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# A Bis(silyl)nickel Complex Containing an *o*-Carboranylene and Its Application in Facile Double Silylation of Alkynes and Alkenes

Youngjin Kang,† Junghyun Lee,‡ Young Kun Kong,‡ Sang Ook Kang,*,† and Jaejung Ko*,†

*Department of Chemistry, Korea University, Chochiwon, Chungnam 339-700, Korea, and Department of Chemistry, Kyonggi University, Suwon, Kyunggido 440-760, Korea*

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The reaction of 1,2-bis(dimethylsilyl)carborane (**1**) with $Ni(PEt_3)_4$ yielded the cyclic bis(silyl)nickel complex (**2**). **2** was found to be a good catalyst for the double silylation reaction of alkynes and alkenes. Thus, the reaction of **1** with $RC\equiv CR'$ in the presence of a catalytic amount of **2** afforded the six-membered disilylene ring compounds $o\text{-}B_{10}H_{10}C_2(SiMe_2)_2(RC{=}CR')$ ($R = R' = Ph$ (**3**); $R = Ph$, $R' = H$ (**4**); $R = R' = Et$ (**5**); $R = Ph$, $R' = Me$ (**6**); $R = R' = Me$ (**7**)). In contrast, the reaction of 1-phenyl-2-(trimethylsilyl)acetylene with **1** in the presence of a catalytic amount of **2** afforded the six-membered disilylene ring compound (**9**) and the five-membered disilylene ring compound (**10**). The stoichiometric reaction of **2** with an active alkyne such as dimethyl acetylenedicarboxylate gave the six-membered disilylene ring compound (**11**). The intermedate **2** also was found to be a good catalyst for the double silylation of some alkenes. Thus, the reaction of **1** with 4-vinylanisole in the presence of a catalytic amount of **2** afforded the five-membered disilylene ring compound (**15**). However, treatment of **1** with 1,1-diphenylethylene under the same reaction conditions yielded a different type of five-membered disilylene ring compound (**17**). The reaction of **1** with 2,3-dimethylbutadiene in the presence of the nickel catalyst also was studied. The crystal structures of **2**, **9**, and **14** are described.

## Introduction

The double silylation of unsaturated organic substrates catalyzed by group 10 metal complexes[1] has been well documented for two decades. Nickel complexes, in particular, provide excellent catalysts for such reactions of silicon-containing linear compounds[2] and 1,2-disilacyclobutene.[3] Bis(silyl)nickel complexes have been implicated as intermediates in the nickel-catalyzed double silylation of arenes,[4] alkynes,[5] alkenes,[6] and aldehydes.[7] In contrast to analogous platinum complexes, bis(silyl)nickel complexes in general have not been isolated due to their instability. The few bis(silyl)nickel complexes that have been isolated possess special stabilization resulting from strongly electron-withdrawing silyl groups (e.g., $SiF_3$ or $SiCl_3$)[8] or from the inclusion of the silyl groups in a chelate ring.[9] Isolation and fundamental knowledge of the reactivity of bis(silyl)nickel complexes are essential to understand their role as catalytic intermediates.

Recently, we reported the double silylation reactions of a cyclic bis(silyl)platinum complex containing an *o*-carboranylene.[10] However, the double silylation reactions were stoichiometric processes involving reaction of a stable $PtSi_2P_2$ complex with a variety of unsaturated organic substrates. A catalytic process would be preferred. Accordingly, we have started a study of the synthesis of bis(silyl)metal complexes that would be suitable as catalysts.

Here we report the general synthesis of a new class of stable cyclic bis(silyl)nickel complex with a bulky

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† Korea University.

‡ Kyonggi University.

(1) (a) Beletskaya, I.; Moberg, C. *Chem. Rev.* **1999**, *99*, 3435. (b) Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351. (c) Braunstein, P.; Knorr, M. *J. Organomet. Chem.* **1995**, *500*, 21. (d) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Organomet. Chem.* **1975**, *86*, C27. (e) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1975**, *97*, 931. (f) Carson, C. W.; West, R. *Organometallics* **1983**, *2*, 1081. (g) Seyferth, D.; Goldman, E. W.; Escudié, J. *J. Organomet. Chem.* **1984**, *271*, 337. (h) Yamashita, H.; Catellani, M.; Tanaka, M. *Chem. Lett.* **1991**, 241. (i) Murakami, M.; Andersson, P. G.; Suginome, M.; Ito, Y. *J. Am. Chem. Soc.* **1991**, *113*, 3987. (j) Finckh, W.; Tang, B.; Lough, A.; Manners, I. *Organometallics* **1992**, *11*, 2904.

(2) (a) Tamao, K.; Miyake, N.; Kiso, Y.; Kumada, M. *J. Am. Chem. Soc.* **1975**, *97*, 5603. (b) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 9263. (c) Ishikawa, M.; Nishimura, Y.; Sakamoto, N.; Ono, T.; Ohshita, J. *Organometallics* **1992**, *11*, 483.

(3) Jzang, T.; Lee, C.; Liu, C. S. *Organometallics* **1988**, *7*, 1265.

(4) (a) Ishikawa, M.; Sakamoto, H.; Okazaki, S.; Naka, A. *J. Organomet. Chem.* **1992**, *439*, 19. (b) Ishikawa, M.; Okazaki, S.; Naka, A.; Sakamoto, H. *Organometallics* **1992**, *11*, 4135.

(5) (a) Naka, A.; Okazaki, S.; Hayashi, M.; Ishikawa, M. *J. Organomet. Chem.* **1995**, *499*, 35. (b) Ishikawa, M.; Ohshita, J.; Ito, Y. *Organometallics* **1986**, *5*, 1518. (c) Kiso, Y.; Tamao, K.; Kumada, M. *J. Organomet. Chem.* **1974**, *76*, 105. (d) Ishikawa, M.; Matsuzawa, S.; Hirotsu, K.; Kamitori, S.; Higuchi, T. *Organometallics* **1984**, *3*, 1930. (e) Ishikawa, M.; Matsuzawa, S.; Higuchi, T.; Kamitori, S.; Hirotsu, K. *Organometallics* **1985**, *4*, 2040.

(6) Ishikawa, M.; Okazaki, S.; Naka, A.; Tachibana, A.; Kawauchi, S.; Yamabe, T. *Organometallics* **1995**, *14*, 114.

(7) Ishikawa, M.; Naka, A.; Okazaki, S.; Sakamoto, H. *Organometallics* **1993**, *12*, 87.

(8) (a) Bierschenk, T. R.; Guerra, M. A.; Juhlke, T. J.; Larson, S. B.; Lagow, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 4855. (b) Kiso, Y.; Tamao, K.; Kumada, M. *J. Organomet. Chem.* **1974**, *76*, 95.

(9) Ohshita, J.; Isomura, Y.; Ishikawa, M. *Organometallics* **1989**, *8*, 2050.

(10) Kang, Y.; Kang, S. O.; Ko. J. *Organometallics* **1999**, *18*, 1818.

