppm due to the olefinic proton. In the olefinic region of the ^{13}C NMR spectrum of **6**, two resonances at 160.42 and 146.69 ppm were present. The ^{29}Si NMR spectrum of **6** showed two resonances at −4.95 and −6.60 ppm arising from the nonequivalent silicon atoms, in accord with the upfield shift for 5,6-benzo-1,4-disilacyclohex-5-enes which appears in the region from −3 to −18 ppm.[1e]

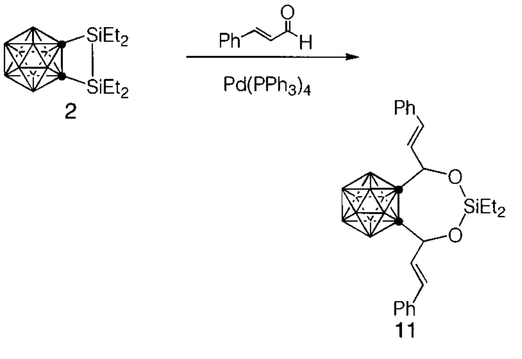
Reaction of 2 with 4-Nitrobenzaldehyde. As the metal complex-catalyzed 1,2-double silylation of the carbonyl groups with cyclic disilanes has been well-established,[1f] we attempted the double silylation of carbonyl compounds such as benzaldehyde, acetone, and acetophenone with **2**. No reactions were observed in all reactions in the presence of a palladium catalyst. However, reactive 4-nitrobenzaldehyde readily reacted with **2** to give the [4+2] cycloadduct (**10**) in 37% yield (eq 5).



(5)

The ^{1}H NMR spectrum of **10** contained a distinguishing low-field methine resonance (δ 4.95), which was used to monitor its formation. The ^{13}C NMR spectrum of product **10** revealed four resonances at δ 7.15, 6.60, 5.56, and 4.42, attributed to the two nonequivalent ethyl carbons. The ^{29}Si NMR spectrum of **10** exhibited two resonances at 9.96 and 0.23 ppm arising from the nonequivalent silicon atoms. Such a 1,2-double-silylation reaction of the carbonyl unit has been reported using a platinum complex as the catalyst with *o*-bis(dimethylsilyl)benzene[14] and with a nickel complex as the catalyst with 1,2-bis(dimethylsilyl)carborane.[2e] The insertion of an aldehyde carbonyl group into the Si–Si bond promoted by a fluoride ion was also noted.[15]

Reaction of 2 with *trans*-Cinnamaldehyde. The treatment of **2** with 4 equiv of *trans*-cinnamaldehyde in the presence of a catalytic amount of Pd(PPh$_3$)$_4$ gave 6,7-carboranylene-1,5-bis(styrenyl)-2,4-dioxa-3,3-diethyl-3-silacyclohept-6-ene (**11**) (eq 6). The ^{1}H NMR spectrum of **11** exhibits the characteristic methine resonance (δ 5.19) in addition to two resonances at 6.62 and 6.23 ppm as a doublet of doublets due to the olefinic protons. The ^{29}Si NMR spectrum of our product exhibited a single resonance at −1.79 ppm. The mass spectrum of the product showed a molecular ion at *m*/*z* 492. As the



(6)

---

(10) Ishikawa, M.; Sakamoto, H.; Okazaki, S.; Naka, A. *J. Organomet. Chem.* **1992**, *439*, 19.

(11) (a) Uchimaru, Y.; Lautenschlager, H.-J.; Wynd, A. J.; Tanaka, M.; Goto, M. *Organometallics* **1992**, *11*, 2639. (b) Tanaka, M.; Uchimaru, Y.; Lautenschlager, H.-J. *J. Organomet. Chem.* **1992**, *482*, 1. (c) Tanaka, M.; Uchimaru, Y. *Bull. Soc. Chim. Fr.* **1992**, *129*, 667.

(12) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans.* **1987**, *1*, 51

(13) Uchimaru, Y.; Brandl, P.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1993**, 744.

(14) Uchimaru, Y.; Lautenschlager, H.-J.; Wynd, A. J.; Tanaka, M.; Goto, M. *Organometallics* **1992**, *11*, 2639.

