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

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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 $o-B_{10}H_{10}C_2(SiMe_2)_2(RC=$ 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 silvlation 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 2,3dimethylbutadiene in the presence of the nickel catalyst also was studied. The crystal structures of 2, 9, and 14 are described.

Introduction

The double silvlation of unsaturated organic substrates catalyzed by group 10 metal complexes¹ has been well documented for two decades. Nickel complexes, in particular, provide excellent catalysts for such reactions of silicon-containing linear compounds² 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 silvl 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 silvlation reactions of a cyclic bis(silyl)platinum complex containing an o-carboranylene.¹⁰ However, the double silvlation reactions were stoichiometric processes involving reaction of a stable PtSi₂P₂ 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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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-(SiMe₂)₂C₂B₁₀H₁₀]Ni(PEt₃)₂ Complex 2. In our search for a stable bis(silyl)nickel complex, we investigated the reaction of o-bis(dimethylsilyl)carborane with Ni(PEt₃)₄. When 1.2 equiv of o-bis(dimethylsilyl) carborane 1 was treated with 1 equiv of Ni(PEt₃)₄ in pentane at 25 °C, an immediate color change from yellow to deep red occurred with evolution of H₂ (eq 1). Standard workup and crystal-



lization from toluene-pentane gave [o-(SiMe₂)₂ C₂B₁₀H₁₀]-Ni(PEt₃)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 ¹H, ¹³C, ³¹P, and ²⁹Si 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 ³¹P NMR signal was shifted from -2.2 ppm for Ni(PEt₃)₃¹² to 5.58 ppm. The structure of 2 was unambiguously established by singlecrystal 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 [(µ-Cl)₂Ni₂(SiCl₃)₄][(CMe₃)₂C₅H₃NH]₂¹³ 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(PPh₃)₂(C₂H₄) (2.15 Å) and Ni(PCy₃)₂-(η-CO₂) (2.15 Å).¹⁴

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 nickelcatalyzed double silylation can be carried out either by reacting **1** and the alkyne in the presence of the Ni-



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).

(PEt₃)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).

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-memberedring 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 fivemembered-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 Me₂Si-(o-C₂B₁₀H₁₀)SiMe₂Pt(PPh₃)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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 Table 1. Nickel-Catalyzed Reactions of Alkynes

 with 1,2-Bis(dimethylsilyl)carborane

entry	reactns	conditns	products(yield, %)
1	PhC≡CPh	r.t. (12 h)	Me ₂ Ph Si Ph Si Ph Me ₂
2	PhC=CH	80 で (4 h)	3 (76%)
3	EtC≕CEt	80 °C (6 h)	Si Et Me ₂ Et
4	MeC≕CPh	r. t. (6 h)	$\begin{array}{c} 5 (7/\%) \\ \mathbf{Me}_{2} \\ \mathbf{Si} \\ \mathbf{Me}_{2} \\ \mathbf{Me}_{3} \\ \mathbf{Me}_{4} \\ \mathbf{Me}_{4} \\ \mathbf{Me}_{4} \\ \mathbf{Me}_{5} \\ $
5	MeC≅CMe	80 ℃ (6 h)	6 (82 %) (-8 %)
6	Bu ⁿ C≡⊂H	80 °C (6 h)	Me ₂ H Si C=C H Si Bu-n Me ₂ Bu-n 8 (71%)
7	PhC≡CSiMe ₃	r.t. (4 h)	Me ₂ Si Ph Si SiMe ₃ 9 (62 %) 10 (~8 %)
8"	MeO ₂ CC=CCO ₂ Me + 2	0 ℃ (3 h)	Me2 CO2Me MeO2 CO2Me SI CO2Me MeO2 CO2Me SI CO2Me MeO2 CO2Me Me2 MeO2 CO2Me CO2Me Me2 MeO2 CO2Me CO2Me Me2 MeO2 CO2Me CO2Me Me2 CO2Me CO2Me CO2Me Me2 CO2Me CO2Me CO2Me
9 ⁴	Me₃SiC≡CSiMe₃ + 2	80 °C (12 h)	Me ₂ Si SiMe ₃ Me ₂ Si SiMe ₃ Me ₂ Si SiMe ₃ Me ₂ Si SiMe ₃ Me ₂ SiMe ₃ Me ₂ SiMe ₃ Me ₂ SiMe ₃ Si C=C SiMe ₃ SiMe ₃ Si C=C SiMe ₃ Me ₂ SiMe ₃ Si C=C SiMe ₃ Me ₂ SiMe ₃ Me ₃ Si C=C SiMe ₃ Me ₂ SiMe ₃ Me ₃ Si C=C SiMe ₃ SiMe ₃