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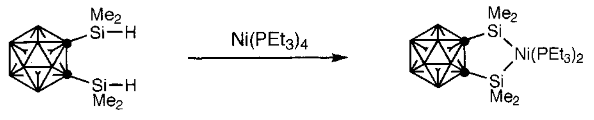
*o*-carboranylene and a variety of their double silylation reactions with unsaturated organic compounds. A portion of this study has already been communicated.[11]

## Results and Discussion

**Synthesis of [$o$-$(SiMe_2)_2C_2B_{10}H_{10}$]Ni($(PEt_3)_2$) Complex 2**. In our search for a stable bis(silyl)nickel complex, we investigated the reaction of *o*-bis(dimethylsilyl)carborane with $Ni(PEt_3)_4$. When 1.2 equiv of *o*-bis(dimethylsilyl) carborane **1** was treated with 1 equiv of $Ni(PEt_3)_4$ in pentane at 25 °C, an immediate color change from yellow to deep red occurred with evolution of $H_2$ (eq 1). Standard workup and crystallization from toluene−pentane gave [$o$-$(SiMe_2)_2$ $C_2B_{10}H_{10}$]-$Ni(PEt_3)_2$ (**2**) in 86% yield as a dark red, crystalline solid which is quite sensitive to air, but stable during brief heating to 100−110 °C. The unusual thermal stability of **2** may be related to the advantageous properties of the carboranylene, including electronic and steric effects. Compound **2** is soluble in toluene, THF, and chloroform and was characterized by $^{1}H$, $^{13}C$, $^{31}P$, and $^{29}Si$ NMR, mass spectroscopy, and elemental analysis. The initial indication of the formulation for **2** stemmed from the observation of a parent ion in the mass spectrum at $m/z$ 553. The $^{31}P$ NMR signal was shifted from −2.2 ppm for $Ni(PEt_3)_3$[12] to 5.58 ppm. The structure of **2** was unambiguously established by single-crystal X-ray analysis and is shown in Figure 1. Crystallographic data and processing parameters are given in Table 3. Complex **2** has a distorted tetrahedral geometry with the dihedral angle between P(1)−Ni(1)−P(2) and Si(1)−Ni(1)−Si(2) being 86.03°. The average Ni−Si bond length [2.2424(9) Å] is slightly longer than the 2.171(3) Å in $[(\mu\text{-}Cl)_2Ni_2(SiCl_3)_4][(CMe_3)_2C_5H_3NH]_2$[13] or 2.182(4) Å in $(SiF_3)_2Ni(PMe_3)_3$,[8a] but shorter than that of the calculated Ni−Si bond length of 2.525 Å for 1-nickela-2,5-disilacyclopent-3-ene.[6] The relatively long Ni−Si bonds of **2** may indicate that they are relatively weak. The Ni−P bond distance [2.2305(8) Å] is comparable to those in $Ni(PPh_3)_2(C_2H_4)$ (2.15 Å) and $Ni(PCy_3)_2$-($\eta$-$CO_2$) (2.15 Å).[14]



(1)

**1** **2**

**Nickel-Catalyzed Reaction with Alkynes**. Although the cyclic bis(silyl)platinum complex $Me_2Si$-($o$-$C_2B_{10}H_{10}$)$SiMe_2Pt(PPh_3)_2$ is not a catalyst for the double silylation reaction due to its strong Pt−Si bond strength, the Ni complex **2** was found to be a good catalyst for the double silylation reaction. The nickel-catalyzed double silylation can be carried out either by reacting **1** and the alkyne in the presence of the $Ni(PEt_3)_4$ catalyst or by reacting **1** and the alkyne in the presence of a catalytic quantity of the nickel intermediate **2**. Because the former procedure may in some cases result in formation of the cyclotrimerization product, the latter procedure is preferred. Thus, the reaction of **1** (0.12 g, 0.46 mmol) with diphenylacetylene (0.09 g, 0.51 mmol) in the presence of a catalytic amount of **2** (0.01 g, 0.018 mmol) was stirred under the conditions specified in Table 1. Subsequent recrystallization gave 5,6-carboranylene-1,1,4,4-tetramethyl-2,3-diphenyl-1,4-disilacyclohex-2-ene (**3**) by insertion of the carbon−carbon triple bond into a silicon−nickel bond of **2** (entry 1).

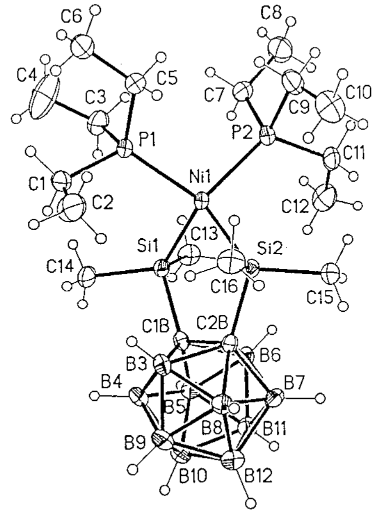


**Figure 1.** X-ray crystal structure of **2** with 50% probability thermal ellipsoids depicted. Selected bond lengths (Å) and angles (deg): Ni(1)−P(1) 2.2265(8), Ni(1)−P(2) 2.2346(8), Ni(1)−Si(1) 2.2371(9), Ni(1)−Si(2) 2.2477(9), Si(1)−C(1B) 1.1941(3), Si(2)−C(2B) 1.940(3), C(1B)−C(2B) 1.669(4), P(1)−Ni(1)−P(2) 101.95(3), Si(1)−Ni(1)−Si(2) 83.69(3), P(1)−Ni(1)−Si(1) 96.06(3), P(2)−Ni(1)−Si(1) 140.35(4).

In a similar fashion, the nickel-catalyzed reaction of **1** with other alkynes such as phenylacetylene, 3-hexyne, and 2-butyne at 80 °C also yielded the six-membered-ring compounds. However, the reaction course was quite sensitive to the reaction conditions. When the reaction of *o*-bis(dimethylsilyl)carborane **1** with 1-phenyl-1-propyne (1 equiv) in the presence of a catalytic amount of **2** (0.03 equiv) was carried out at 70−80 °C, the major product was identified as 1,3,5-trimethyl-2,4,6-triphenylbenzene, which was characterized by spectroscopic techniques. However, the same reaction when carried out at room temperature gave the six-membred-ring compound **6** in high yield (entry 4). The spectral data for **3**−**5** and **7** were identical with those of the authentic samples.[15]

When 1-hexyne was employed as a terminal alkyne in the nickel-catalyzed reaction of **1** at 80 °C, the five-membered-ring compound **8** was isolated as a colorless liquid in 71% yield (entry 6). The isolation of **8** is interesting because a 1,2-hydrogen shift must be involved in its formation. Such a 1,2-hydrogen shift has been observed in the stoichiometric reaction of $Me_2Si$-($o$-$C_2B_{10}H_{10}$)$SiMe_2Pt(PPh_3)_2$ with 1-hexyne.[10] Similar reaction of **1** with 1-phenyl-2-(trimethylsilyl)acetylene at room temperature afforded 5,6-carboranylene-1,1,

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[11] Kang, Y.; Lee, J.; Kong, Y. K.; Kang, S. O.; Ko, J. *Chem. Commun.* **1998**, 2343.

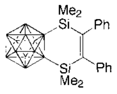
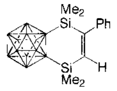
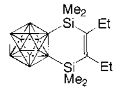
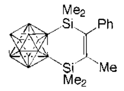
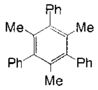
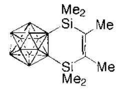
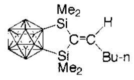
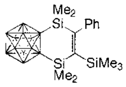
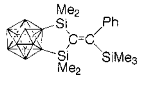
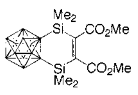
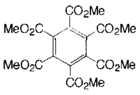
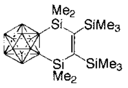
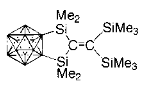
[12] Tolman, C. A.; Gerlach, D. H.; Jesson, J. P.; Schunn, R. A. *J. Organomet. Chem.* **1974**, *65*, C23.