(15) Hiyama, T.; Obayashi, M. *Tetrahedron Lett.* **1983**, *24*, 4109.

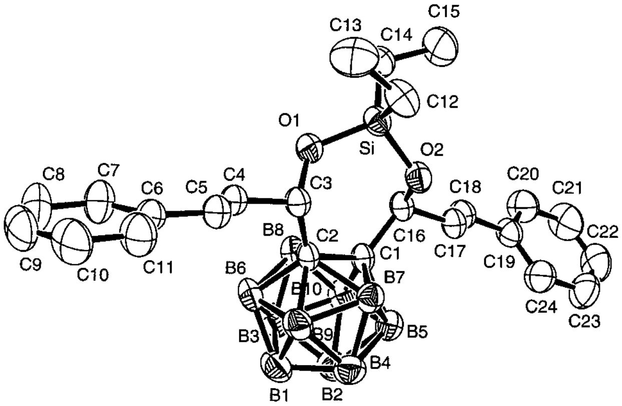


Figure 3. X-ray crystal structure of **11** with 50% probability thermal ellipsoids depicted. Selected bond lengths (Å) and angle (deg): Si−O(2) = 1.6552(16), O(1)−C(3) = 1.425(2), O(2)−C(16) = 1.416(2), C(1)−C(16) = 1.562(3), C(1)−C(2) = 1.701(3), C(2)−C(3) = 1.555(3), C(3)−C(4) = 1.497(3), C(4)−C(5) = 1.319(3), C(5)−C(6) = 1.470(3), O(2)−Si−O(1) = 103.52(7), C(3)−O(1)−Si = 117.35(12), C(16)−C(1)−C(2) = 121.17(16), C(3)−C(2)−C(1) = 122.03(15), O(1)−C(3)−C(2) = 111.80(15), C(5)−C(4)−C(3) = 123.3(2), C(4)−C(5)−C(6) = 127.2(6), O(2)−C(16)−C(1) = 111.21(15), C(18)−C(17)−C(16) = 125.3(2), C(17)−C(18)−C(19) = 125.3(2).

structure of the product was not deduced on the basis of the spectroscopic data, a single-crystal X-ray diffraction study was undertaken. The molecular structure of **11** is shown in Figure 3. The X-ray study of **11** showed it to be the insertion product of two carbonyl ligands into the C−Si bond of **2**. The molecule contains a C_4SiO_2 seven-membered ring. Such an insertion of the carbonyl unit into *o*-carborane has been observed in the reaction of the cyclic bis(silyl)platinum complex and *trans*-cinnamaldehyde[2c] in Yamamoto's work on the chemoselective addition of *o*-carborane to aldehyde groups,[14] and in the fluoride-promoted reaction of *o*-carborane with aldehydes.[15]

In conclusion, we have prepared a strained 3,4-carboranylene-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene (**2**). In marked contrast to the *o*-bis(dimethylsilyl)carborane, which reacted with a variety of unsaturated organic substrates in the presence of the Ni and Pt complexes, compound **2** reacted with a few activated alkynes and aldehydes only in the presence of the Pd catalyst to afford the double-silylated products. The present reaction provides a new route to a novel class of heterocyclic compounds.

Experimental Section

General Considerations. For the general experimental procedure see ref 2c. *o*-Carborane was purchased from the Katchem, Ltd., and used without purification. All the alkynes, aldehydes, and ethylenesulfide were purchased from Aldrich. $Pd(PPh_3)_4$[16] and 1,2-dichlorotetraethyldisilane[17] were prepared according to the literature.

3,4-Carboranylene-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene (2). To a stirred diethyl ether (200 mL) solution of *o*-carborane (1.44 g, 10 mmol) at 0 °C was added *n*-BuLi (20 mmol), and the reaction solution was warmed to room temperature. The solution of 1,2-dichlorotetraethyldisilane (2.43 g, 10 mmol) in diethyl ether (15 mL) was slowly added to the reaction mixture at 0 °C. The reaction mixture was warmed to room temperature and stirred for 3 h. All volatiles were removed under reduced pressure, followed by extraction of the residues with *n*-hexane (30 mL). The extracts were concentrated to 15 mL and cooled to −10 °C to furnish 1.68 g (53%) of colorless crystals of **2**. Mp: 100 °C. ^1H NMR ($CDCl_3$): δ 1.12−0.96 (m, *Et*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 7.69 (CH_2), 4.63 (CH_3). ^{29}Si NMR ($CDCl_3$): δ 21.68. MS: *m*/*z* 314 [M^+]. Anal. Calcd for $C_{10}H_{30}B_{10}Si_2$: C, 38.17; H, 9.60. Found: C, 38.64; H, 9.86.