^a Stoichiometric reaction.

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 ¹H 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 ¹³C NMR spectrum of 9, two resonances at 172.77 and 157.41 ppm of equal intensity were present. The ²⁹Si NMR spectrum of **9** shows three resonances at -6.2, -10.2, and -13.4 ppm. The two resonances at -10.2and -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

 Table 2. Nickel-Catalyzed Reactions of Alkenes

 with 1,2-Bis(dimethylsilyl)carborane

entry	reactns	conditns	products(yield, %)
10^{d}	PhHC=CH ₂ + 2	110 °C (12 h)	Me ₂ Si Si Me ₂ H 14(76 %)
11	H ₂ C=CHC ₆ H ₄ OCH ₃	80 °C (12 h)	Me ₂ H Si C=C Si Me ₂ / 15 (52 %) OMe
12	H ₂ C==CH(CH ₂) ₅ CH ₃	80 °C (12 h)	Me ₂ Si C=C H Si Me ₂ (CH ₂) ₅ CH ₃ 16 (~45 %)
13	H ₂ C=CPh ₂	80 °C (12 h)	Me ₂ Si CHPh ₂ Me ₂ 17 (74 %)
14	H ₃ C CH ₃	r. t. (6 h)	Me2 Si Me2 CH3 18 (84 %)

^a Stoichiometric reaction.

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

	2	9	14
empirical formula	$C_{18}H_{52}B_{10}NiP_2PtSi_2$	C17H36B10Si3	C14H28B10Si2
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		
β (deg)	93.029(2)	96.944(5)	106.587(4)
γ (deg)	90		
V, Å ³	3068.8(3)	2683.6(3)	2160.2(2)
Z value	4	4	4
D(calcd),	1.198	1.071	1.109
(g cm ⁻³)			
F(000)	1184	920	760
abs coeff, mm ⁻¹	0.823	0.181	0.160
λ, (Å)	0.71073	0.71073	0.71073
monochromator	graphite	graphite	graphite
scan type	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$
2θ 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
$R_{\rm w}$	0.1072	0.1537	0.1316
goodness of fit	1.083	0.970	0.967

field (-8 to -16 ppm) than those of the five-membered 4,5-carboranylene-1,3-disilacyclopentane (5 to -4 ppm).^{10,17} The ¹³C 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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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 ²⁹Si NMR of **10** provide evidence for the fivemembered-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 alkynes¹⁶ 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 singlecrystal 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-2ene (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.



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). ¹H, ¹³C, and ²⁹Si 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 4,5carboranylene-1,1,3,3-tetramethyl-2-[bis(trimethylsilyl)methylene]-1,3-disilacyclopentane (13), in 66% and \sim 6% yield, respectively. All spectral data for 12 and 13 support the proposed structures. In particular, the ²⁹Si NMR chemical shift of -9.98 and -11.02 ppm for **12** resembles the values reported for the six-memberedring compounds.¹⁵ In contrast, the ²⁹Si 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-workers¹⁹ have recently suggested the mechanistic pathways in the nickel-catalyzed reaction of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3ene 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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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 sixmembered 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 silvlation reaction with styrene. However, the stoichiometric reaction of **2** with styrene afforded 4,5-carboranylene-1,1,3,3-tetramethyl-2-phe-nylmethylene-1,3-disilacyclopentane (**14**) in 76% yield (entry 10). A key feature in the ¹H NMR spectrum of **14** includes a singlet at 7.71 ppm assigned to the vinyl proton. A characteristic low-frequency ¹³C NMR resonance at 139.75 ppm provides evidence for a tethered carbon atom of the two silicon moieties. The ²⁹Si 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 silvlation 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 fivemembered disilylene ring compound 16 as a colorless liquid. However, treatment of 1 with 1.2 equiv of 1,1diphenylethylene 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 ¹H NMR spectrum of **17** are assigned to the two methine protons. A large coupling constant ($J_{\rm HH} = 13.19$ Hz) indicates that the two methine protons are in a trans configuration due to the steric hindrance of the phenyl groups. A low-frequency ¹³C 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-1,3disilacyclopent-4-ene.²⁰ Its ²⁹Si 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 $130.2(3)^{\circ}$ 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 ¹H NMR spectrum of **18** shows a single resonance at δ 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 ¹³C NMR spec-