[13] Brezinski, M. M.; Schneider, J.; Radonovich, L. J.; Klabunde, K. J. *Inorg. Chem.* **1989**, *28*, 2414.

[14] Aresta, M.; Nobile, C. F.; Albano, V. G.; Forni, E.; Manassero, M. *J. Chem. Soc., Chem. Commun.* **1975**, 636.

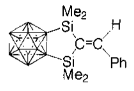
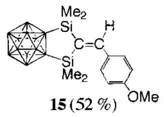
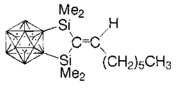
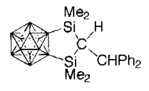
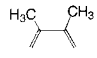
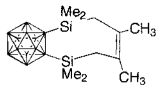
[15] Kang, Y.; Kang, S. O.; Ko, J. *Organometallics*, in press.

**Table 1. Nickel-Catalyzed Reactions of Alkynes with 1,2-Bis(dimethylsilyl)carborane**

| entry | reactns | conditns | products(yield, %) |
|---|---|---|---|
| 1 | $PhC\equiv CPh$ | r.t. (12 h) |  **3** (76 %) |
| 2 | $PhC\equiv CH$ | 80 ℃ (4 h) |  **4** (64 %) |
| 3 | $EtC\equiv CEt$ | 80 ℃ (6 h) |  **5** (77 %) |
| 4 | $MeC\equiv CPh$ | r. t. (6 h) |  **6** (82 %)  (~8 %) |
| 5 | $MeC\equiv CMe$ | 80 ℃ (6 h) |  **7** (58 %) |
| 6 | $Bu^nC\equiv CH$ | 80 ℃ (6 h) |  **8** (71 %) |
| 7 | $PhC\equiv CSiMe_3$ | r.t. (4 h) |  **9** (62 %)  **10** (~8 %) |
| 8[a] | $MeO_2CC\equiv CCO_2Me$ + **2** | 0 ℃ (3 h) |  **11** (57 %)  (22 %) |
| 9[a] | $Me_3SiC\equiv CSiMe_3$ + **2** | 80 ℃ (12 h) |  **12** (66 %)  **13** (~6%) |

[a] Stoichiometric reaction.

**Table 2. Nickel-Catalyzed Reactions of Alkenes with 1,2-Bis(dimethylsilyl)carborane**

| entry | reactns | conditns | products(yield, %) |
|---|---|---|---|
| 10[a] | $PhHC=CH_2$ + **2** | 110 ℃ (12 h) |  **14** (76 %) |
| 11 | $H_2C=CHC_6H_4OCH_3$ | 80 ℃ (12 h) |  **15** (52 %) |
| 12 | $H_2C=CH(CH_2)_5CH_3$ | 80 ℃ (12 h) |  **16** (~45 %) |
| 13 | $H_2C=CPh_2$ | 80 ℃ (12 h) |  **17** (74 %) |
| 14 |  | r. t. (6 h) |  **18** (84 %) |

[a] Stoichiometric reaction.

**Table 3. Crystal Data of 2, 9, and 14**

| | 2 | 9 | 14 |
|---|---|---|---|
| empirical formula | $C_{18}H_{52}B_{10}NiP_2PtSi_2$ | $C_{17}H_{36}B_{10}Si_3$ | $C_{14}H_{28}B_{10}Si_2$ |
| molecular wt | 553.53 | 432.83. | 360.64 |
| cryst syst | monoclinic | monoclinic | monoclinic |
| space group | $P2(1)/n$ | $P21/n$ | $P21/n$ |
| $a$ (Å) | 9.4833(6) | 10.1510(8) | 9.6874(4) |
| $b$ (Å) | 19.2061(13) | 21.3249(10) | 18.2763(15) |
| $c$ (Å) | 16.8724(10) | 12.4886(5) | 12.7310(7) |
| α (deg) | 90 | | |
| $\beta$ (deg) | 93.029(2) | 96.944(5) | 106.587(4) |
| $\gamma$ (deg) | 90 | | |
| $V$, Å$^3$ | 3068.8(3) | 2683.6(3) | 2160.2(2) |
| $Z$ value | 4 | 4 | 4 |
| $D$(calcd), (g cm$^{-3}$) | 1.198 | 1.071 | 1.109 |
| $F$(000) | 1184 | 920 | 760 |
| abs coeff, mm$^{-1}$ | 0.823 | 0.181 | 0.160 |
| $\lambda$, (Å) | 0.71073 | 0.71073 | 0.71073 |
| monochromator | graphite | graphite | graphite |
| scan type | $\omega-2\theta$ | $\omega-2\theta$ | $\omega-2\theta$ |
| $2\theta$ range, deg | 4.80−58.40 | 3.80−51.94 | 4.02−51.94 |
| no. of reflns measd | 14984 | 5513 | 4494 |
| no. of obsd reflns ($I > 3.00\sigma(I)$) | 6498 | 5268 | 4239 |
| $R$ | 0.0545 | 0.0665 | 0.0506 |
| $R_w$ | 0.1072 | 0.1537 | 0.1316 |
| goodness of fit | 1.083 | 0.970 | 0.967 |

4,4-tetramethyl-2-phenyl-3-trimethysilyl-1,4-disilacyclohex-2-ene (**9**) and 4,5-carboranylene-1,1,3,3-tetramethyl-2-[phenyl(trimethylsilyl)methylene]-1,3-disilacyclopentane (**10**) in 62% and 8% yield, respectively. The products **9** and **10** could readily be isolated by preparative GLC. The $^1$H NMR spectrum of **9** contains three resonances at 0.50, 0.13, and −0.21 ppm, assigned to three kinds of methyl groups. In the olefinic region of the $^{13}$C NMR spectrum of **9**, two resonances at 172.77 and 157.41 ppm of equal intensity were present. The $^{29}$Si NMR spectrum of **9** shows three resonances at −6.2, −10.2, and −13.4 ppm. The two resonances at −10.2 and −13.4 ppm were assigned to the ring silicon atoms and the peak at −6.2 ppm to the trimethylsilyl silicon atom. The chemical shifts of **9** are in the range of those of the other six-membered-ring compounds because the resonances of the silicon atoms in the 5,6-carboranylene-1,4-disilacyclohex-2-ene observed so far appear at higher field (−8 to −16 ppm) than those of the five-membered 4,5-carboranylene-1,3-disilacyclopentane (5 to −4 ppm).[10,17] The $^{13}$C NMR spectrum of **10** shows two olefinic resonances at 180.22 and 156.02 ppm. Characteristic low-frequency resonances at 1.08 and −1.44 ppm

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(16) (a) Schneider, D.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1991**, 700. (b) Werner, H.; Baum, M.; Schneider, D.; Windmüller, B. *Organometallics* **1994**, *13*, 1089.