4,5-Caboranylene-1,1,3,3-tetraethyl-1,3-disila-2-oxacyclopent-4-ene (3). Oxygen gas was bubbled into a solution of **2** (0.1 g, 0.32 mmol) in toluene (20 mL) for 20 min. The solvent was removed under reduced pressure, yielding a white solid. The pure product **3** was obtained by crystallization from a saturated solution of ether at −20 °C in 92% yield. Mp: 43 °C. ^1H NMR ($CDCl_3$): δ 1.08−0.82 (m, *Et*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 6.41 (CH_2), 5.53 (CH_3). MS: *m*/*z* 331 [M^+]. Anal. Calcd for $C_{10}H_{30}B_{10}OSi_2$: C, 36.33; H, 9.13. Found: C, 36.88; H, 9.01.

4,5-Caboranylene-1,1,3,3-tetraethyl-1,3-disila-2-thiacyclopent-4-ene (4). A mixture of 0.1 g (0.32 mmol) of **2** and 0.19 g (3.2 mmol) of ethylene sulfide in toluene (20 mL) was refluxed for 8 h. The solvent was removed in vacuo, and the residue was sublimed to give **4** in 82% yield. ^1H NMR ($CDCl_3$): δ 1.01−0.81 (m, *Et*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 10.64, 7.22 (*Et*). MS: *m*/*z* 346 [M^+]. Anal. Calcd for $C_{10}H_{30}B_{10}SSi_2$: C, 34.64; H, 8.71. Found: C, 34.48; H, 8.54.

1-(Diethylphenylsilyl)-2-(diethylsilyl)carborane (5). A mixture of **2** (0.15 g, 0.48 mmol) and $Pd(PPh_3)_4$ (0.027 g) in benzene (15 mL) was heated to reflux for 72 h. The solvent was removed in vacuo, and the residue was chromatographed using benzene/hexane (1:2) as the eluent ($R_f = 0.46$) to give **5** in 38% yield. Mp: 108 °C. ^1H NMR ($CDCl_3$): δ 7.44−7.04 (m, 5H, *Ph*), 4.30 (quint, 1H, J = 3.38 Hz, Si*H*), 1.16−0.82 (m, 20H, *Et*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 143.26, 138.64, 134.02, 128.84, 127.74, 127.29, 7.62, 7.24, 5.76, 4.85. ^{29}Si NMR ($CDCl_3$): δ −2.74, −6.46. IR (KBr pellet; cm^{-1}): 2096. Anal. Calcd for $C_{16}H_{36}B_{10}Si_2$: C, 47.96; H, 9.04. Found: C, 47.58; H, 8.82.

Reaction of 2 with Phenylacetylene (6). A mixture of 0.1 g (0.32 mmol) of **2** and 0.13 g (1.28 mmol, 4 equiv) of phenylacetylene in the presence of a catalytic amount of $Pd(PPh_3)_4$ (0.018 g, 5 mol %) in toluene (30 mL) was refluxed for 24 h. The solvent was removed in vacuo, and the residue was chromatographed using benzene/hexane (1:2) as the eluent (R_f = 0.8). The first band was crystallized from hexane at −10 °C to give 5,6-carboranylene-1,1,4,4-tetraethyl-2-phenyl-1,4-disilacyclohex-2-ene (**6**) as colorless crystals in 62% yield. Mp: 90 °C. ^1H NMR ($CDCl_3$): δ 7.36−7.07 (m, 5H, *Ph*), 6.61(s, 1H, C*H*), 1.12−0.85 (m, 20H, *Et*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 160.42, 146.69, 142.70, 128.64, 127.45, 127.05, 126.36, 126.02, 68.95, 67.43, 7.66, 7.48, 6.56, 5.90. ^{29}Si NMR ($CDCl_3$): δ −4.95, −6.60. MS: *m*/*z* 416 [M^+]. Anal. Calcd for $C_{18}H_{36}B_{10}Si_2$: C, 51.87; H, 8.69. Found: C, 51.62; H, 8.52.