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trum consists of three lines at δ 21.19, -0.41, and -0.86. The value of δ 21.19 is assigned to *C*-CH₃ and two higher values of δ -0.41 and -0.86 assigned to Si-*C*H₃. 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 CaH₂. ¹H, ¹³C, and ³¹P NMR spectra were recorded on a Varian Gemini 200 spectrometer operating at 200.1, 50.3, and 80.9 MHz, respectively. ²⁹Si NMR spectra were recorded on a JEOL Model EX-270 spectrometer. Chemical shifts are referenced relative to TMS(¹H), benzene- d_6 (¹H, δ 7.156; ¹³C{¹H}, δ 128.00), and external 85% H_3PO_4 (³¹P). 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, PEt₃, and Me₂SiHCl, were purchased from Strem Chemicals. The alkynes and alkenes were purchased from Aldrich. 1,2-Bis(dimethylsilyl)carborane¹⁰ and Ni(PEt₃)₄²² were prepared according to the known procedures.

Me₂Si(1,2-C₂B₁₀H₁₀)SiMe₂Ni(PEt₃)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(PEt₃)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. ¹H NMR (C_6D_6): δ 1.13 (dq, 12H, $J_{\text{HH}} = 5.6$ Hz, $J_{\text{HP}} = 6.4$ Hz, CH_2), 0.63 (dt, 18H, J_{HH} = 5.6 Hz, J_{HP} = 14.2 Hz, CH_3), 0.42(s, 12H, SiCH₃). ¹³C{¹H} NMR (C₆D₆): δ 71.08, 17.05 (d, $J_{CP} = 16.64$ Hz, CH_2), 6.74 (s, CH₃), 4.11 (s, SiCH₃). ³¹P{¹H} NMR (C₆D₆): ∂ 5.58. ²⁹Si NMR-(C₆D₆): δ 43.19 (t, J_{SiP} = 40.11 Hz). MS m/z 553 [M⁺]. Anal. Calcd for C₁₈H₅₂B₁₀NiP₂Si₂: 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 5,6carboranylene-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. ¹H NMR (CDCl₃): 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). ¹³C-{¹H} NMR(CDCl₃): δ 160.82 (*C*Ph), 157.04 (*C*Me), 128.59, 127.39, 126.42 (*Ph*), 19.71 (C–*C*H₃), -1.41 (Si–*C*H₃), -1.86 (Si–*C*H₃). ²⁹Si NMR (CDCl₃): δ -8.92, -10.34. MS: *m/z* 374 [M⁺]. Anal. Calcd for C₁₅H₃₀B₁₀Si₂: C, 48.11; H, 8.01. Found: C, 47.87; H, 7.93.