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

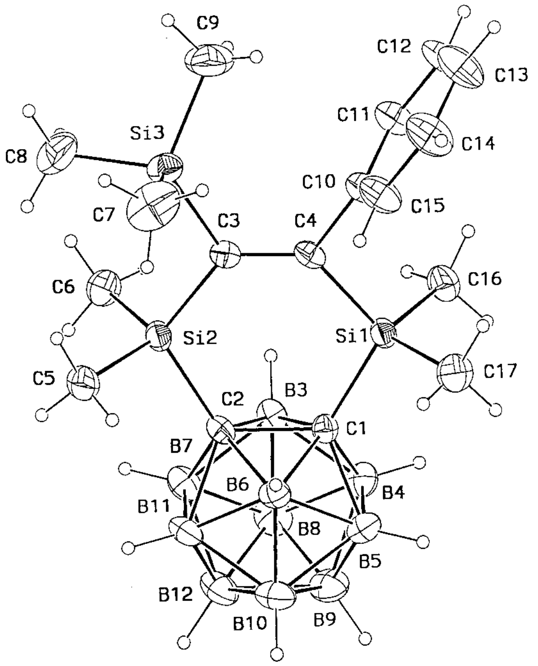
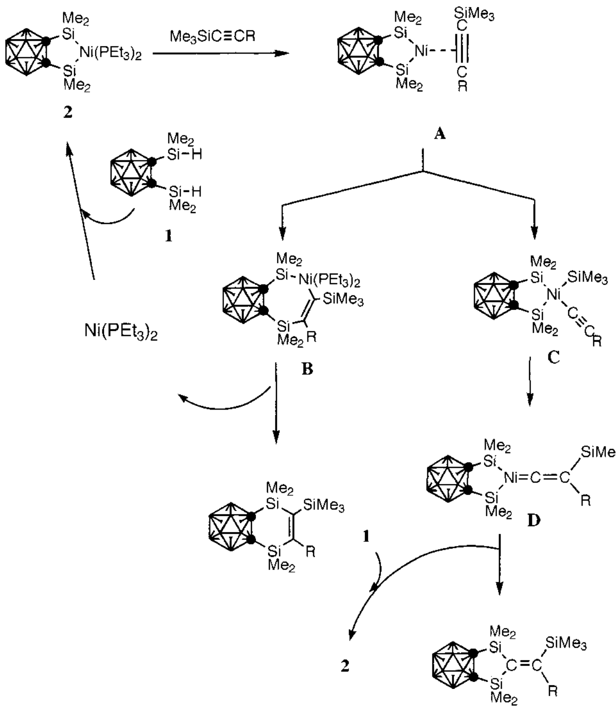


**Figure 2.** X-ray crystal structure of **9** with 50% probability thermal ellipsoids depicted. Selected bond lengths (Å) and angles (deg): Si(1)–C(1) 1.905(4), Si(2)–C(2) 1.910(4), C(1)–C(2) 1.677(6), Si(1)–C(4) 1.885(5), Si(2)–C(3) 1.869(4), C(3)–C(4) 1.366(6), C(3)–Si(3) 1.919(5), C(14)–C(10) 1.516, Si(1)–C(1)–C(2) 119.8(3), C(1)–C(2)–Si(2) 121.2(3) C(2)–Si(2)–C(3) 113.33(19), Si(2)–C(3)–C(4) 123.2(3), C(3)–C(4)–Si(1) 130.3(3), C(4)–Si(1)–C(1) 111.28(18).

in the $^{29}$Si NMR of **10** provide evidence for the five-membered-ring structure. The formation of **10** involves a 1,2-trimethylsilyl shift during the reaction via an oxidative addition reaction of a Si–C bond to the intermediate. Such a trimethylsilyl shift has been observed in the reaction of chloro(triisopropylphosphine)rhodium(I) with trimethylsilyl-substituted alkynes[16] and in the nickel-catalyzed reaction of 3,4-benzo-1,1,2,2,-tetraethyl-1,2-disilacyclobut-3-ene with silyl-substituted alkynes.[5a]

Although all the spectra of **3**–**10** are consistent with the proposed formulations, this does not provide an unambiguous proof of structure. Accordingly, a single-crystal X-ray diffraction study of the 1-phenyl-2-(trimethylsilyl)acetylene insertion product **9** was undertaken. The molecule structure of **9** is shown in Figure 2. A summary of data collection parameters is included in Table 3. The X-ray crystal structure of **9** confirmed the presence of a six-membered-ring compound comprising a carboranylene, two silicon atoms, and an unsaturated hydrocarbon fragment with a C=C bond. An interesting structural feature of **9** is that the two planes consisting of Si1, Cl, C2, Si2 and Si2, C3, C4, Si1 are slightly bent (165.4°). The C3–C4 bond length (1.366(6) Å) is slightly longer than the typical value for the carbon–carbon double bond (1.317 Å)[17] and that of 5,6-carboranylene-1,1,4,4-tetramethyl-2,3-diphenyl-1,4-disilacyclohex-2-ene (1.33(1) Å)[15] and the tricyclic product (1.346(3) Å) formed in the reaction between diphenylacetylene and tetrakis(dimethylsilyl)benzene.[18] The bond lengthening of C3–C4 may be related to the wideness of the Si2–C3–C4 bond angle (123.2(3)°), resulting in the diminishment of the s character of the C4 atom.

**Scheme 1**



In contrast to the nickel-catalyzed double silylation reactions of the above alkynes, when dimethyl acetylenedicarboxylate was employed as the alkyne in the nickel-catalyzed reaction of **1** at 80 °C, the alkyne cyclotrimerization product was isolated in a quantitative yield. However, the reaction of the nickel intermediate with dimethyl acetylenedicarboxylate under mild conditions (0 °C) gave the six-membered-ring compound **11** in 57% yield, together with the cyclotrimerization product (entry 8). $^{1}$H, $^{13}$C, and $^{29}$Si NMR spectra for **11** were identical with those of an authentic sample.[15] A similar stoichiometric reaction of the nickel intermediate **2** with bis(trimethylsilyl)acetylene afforded two products, 5,6-carboranylene-1,1,4,4-tetramethyl-2,3-bis(trimethylsilyl)1,4-disilacyclohex-2-ene (**12**) and 4,5-carboranylene-1,1,3,3-tetramethyl-2-[bis(trimethylsilyl)-methylene]-1,3-disilacyclopentane (**13**), in 66% and ~6% yield, respectively. All spectral data for **12** and **13** support the proposed structures. In particular, the $^{29}$Si NMR chemical shift of $-9.98$ and $-11.02$ ppm for **12** resembles the values reported for the six-membered-ring compounds.[15] In contrast, the $^{29}$Si NMR of **13** shows two resonances at 1.74 and 0.87 ppm, clearly indicating that product **13** is a five-membered-ring compound. Such a trimethylsilyl shift has been observed in the nickel-catalyzed reaction.[19]

Ishikawa and co-workers[19] have recently suggested the mechanistic pathways in the nickel-catalyzed reaction of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene with disubstituted acetylenes. Therefore, the formation of six- and five-membered disilylene ring compounds may be explained by a series of steps, as shown in Scheme 1.

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[18] Uchimaru, Y.; Brandl, P.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1993**, 744.

[19] (a) Naka, A.; Hayashi, M.; Okazaki, S.; Kunai, A.; Ishikawa, M. *Organometallics* **1996**, *15*, 1101. (b) Ishikawa, M.; Nomura, Y.; Tozaki, E.; Kunai, A.; Ohshita, J. *J. Organomet. Chem.* **1990**, *399*, 205.