Reaction of 2 with 1-Phenylpropyne (7). The same procedure was used as described for **6**, except 1-phenylpropyne was used instead of phenylacetylene. Pure **7** was isolated by chromatographic workup (eluent: benzene/hexane (1:6), R_f = 0.4) in 53% yield. Mp: 98 °C. ^1H NMR ($CDCl_3$): δ 7.37−6.86 (m, 5H, *Ph*), 1.61 (s, 3H, CH_3), 1.11−0.73 (m, 20H, *Et*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 154.66, 148.40, 142.61, 132.26, 130.76, 128.83, 127.36, 126.51, 67.72, 67.42, 21.12, 7.74, 7.55, 5.62, 5.52. ^{29}Si NMR ($CDCl_3$): δ −5.13, −8.41. MS: *m*/*z* 430 [M^+]. Anal. Calcd for $C_{19}H_{38}B_{10}Si_2$: C, 52.97; H, 8.88. Found: C, 53.25; H, 9.02.

Reaction of 2 with Dimethyl Acetylenedicarboxylate (8). The same procedure was used as described for **6**, except dimethyl acetylenedicarboxylate was used instead of pheny-

---

[16] Brauer, G. *Handbuch der Präparativen Anorganischen Chemie*; Ferdinand Enke Verlag: Stuttgart, 1981; p 2013.

[17] Matsumoto, H.; Motegi, T.; Hasegawa, M.; Nagai, Y. *J. Organomet. Chem.* **1977**, *142*, 149.

lacetylene. Pure **8** was isolated by chromatographic workup (eluent: ethyl acetate/hexane (1:2), $R_f = 0.9$) as a yellow oil in 61% yield. ^{1}H NMR (CDCl$_3$): δ 3.75 (s, 6H, C*H$_3$*), 1.05−0.98 (m, 20H, *Et*). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 169.14, 151.91, 66.18, 52.53, 7.25, 6.15. ^{29}Si NMR (CDCl$_3$): δ −3.73. MS: *m*/*z* 457 [M$^+$]. Anal. Calcd for $C_{16}H_{36}B_{10}O_4Si_2$: C, 42.07; H, 7.93. Found: C, 41.88; H, 7.74.

Reaction of 2 with 1-Hexyne (9). The same procedure was used as described for **6**, except 1-hexyne was used instead of phenylacetylene. Pure **9** was isolated by chromatographic workup (eluent: benzene/hexane (1:9), $R_f = 0.4$) as a colorless oil in 65% yield. ^{1}H NMR (CDCl$_3$): δ 6.41 (t, 1H, $J_{HH} = 1.52$ Hz, =C*H*), 2.16 (t, 2H, $J_{HH} = 1.52$ Hz, =CC*H$_2$*), 1.46−1.25 (m, 7H, C*H$_2$*C*H$_2$* C*H$_3$*), 1.06−0.75 (m, 20H, *Et*). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 160.19, 156.50, 68.74, 67.81, 39.40, 38.81, 22.62, 14.16, 7.72, 7.51, 6.00, 5.60. ^{29}Si NMR (CDCl$_3$): δ −5.77, −6.95. MS: *m*/*z* 396 [M$^+$]. Anal. Calcd for $C_{16}H_{40}B_{10}Si_2$: C, 48.43; H, 10.15. Found: C, 48.08; H, 10.02.

Reaction of 2 with 4-Nitrobenzaldehyde (10). The same procedure was used as described for **6**, except 4-nitrobenzaldehyde was used instead of phenylacetylene. Pure 5,6-carboranylene-1,1,4,4-tetraethyl-2-oxa-3-(4-nitrobenz-yl)-1,4-disilacyclohex-5-ene (**10**) was isolated by chromatographic workup (eluent: ethyl acetate/hexane (1:9), $R_f = 0.3$) as a colorless crystal in 37% yield. Mp: 181 °C. ^{1}H NMR (CDCl$_3$): δ 8.21−7.34 (m, 5H, *Ph*), 4.95 (s, 1H, C*H*), 1.05−0.79 (m, 20H, *Et*). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 148.41, 129.18, 129.02, 128.37, 127.22, 126.64, 124.84, 124.01, 70.62, 7.15, 6.60, 5.56, 4.42. ^{29}Si NMR (CDCl$_3$): δ 9.96, 0.23. MS: *m*/*z* 465 [M$^+$]. Anal. Calcd for $C_{17}H_{35}B_{10}$ NO_3Si_2: C, 43.84; H, 7.56. Found: C, 43.62; H, 7.72.