(ii) 8 from the Reaction with 1-Hexyne. ¹H NMR (CDCl₃): 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). ¹³C{¹H} NMR (CDCl₃): δ 160.4 (=*C*H), 138.5 (Si*C*=), 40.1, 31.7, 23.3, 14.9, -0.04 (Si–CH₃), -0.49 (Si–C*H*₃). ²⁹Si NMR (CDCl₃): δ 4.42, 0.92. MS: *m/z* 340 [M⁺]. Anal. Calcd for C₁₂H₃₂B₁₀Si₂: 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. ¹H NMR (CDCl₃): δ 7.25–6.82 (m, 5H, *Ph*), 0.50 (s, 6H, Si–*CH*₃), 0.13 (s, 6H, Si–*CH*₃), -0.21 (s, 9H, Si–*CH*₃). ¹³C{¹H} NMR (CDCl₃): δ 172.77 (=*C*Ph), 157.41 (=*C*SiMe₃), 145.95, 128.33, 126.94, 126.76 (*Ph*), 68.15, 66.67 (*carborane carbons*), 2.42, 1.44, -0.92. ²⁹Si NMR (CDCl₃): δ -6.2, -10.2, -13.4. MS: *m/z* 432 [M⁺], 417 [M⁺ - CH₃]. Anal. Calcd for C₁₇H₃₆B₁₀Si₃: C, 47.20; H, 8.32. Found: C, 46.85; H, 8.09. For **10**: mp 110– 112 °C. ¹H NMR (CDCl₃): δ 7.22–6.76 (m, 5H, *Ph*), 0.54 (s, 6H, Si–*CH*₃), 0.18 (s, 6H, Si–*CH*₃), -0.08 (s, 9H, Si–*CH*₃). ¹³C{¹H} NMR (CDCl₃): δ 180.22, 156.02 (*olefinic carbons*), 145.22, 129.58, 127.22, 126.92 (*Ph*), 4.42, 1.42, 0.12. ²⁹Si NMR (CDCl₃): δ 2.82, 1.08. -1.44. Anal. Calcd for C₁₇H₃₆B₁₀Si₃: 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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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. ¹H NMR (CDCl₃): δ 0.40 (s, 12H, Si-CH₃), 0.27 (s, 18H, Si-CH₃). ¹³C{¹H} NMR (CDCl₃): δ 168.51 (C=C), -4.37 (Si-CH₃), -5.94 $(Si-CH_3)$. ²⁹Si NMR (CDCl₃): δ -1.86, -9.98, -11.02. MS: m/z413 $[M^+ - CH_3]$, 342 $[M^+ - 2CH_3]$. Anal. Calcd for $C_{14}H_{40}B_{10}$ -Si₄: C, 39.23; H, 9.33. Found: C, 39.42; H, 9.51. For 13: mp 110 °C. ¹H NMR (CDCl₃): δ 0.32 (s, 12H, Si-CH₃), 0.18 (s, 12H, Si-CH₃). ¹³C{¹H} NMR (CDCl₃): δ 174.33 (C=C), -0.64 (Si-CH₃), -1.74 (Si-CH₃). ²⁹Si NMR (CDCl₃): δ 1.74, 0.87, -0.92. Anal. Calcd for C₁₄H₄₀B₁₀Si₄: 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. ¹H NMR (CDCl₃): δ 7.71 (s, 1H, *H*C=C), 7.39–7.24 (m, 5H, *Ph*), 0.41 (s, 6H, Si-*C*H₃), 0.28 (s, 6H, Si-*C*H₃). ¹³C{¹H} NMR (CDCl₃): δ 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*H₃). ²⁹Si NMR (CDCl₃): δ 4.32, 0.42. MS *m*/*z* 360 [M⁺]. Anal. Calcd for C₁₄H₂₈B₁₀Si₂: 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 1,1diphenylethylene, 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-1,1,3,3tetramethyl-2-(diphenylmethyl)-1,3-disilacyclopentane, 17, in 74% yield, mp 185-189 °C (dec). ¹H NMR (CDCl₃): δ 7.35-7.15 (m, 10H, *Ph*), 3.96 (d, 1H, $J_{\rm HH} = 13.19$ Hz, *CH*), 1.82 (d, 1H, $J_{\text{HH}} = 13.19$ Hz, CH), 0.13 (s, 6H, Si-CH₃), -0.08 (s, 6H, Si-CH₃). ¹³C{¹H} NMR (CDCl₃): δ 144.93, 128.73, 127.45, 127.15 (Ph), 49.87 (CH), 22.68 (CH), -0.13, -2.92 (Si-CH₃). ²⁹Si NMR (CDCl₃): δ -0.48, -3.42. MS: m/z 438 [M⁺]. Anal. Calcd for C₂₀H₃₄B₁₀Si₂: C, 54.78; H, 7.75. Found: C, 54.32; H, 7.50