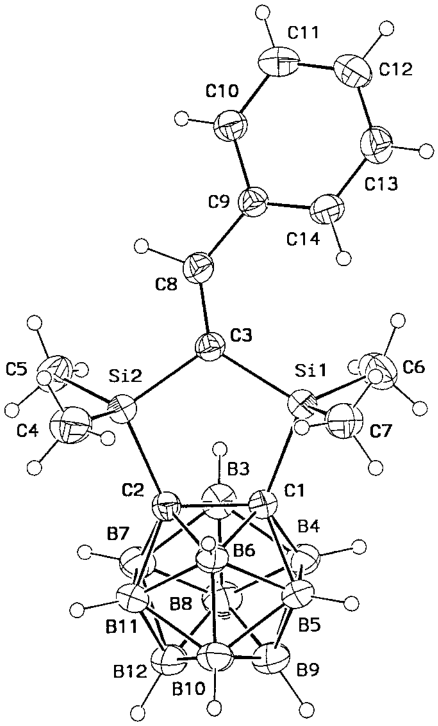

**Figure 3.** X-ray crystal structure of **14** with 50% probability thermal ellipsoids depicted. Selected bond lengths (Å) and angles (deg): C(1)−C(2) 1.685(4), C(1)−Si(1) 1.919(3), Si(1)−C(3) 1.870(3), C(3)−Si(2) 1.870(3), Si(2)−C(2) 1.904(3), C(3)−C(8) 1.354(4), Si(1)−C(1)−C(2) 112.55(18), C(1)−C(2)−Si(2) 111.98(18), C(2)−Si(2)−C(3) 100.10(12), Si(1)−C(3)−Si(2) 113.85(14), Si(1)−C(3)−C(8) 130.3(2), Si(2)−C(3)−C(8) 115.6(2), C(3)−C(8)−C(9) 130.2(3).

In the first stage, the intermediate **2** coordinates to an alkyne (**A**). This is followed by insertion of the triple bond into a Ni−Si bond to give a seven-membered intermediate (**B**) or by oxidative addition of the Si−C bond to a nickel center (**C**). Reductive elimination of the nickel fragment from intermediate **B** leads to the six-membered disilylene ring compound. On the other hand, formation of the five-membered disilylene ring compound may be explained in terms of a shift of trimethylsilyl groups to the CR carbon atom, giving a (vinylidene)nickel intermediate (**D**).

The disilanickela compound **2** is not effective in the nickel-catalyzed double silylation reaction with styrene. However, the stoichiometric reaction of **2** with styrene afforded 4,5-carboranylene-1,1,3,3-tetramethyl-2-phenylmethylene-1,3-disilacyclopentane (**14**) in 76% yield (entry 10). A key feature in the $^1$H NMR spectrum of **14** includes a singlet at 7.71 ppm assigned to the vinyl proton. A characteristic low-frequency $^{13}$C NMR resonance at 139.75 ppm provides evidence for a tethered carbon atom of the two silicon moieties. The $^{29}$Si NMR spectrum of **14** shows two resonances at 4.32 and 0.42 ppm, which are consistent with our prior observation with the five-membered disilylene ring compounds.

Unambiguous confirmation was provided by an X-ray crystallographic analysis of **14**. The molecular structure of **14** is shown in Figure 3. The molecule contains one $C_2Si_2C$ five-membered ring comprising a carboranylene, two silicon atoms, and an unsaturated carbon fragment containing a C=C bond. The C3−C8 bond length (1.354(4) Å) is slightly longer than the typical value for the carbon−carbon bond (1.317 Å) and comparable to that of 5,6-carboranylene-1,1,4,4-tetramethyl-2,3-diphenyl-1,4-disilacyclohex-2-ene (1.33(1) Å).[15]

**Nickel-Catalyzed Reaction with Alkenes.** The disilanickela complex **2** is an effective catalyst for the double silylation of some alkenes. Thus, reaction of **1** with 2 equiv of 4-vinylanisole in the presence of a catalytic amount of **2** afforded a moderate yield of the five-membered disilylene compound **15** (entry 11). A similar reaction of **1** with 1-octene also gave a five-membered disilylene ring compound **16** as a colorless liquid. However, treatment of **1** with 1.2 equiv of 1,1-diphenylethylene in the presence of a catalytic amount of **2** gave five-membered disilylene ring compound **17**, which contained a saturated side chain in 74% yield (entry 13). The formulation of **17** was confirmed by spectrometric analysis. The mass spectrum of the product showed a molecular ion at $m/z$ 438. Two characteristic doublets at 3.93 and 1.81 ppm in the $^1$H NMR spectrum of **17** are assigned to the two methine protons. A large coupling constant ($J_{HH}$ = 13.19 Hz) indicates that the two methine protons are in a trans configuration due to the steric hindrance of the phenyl groups. A low-frequency $^{13}$C NMR resonance at 22.68 ppm provides evidence for the tethered carbon atom of the silicon moieties. The value is comparable to that observed for *cis*-4,5-benzo-1,1,3-triethyl-2-methyl-1,3-disilacyclopent-4-ene.[20] Its $^{29}$Si NMR spectrum reveals two resonances at −0.48 and −3.42 ppm due to two nonequivalent silicon atoms. These results are wholly consistent with the proposed structure.

The formation of **14** in the reaction with styrene and **17** in the reaction with 1,1-diphenylethylene can be rationalized in terms of steric factors. As indicated in the crystal structure of **14**, the bond angle of C3−C8−C9 is 130.2(3)° and the phenyl ring lies in the plane Si1−C3−C8−C9 in a horizontal configuration. The reaction of **1** with 1,1-diphenylethylene then must have given **17** by intramolecular hydrosilylation due to the steric hindrance of the two phenyl groups. The routes to **14** and **17** may have in common an initial oxidative addition reaction of an olefinic C−H bond to the nickel center **E**, followed by the shift of a phenylethyl group from the nickel atom to one of two silicon atoms (**F**), as shown in Scheme 2. Another olefinic C−H oxidative addition followed by elimination of nickel dihydride then could lead to compound **14**. On the other hand, when R = Ph in **F**, such a second C−H oxidative addition may not be possible and an intramolecular hydrosilylation takes place instead, leading to compound **17**. We emphasize that these suggested reaction courses have no experimental support and are entirely speculative.