Reaction of 2 with *trans*-Cinnamaldehyde (11). The same procedure was used as described for **6**, except *trans*-cinnamaldehyde was used instead of phenylacetylene. Pure 6,7-carboranylene-1,5-bis(styrenyl)-2,4-dioxa-3,3-diethyl-3-silacyclohept-6-ene (**11**) was isolated by chromatographic workup (eluent: benzene/hexane (1:4), $R_f = 0.1$) as a colorless crystal in 26% yield. Mp: 68 °C. ^{1}H NMR (CDCl$_3$): δ 7.44−7.29 (m, 10H, *Ph*), 6.62 (d, 2H, $J_{HH} = 15.90$ Hz, =C*H*), 6.23 (dd, 2H, $J_{HH} = 15.90$ Hz, $J_{HH} = 6.60$ Hz, =C*H*), 5.19 (d, 2H, $J_{HH} = 6.60$ Hz, C*H*), 1.06−0.78 (m, 10H, *Et*), ^{13}C{^{1}H} NMR (CDCl$_3$): δ 139.03, 135.89, 132.03, 128.86, 128.53, 128.00, 127.05, 75.02, 6.39, 2.79. ^{29}Si NMR (CDCl$_3$): δ −1.79. MS: *m*/*z* 492 [M$^+$]. Anal. Calcd for $C_{24}H_{36}B_{10}O_2Si$: C, 58.50; H, 7.35. Found: C, 58.28; H, 7.16.

Table 1. Crystal Data of 2, 6, and 11

	2	**6**	**11**
empirical formula	$C_{10}H_{30}B_{10}Si_2$	$C_{18}H_{36}B_{10}Si_2$	$C_{24}H_{36}B_{10}O_2Si$
mol wt	314.62	416.75	492.72
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a (Å)	7.5845(9)	9.663(1)	10.6814(9)
b (Å)	16.346(2)	24.421(2)	11.6686(11)
c (Å)	16.3645(16)	9.979(1)	12.4992(12)
α (deg)			75.755(2)
β (deg)	90.629(8)	96.281(9)	74.570(2)
γ (deg)			73.167(2)
V, Å^3	2028.6(4)	2532.5(5)	1413.0(2)
Z	4	4	2
D(calcd) (g cm^{-3})	1.030	1.093	1.158
F(000)	672	888	520
μ (mm^{-1})	0.162	0.145	0.105
λ(Mo Kα) (Å)	0.7107	0.7107	0.7107
monochromator	graphite	graphite	graphite
scan type	ω	ω	ω−2θ
no. of reflns measd	3794	4722	9323
no. of reflns with $I > 2\sigma(I)$	1248	3108	6541
R	0.0836	0.0574	0.0542
R_w	0.1947	0.1419	0.1338
goodness of fit	1.007	1.042	1.022

X-ray Crystallography. Details of the crystal data and a summary of intensity data collection parameters for **2**, **6**, and **11** are gave in Table 1. Crystals of **2** and **6** were grown from hexane at −10 °C, and a crystal of **11** was grown from CH_2Cl_2/hexane. Crystals of **2**, **6**, and **11** were mounted in thin-walled glass capillaries and sealed under argon. The data sets of **2** and **6** were collected on an Enraf CAD 4 automated diffractometer, and those of **11** on a Siemens P4 diffractometer. Mo Kα radiation (λ = 0.7107 Å) was used for all structures. Each structure was solved by the application of direct methods using the SHELX-96 program and least-squares refinement using SHELXL-97. All non-hydrogen atoms in compound **2**, **6**, and **11** were refined anisotropically. All other hydrogen atoms were included in the calculated positions.

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

OM010535G