(vii) 15 from the Reaction with 4-Vinylanisole. Mp: 131 °C. ¹H NMR (CDCl₃): δ 7.61 (s, 1H, *H*C=C), 7.26–6.87 (m, 4H, *Ph*), 3.84 (s, 3H, *CH*₃), 0.39 (s, 6H, Si–*CH*₃), 0.33 (s, 6H, Si–*CH*₃). ¹³C{¹H} NMR (CDCl₃): δ 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*H₃), -0.69 (Si–*C*H₃), -1.27 (Si–*C*H₃). ²⁹Si NMR (CDCl₃): δ 2.64, 0.28. MS: *m/z* 390 [M⁺], 375 [M⁺ – CH₃]. Anal. Calcd for C₁₅H₃₀B₁₀OSi₂: C, 46.14; H, 7.68. Found: C, 45.76; H, 7.36.

(viii) 16 from the Reaction with 1-Octene. ¹H NMR (CDCl₃): δ 6.78 (t, 1H, $J_{HH} = 13.78$ Hz, =CH), 2.19 (q, 2H, $J_{HH} = 12.14$ Hz, CH₂), 1.54–1.20 (m, 8H, (CH₂)₄), 0.88 (t, 3H, $J_{HH} = 7.82$ Hz, CH₃), 0.38 (s, 6H, Si–CH₃), 0.25 (s, 6H, Si– CH₃). ¹³C{¹H} NMR (CDCl₃): δ 162.51, 140.44 (*olefinic carbons*), 36.92, 30.09, 27.40, 27.23, 20.98, 1.47, -2.69 (Si–CH₃), -2.97 (Si–CH₃). ²⁹Si NMR (CDCl₃): δ 3.82, 0.12. MS: *m/z* 368 [M⁺]. Anal. Calcd for C₁₄H₃₆B₁₀Si₂: 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. ¹H NMR (CDCl₃): δ 1.64 (s, 4H, *CH*₂), 1.56 (s, 6H, *CH*₃), 0.35 (s, 6H, Si–*CH*₃), 0.27 (s, 6H, Si–*CH*₃). ¹³C{¹H} NMR (CDCl₃): δ 120.58 (*C*=C), 74.94 (*carborane carbon*), 21.48 (*CH*₂), 21.19 (*CH*₃), -0.41 (Si–*CH*₃), -0.86 (Si– *CH*₃). ²⁹Si NMR (CDCl₃): δ 6.32. MS: *m*/*z* 340 [M⁺], 325 [M⁺ – CH₃]. Anal. Calcd for C₁₂H₃₂B₁₀Si₂: 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 \times 0.20 \times 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 α radiation ($\lambda = 0.71073$ Å). The sample was cooled to 153 K. The intensity data were measured as a series of ϕ oscillation frames each of 0.4° for 30 s/frame. A colorless crystal of dimensions $0.4 \times 0.4 \times 0.5$ mm of $\boldsymbol{9}$ was mounted at the tip of a glass fiber. The cell parameters were obtained by leastsquares refinement from 25 reflections in the range $1.9^{\circ} < \theta$ $< 25.97^{\circ}$ measured with graphite-monochromated Mo K α radiation on Enraf-Nonious CAD-4 diffractometer. X-ray intensity data were collected by the $\omega - 2\theta$ scan method with θ = 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 $2.01^{\circ} < \theta < 25.97^{\circ}$ on Enraf-Nonious CAD-4 diffractometer. X-ray intensity data were collected by the ω -2 θ scan method with θ = 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 leastsquares methods on F². Hydrogen atom positions were initially determined by geometry and refined by a riding model. Nonhydrogen 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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