The nickel-catalyzed reaction of **1** with 2,3-dimethylbutadiene afforded 7,8-carboranylene-1,1,6,6-tetramethyl-3,4-dimethyl-1,6-disilacycloocta-3-ene **18** via an addition reaction in 84% yield (entry 14). The elemental analysis and mass spectrum of **18** were consistent with the foumula $C_{12}H_{32}B_{10}Si_2$. The $^1$H NMR spectrum of **18** shows a single resonance at $\delta$ 1.56, attributed to methyl protons on carbon, as well as two resonances due to methyl protons on silicon which show the presence of two nonequivalent methyl protons. Its $^{13}$C NMR spec-

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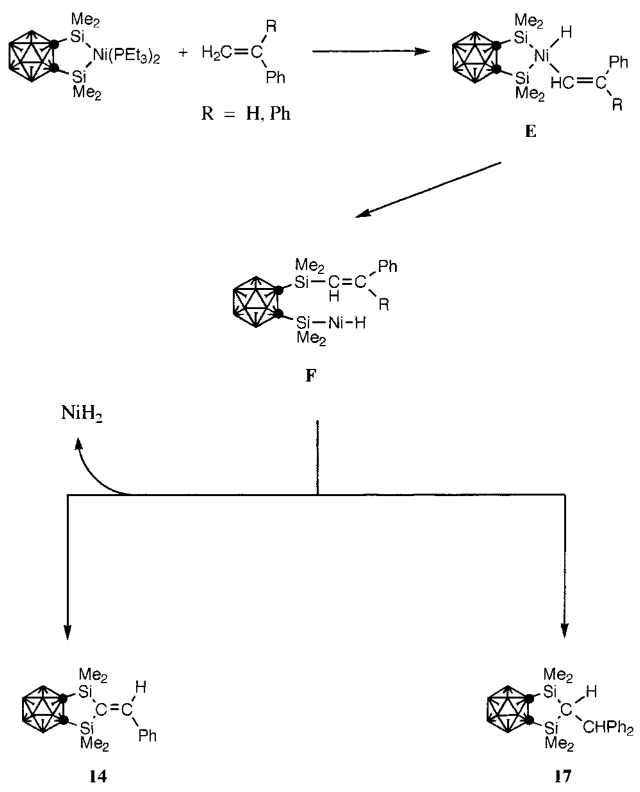
(20) Ishikawa, M.; Naka, A.; Ohshita, J. *Organometallics* **1993**, *12*, 4987.

**Scheme 2**



trum consists of three lines at *δ* 21.19, −0.41, and −0.86. The value of *δ* 21.19 is assigned to *C*−CH$_3$ and two higher values of *δ* −0.41 and −0.86 assigned to Si−*C*H$_3$. These spectral features are wholly consistent with the proposed structure of **18**. The formation of **18** may be interpreted in terms of initial activation of a terminal olefinic C−H bond by the nickel species followed by a 1,4-addition reaction. Such a 1,4-addition has been observed in the Ni-, Pd-, and Pt-mediated cycloaddition reactions of disilabutenes to conjugated dienes.[21]

## Experimental Section

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques. Benzene, diethyl ether, toluene, and THF were freshly distilled from sodium benzophenone. Dichloromethane and hexane were dried and distilled from CaH$_2$. $^1$H, $^{13}$C, and $^{31}$P NMR spectra were recorded on a Varian Gemini 200 spectrometer operating at 200.1, 50.3, and 80.9 MHz, respectively. $^{29}$Si NMR spectra were recorded on a JEOL Model EX-270 spectrometer. Chemical shifts are referenced relative to TMS($^1$H), benzene-*d*$_6$ ($^1$H, *δ* 7.156; $^{13}$C{$^1$H}, *δ* 128.00), and external 85% H$_3$PO$_4$ ($^{31}$P). IR spectra were recorded on a Biorad FTS-165 spectrophotometer. Mass spectra were recorded on a high-resolution VG 70-VSEG instrument operating with an electron beam energy of 60 eV for EI mass spectra, and elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA 1108 analyzer.

*o*-Carborane was purchased from the Callery Chemical Co. and used without purification. The starting materials, Ni(cod)$_2$, PEt$_3$, and Me$_2$SiHCl, were purchased from Strem Chemicals. The alkynes and alkenes were purchased from Aldrich. 1,2-Bis(dimethylsilyl)carborane[10] and Ni(PEt$_3$)$_4$[22] were prepared according to the known procedures.

**Me$_2$Si(1,2-C$_2$B$_{10}$H$_{10}$)SiMe$_2$Ni(PEt$_3$)$_2$ (2).** 1,2-Bis(dimethylsilyl)carborane **1** (0.48 g, 1.85 mmol) in 20 mL of pentane was added to a stirred solution of Ni(PEt$_3$)$_4$ (0.98 g, 1.85 mmol) in 20 mL of pentane at −20 °C. The solution was warmed to room temperature for 2 h and then was filtered. The residue was dissolved in toluene (20 mL), and this solution was layered with pentane (20 mL) at −15 °C. Dark red crystals of **2** were formed over a period of several days (0.88 g, 86% yield). Compound **2** remained unchange when kept for 3 days in an inert atmosphere at room temperature. $^1$H NMR (C$_6$D$_6$): *δ* 1.13 (dq, 12H, $J_{HH}$ = 5.6 Hz, $J_{HP}$ = 6.4 Hz, C*H$_2$*), 0.63 (dt, 18H, $J_{HH}$ = 5.6 Hz, $J_{HP}$ = 14.2 Hz, C*H$_3$*), 0.42(s, 12H, SiC*H$_3$*). $^{13}$C{$^1$H} NMR (C$_6$D$_6$): *δ* 71.08, 17.05 (d, $J_{CP}$ = 16.64 Hz, *C*H$_2$), 6.74 (s, *C*H$_3$), 4.11 (s, Si*C*H$_3$). $^{31}$P{$^1$H} NMR (C$_6$D$_6$): *δ* 5.58. $^{29}$Si NMR-(C$_6$D$_6$): *δ* 43.19 (t, $J_{SiP}$ = 40.11 Hz). MS *m*/*z* 553 [M$^+$]. Anal. Calcd for C$_{18}$H$_{52}$B$_{10}$NiP$_2$Si$_2$: C, 39.11; H, 9.40. Found: C, 38.84; H, 9.22.

**Nickel-Catalyzed Reaction of 1 with Various Alkynes. General Procedure.** Compounds **3**−**10** were prepared by the reaction of **1** with the corresponding alkyne in the presence of a catalytic amount of **2**. In a typical synthesis, a mixture of 0.09 g (0.51 mmol) of diphenylacetylene, 0.12 g (0.46 mmol) of **1**, and 0.01 g (0.018 mmol) of **2** in toluene (20 mL) was stirred at room temperature for 12 h. The mixture was filtered through a short silica gel column to remove the nickel species from the reaction mixture. The solvent was then removed and chromatography using benzene/hexane (1:1) as eluent followed. Recrystallization from hexane at −20 to −10 °C afforded 5,6-carboranylene-1,1,4,4-tetramethyl-2,3-diphenyl-1,4-disilacyclohex-2-ene (0.17 g, 76% yield). All spectral data for **3**−**5** and **7** were identical with their authentic samples.[15]

**(i) 6 from the Reaction with 1-Phenyl-1-propyne**. Mp: 188 °C. $^1$H NMR (CDCl$_3$): *δ* 7.33−6.81 (m, 5H, *Ph*), 1.56 (s, 3H, C−C*H$_3$*), 0.39 (s, 6H, Si−C*H$_3$*), 0.17 (s, 6H, Si−C*H$_3$*). $^{13}$C{$^1$H} NMR(CDCl$_3$): *δ* 160.82 (*C*Ph), 157.04 (*C*Me), 128.59, 127.39, 126.42 (*Ph*), 19.71 (C−*C*H$_3$), −1.41 (Si−*C*H$_3$), −1.86 (Si−*C*H$_3$). $^{29}$Si NMR (CDCl$_3$): *δ* −8.92, −10.34. MS: *m*/*z* 374 [M$^+$]. Anal. Calcd for C$_{15}$H$_{30}$B$_{10}$Si$_2$: C, 48.11; H, 8.01. Found: C, 47.87; H, 7.93.

**(ii) 8 from the Reaction with 1-Hexyne.** $^1$H NMR (CDCl$_3$): *δ* 6.24 (s, 1H, =C*H*), 2.17 (t, 2H, $J_{HH}$ = 9.4 Hz, CC*H$_2$*), 1.57−1.24 (m, 4H, C*H$_2$*), 0.92 (t, 3H, $J_{HH}$ = 4.4 Hz, C*H$_3$*), 0.33 (s, 6H, Si−C*H$_3$*), 0.29 (s, 6H, Si−C*H$_3$*). $^{13}$C{$^1$H} NMR (CDCl$_3$): *δ* 160.4 (=*C*H), 138.5 (Si*C*=), 40.1, 31.7, 23.3, 14.9, −0.04 (Si−*C*H$_3$), −0.49 (Si−*C*H$_3$). $^{29}$Si NMR (CDCl$_3$): *δ* 4.42, 0.92. MS: *m*/*z* 340 [M$^+$]. Anal. Calcd for C$_{12}$H$_{32}$B$_{10}$Si$_2$: C, 42.34; H, 9.40. Found: C, 42.02; H, 9.24.

**(iii) 9 and 10 from the Reaction with 1-Phenyl-2-(trimethylsilyl)acetylene**. For **9**: mp 118−120 °C. $^1$H NMR (CDCl$_3$): *δ* 7.25−6.82 (m, 5H, *Ph*), 0.50 (s, 6H, Si−C*H$_3$*), 0.13 (s, 6H, Si−C*H$_3$*), −0.21 (s, 9H, Si−C*H$_3$*). $^{13}$C{$^1$H} NMR (CDCl$_3$): *δ* 172.77 (=*C*Ph), 157.41 (=*C*SiMe$_3$), 145.95, 128.33, 126.94, 126.76 (*Ph*), 68.15, 66.67 (*carborane carbons)*, 2.42, 1.44, −0.92. $^{29}$Si NMR (CDCl$_3$): *δ* −6.2, −10.2, −13.4. MS: *m*/*z* 432 [M$^+$], 417 [M$^+$ − CH$_3$]. Anal. Calcd for C$_{17}$H$_{36}$B$_{10}$Si$_3$: C, 47.20; H, 8.32. Found: C, 46.85; H, 8.09. For **10**: mp 110−112 °C. $^1$H NMR (CDCl$_3$): *δ* 7.22−6.76 (m, 5H, *Ph*), 0.54 (s, 6H, Si−C*H$_3$*), 0.18 (s, 6H, Si−C*H$_3$*), −0.08 (s, 9H, Si−C*H$_3$*). $^{13}$C{$^1$H} NMR (CDCl$_3$): *δ* 180.22, 156.02 (*olefinic carbons*), 145.22, 129.58, 127.22, 126.92 (*Ph*), 4.42, 1.42, 0.12. $^{29}$Si NMR (CDCl$_3$): *δ* 2.82, 1.08. −1.44. Anal. Calcd for C$_{17}$H$_{36}$B$_{10}$Si$_3$: C, 47.20; H, 8.32. Found: C, 46.72; H, 8.13.

**(iv) Reaction of 2 with Dimethyl Acetylenedicarboxylate (11).** To a stirred toluene solution (10 mL) of **2** (0.2 g, 0.36 mmol) was added dimethyl acetylenedicarboxylate (0.12

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[21] (a) Tsuji, Y.; Lago, R. M.; Tomohiro, S.; Tsuneishi, H. *Organometallics* **1992**, *11*, 2353. (b) Tamao, K.; Okazaki, S.; Kumada, M. *J. Organomet. Chem.* **1978**, *146*, 87. (c) Obora, Y.; Tsuji, Y.; Kawamura, T. *Organometallics* **1993**, *12*, 2853. (d) Tanaka, M.; Uchimaru, Y.; Lautenschlager, H.-J. *Organometallics* **1991**, *10*, 16. (e) Matsumoto, H.; Shono, K.; Wada, A.; Matsubara, I.; Watanabe, H.; Nagai, Y. *J. Organomet. Chem.* **1980**, *199*, 185.

[22] Browning, J.; Cundy, C. S.; Green, M.; Stone, F. G. A. *J. Chem. Soc. A* **1969**, 20.

mL, 1 mmol) at −80 °C. The mixture was warmed to 0 °C and stirred for 3 h at that temperature. The solvent was removed in vacuo, and chromatography using ethyl acetate/hexane (1:9) as eluent followed. Pure **11** was obtained in 55−60% yield. All spectral data for product **11** were identical with those of an authentic sample.[15]

**(v) Reaction of 2 with Bis(trimethylsilyl)acetylene (12 and 13).** To a stirred solution (10 mL) of **2** (0.3 g, 0.54 mmol) was added bis(trimethyl silyl)acetylene (0.32 mL, 1.4 mmol). The mixture was heated to 80 °C and stirred overnight. Products **12** and **13** were isolated by chromatography using benzene/hexane (1:1) as eluent. For **12**: mp 114−116 °C. $^{1}$H NMR ($CDCl_3$): $\delta$ 0.40 (s, 12H, Si−C$H_3$), 0.27 (s, 18H, Si−C$H_3$). $^{13}$C{$^{1}$H} NMR ($CDCl_3$): $\delta$ 168.51 (C═*C*), −4.37 (Si−*C*H$_3$), −5.94 (Si−*C*H$_3$). $^{29}$Si NMR ($CDCl_3$): $\delta$ −1.86, −9.98, −11.02. MS: *m*/*z* 413 [M$^+$ − CH$_3$], 342 [M$^+$ − 2CH$_3$]. Anal. Calcd for $C_{14}H_{40}B_{10}Si_4$: C, 39.23; H, 9.33. Found: C, 39.42; H, 9.51. For **13**: mp 110 °C. $^{1}$H NMR ($CDCl_3$): $\delta$ 0.32 (s, 12H, Si−C$H_3$), 0.18 (s, 12H, Si−C$H_3$). $^{13}$C{$^{1}$H} NMR ($CDCl_3$): $\delta$ 174.33 (C═*C*), −0.64 (Si−*C*H$_3$), −1.74 (Si−*C*H$_3$). $^{29}$Si NMR ($CDCl_3$): $\delta$ 1.74, 0.87, −0.92. Anal. Calcd for $C_{14}H_{40}B_{10}Si_4$: C, 39.23; H, 9.33. Found: C, 38.82; H, 9.02.

**(vi) Reaction of 2 with Styrene (14).** A mixture of 0.2 g (0.36 mmol) of **2** and 0.07 mL (0.7 mmol) of styrene in toluene (10 mL) was refluxed overnight. The solvent was removed in vacuo, and chromatography using benzene/hexane (1:3) as eluent followed. Recrystallization from hexane at −20 °C afforded 4,5-carboranylene-1,1,3,3-tetramethyl-2-(phenylmethylene)-1,3-disilacyclopentane, **14**, in 76% yield, mp 116 °C. $^{1}$H NMR ($CDCl_3$): $\delta$ 7.71 (s, 1H, *H*C═C), 7.39−7.24 (m, 5H, *Ph*), 0.41 (s, 6H, Si-*C*H$_3$), 0.28 (s, 6H, Si−*C*H$_3$). $^{13}$C{$^{1}$H} NMR ($CDCl_3$): $\delta$ 159.44, 139.75 (*olefinic carbons*), 130.19, 129.25, 128.54, 128.46, 127.72 (*Ph*), 75.04, 72.60 (*carborane carbons*), −0.86−1.52 (Si-*C*H$_3$). $^{29}$Si NMR ($CDCl_3$): $\delta$ 4.32, 0.42. MS *m*/*z* 360 [M$^+$]. Anal. Calcd for $C_{14}H_{28}B_{10}Si_2$: C, 46.65; H, 7.76. Found: C, 46.24; H, 7.58.

**Nickel-Catalyzed Reaction of 1 with Various Alkenes. General Procedure.** Compounds **15**−**19** were prepared by the reaction of **1** with the corresponding alkenes in the presence of a catalytic amount of **2**. In a typical reaction, a mixture of 0.12 g (0.46 mmol) of **1**, 0.1 mL (0.55 mmol) of 1,1-diphenylethylene, and 0.01 g (0.018 mmol) of **2** in toluene (15 mL) was heated to 80 °C and stirred for 12 h. The solvent was removed in vacuo, and chromatography using benzene/hexane (1:3) as eluent ($R_f$ = 0.6) followed. Recrystallization from hexane (5 mL) at −5 °C afforded 4,5-carboranylene-1,1,3,3-tetramethyl-2-(diphenylmethyl)-1,3-disilacyclopentane, **17**, in 74% yield, mp 185−189 °C (dec). $^{1}$H NMR ($CDCl_3$): $\delta$ 7.35−7.15 (m, 10H, *Ph*), 3.96 (d, 1H, $J_{HH}$ = 13.19 Hz, C*H*), 1.82 (d, 1H, $J_{HH}$ = 13.19 Hz, C*H*), 0.13 (s, 6H, Si−C$H_3$), −0.08 (s, 6H, Si−C$H_3$). $^{13}$C{$^{1}$H} NMR ($CDCl_3$): $\delta$ 144.93, 128.73, 127.45, 127.15 (*Ph*), 49.87 (*C*H), 22.68 (*C*H), −0.13, −2.92 (Si-*C*H$_3$). $^{29}$Si NMR ($CDCl_3$): $\delta$ −0.48, −3.42. MS: *m*/*z* 438 [M$^+$]. Anal. Calcd for $C_{20}H_{34}B_{10}Si_2$: C, 54.78; H, 7.75. Found: C, 54.32; H, 7.50.

**(vii) 15 from the Reaction with 4-Vinylanisole**. Mp: 131 °C. $^{1}$H NMR ($CDCl_3$): $\delta$ 7.61 (s, 1H, *H*C═C), 7.26−6.87 (m, 4H, *Ph*), 3.84 (s, 3H, C$H_3$), 0.39 (s, 6H, Si−C$H_3$), 0.33 (s, 6H, Si−C$H_3$). $^{13}$C{$^{1}$H} NMR ($CDCl_3$): $\delta$ 160.74, 159.05 (*olefinic carbons*), 136.06, 132.44, 129.72, 114.01 (*Ph*), 73.35, 72.86 (*carborane carbons*), 55.53 (O−*C*H$_3$), −0.69 (Si−*C*H$_3$), −1.27 (Si−*C*H$_3$). $^{29}$Si NMR ($CDCl_3$): $\delta$ 2.64, 0.28. MS: *m*/*z* 390 [M$^+$], 375 [M$^+$ − CH$_3$]. Anal. Calcd for $C_{15}H_{30}B_{10}OSi_2$: C, 46.14; H, 7.68. Found: C, 45.76; H, 7.36.

**(viii) 16 from the Reaction with 1-Octene.** $^{1}$H NMR ($CDCl_3$): $\delta$ 6.78 (t, 1H, $J_{HH}$ = 13.78 Hz, ═C*H*), 2.19 (q, 2H, $J_{HH}$ = 12.14 Hz, C$H_2$), 1.54−1.20 (m, 8H, (C$H_2$)$_4$), 0.88 (t, 3H, $J_{HH}$ = 7.82 Hz, C$H_3$), 0.38 (s, 6H, Si−C$H_3$), 0.25 (s, 6H, Si−C$H_3$). $^{13}$C{$^{1}$H} NMR ($CDCl_3$): $\delta$ 162.51, 140.44 (*olefinic carbons*), 36.92, 30.09, 27.40, 27.23, 20.98, 1.47, −2.69 (Si−*C*H$_3$), −2.97 (Si−*C*H$_3$). $^{29}$Si NMR ($CDCl_3$): $\delta$ 3.82, 0.12. MS: *m*/*z* 368 [M$^+$]. Anal. Calcd for $C_{14}H_{36}B_{10}Si_2$: C, 45.64; H, 9.77. Found: C, 45.18; H, 9.46.

**(ix) 18 from the Reaction with 2,3-Dimethyl-1,3-butadiene**. Mp: 149 °C. $^{1}$H NMR ($CDCl_3$): $\delta$ 1.64 (s, 4H, C$H_2$), 1.56 (s, 6H, C$H_3$), 0.35 (s, 6H, Si−C$H_3$), 0.27 (s, 6H, Si−C$H_3$). $^{13}$C{$^{1}$H} NMR ($CDCl_3$): $\delta$ 120.58 (*C*═C), 74.94 (*carborane carbon*), 21.48 (*C*H$_2$), 21.19 (*C*H$_3$), −0.41 (Si−*C*H$_3$), −0.86 (Si−*C*H$_3$). $^{29}$Si NMR ($CDCl_3$): $\delta$ 6.32. MS: *m*/*z* 340 [M$^+$], 325 [M$^+$ − CH$_3$]. Anal. Calcd for $C_{12}H_{32}B_{10}Si_2$: C, 42.34; H, 9.40. Found: C, 41.98; H, 9.24.

**X-ray Crystallography.** Details of the crystal data and a summary of intensity data collection parameters for **2**, **9**, and **14** are given in Table 1. A red prism-shaped crystal of dimensions 0.38 × 0.20 × 0.40 mm of **2** was selected for structural analysis. Intensity data for **2** were collected using a Siemens SMART ccd area detector mounted on a Siemens P4 diffractometer equipped with graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å). The sample was cooled to 153 K. The intensity data were measured as a series of $\phi$ oscillation frames each of 0.4° for 30 s/frame. A colorless crystal of dimensions 0.4 × 0.4 × 0.5 mm of **9** was mounted at the tip of a glass fiber. The cell parameters were obtained by least-squares refinement from 25 reflections in the range $1.9° < \theta < 25.97°$ measured with graphite-monochromated Mo K$\alpha$ radiation on Enraf-Nonious CAD-4 diffractometer. X-ray intensity data were collected by the $\omega-2\theta$ scan method with $\theta = 25.97$ for the ranges $-12 < h < 12$, $0 < k < 26$, $0 < l < 15$. The cell parameters of **14** were obtained by least-squares refinement from 25 reflections in the range $2.01° < \theta < 25.97°$ on Enraf-Nonious CAD-4 diffractometer. X-ray intensity data were collected by the $\omega$-2$\theta$ scan method with $\theta = 25.97$ for the ranges $0 < h < 11$, $0 < k < 22$, $-15 < l < 15$. The structures were solved by direct methods and refined by full-matrix least-squares methods on $F^2$. Hydrogen atom positions were initially determined by geometry and refined by a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters.

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**Supporting Information Available:** Tables listing crystallographic information, atomic coordinates and $B_{eq}$ values, anisotropic thermal parameters, and intramolecular bond distances, angles, and torsion angles for **2**, **9**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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