Nickel-Catalyzed Double Silylation of a Variety of Carbonyl Compounds with 1,2-Bis(dimethylsilyl)carborane

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The nickel-catalyzed reactions of 1,2-bis(dimethylsilyl)carborane **1** with aldehydes such as isobutyraldehyde, trimethylacetaldehyde, hexanal, and benzaldehyde afforded 5,6-carboranylene-2-oxa-1,4-disilacyclohexanes. The dehydrogenative 1,4-double silylation of methacrolein and *trans*-4-phenyl-3-buten-2-one in the presence of a catalytic amount of Ni-(PEt₃)₄ took place under similar conditions. In contrast, the reaction of **1** with α-methyl-*trans*-cinnamaldehyde and *trans*-cinnamaldehyde under the same reaction conditions yielded the insertion compounds formed via insertion of a carbonyl group into each of the C−Si bonds of **1**. The reaction of **1** with diphenylketene gave the 1,2-adduct across the carbonyl group. The structures of compounds **8**, **11**, and **14** were determined by single-crystal X-ray crystallography.

Introduction

The double silylation of unsaturated organic substrates catalyzed by group 10 metal complexes is a useful route to disilyl organic compounds in which two Si−C bonds are created by the addition of two silicon units to unsaturated organic substrates such as alkynes,[1] alkenes,[2] and 1,3-dienes.[3] Nickel complexes, in particular, are excellent catalysts for such reactions of silicon-containing linear compounds[4] and cyclic disilanes.[5]

Recently, we[6] reported the double silylation reactions of [*o*-(SiMe₂)₂C₂B₁₀H₁₀]Pt(PPh₃)₂, **A**, containing an *o*-carboranylene unit with a variety of unsaturated organic substrates. Interestingly, its reaction with *trans*-cinnamaldehyde afforded the insertion compound **B** formed through the insertion of a carbonyl ligand into each of the C−Si bonds. Usually, α,β-unsaturated ketones undergo double silylation to give 1,4-adducts.[7]

A   **B**   **C**
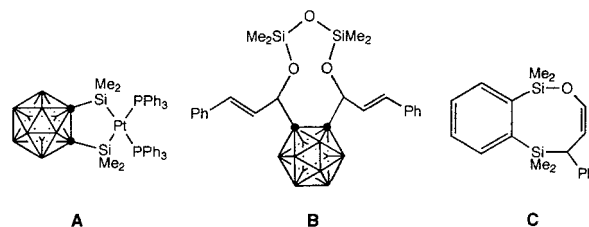
Recently, Tanaka and co-workers[8] reported that a metal complex catalyzed double silylation of *trans*-cinnamaldehyde with *o*-bis(dimethylsilyl)benzene afforded 1,2 and 1,4 adducts **C**. The peculiar behavior of the 1,2-bis(dimethylsilyl)carborane **1** has allowed novel transformations of some carbonyl compounds. The double silylation of the carbonyl by the cyclic bis(silyl)-platinum complex was a stoichiometric process and thus was limited. Accordingly, we have started a systematic study of the double silylation of carbonyl compounds catalyzed by a nickel complex. Here we report the double silylation reactions of carbonyl compounds such as aldehydes, α,β-unsaturated aldehydes, α,β-unsaturated ketones, and a ketene with 1,2-bis(dimethylsilyl)carborane.

Results and Discussion

Nickel-Catalyzed Reactions with Aldehydes. Although the platinum complex (C₂H₄)Pt(PPh₃)₂ is not a catalyst for the 1,2-double silylation of aldehydes when 1,2-bis(dimethylsilyl)carborane **1** is used, due to its

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Table 1. Crystal Data of Compounds 8, 11, and 14

	8	**11**	**14**
empirical formula	$C_{14}H_{27}B_{10}NOSi_2$	$C_{16}H_{34}B_{10}O_2Si_2$	$C_{20}H_{32}B_{10}OSi_2$
molecular weight	389.65	422.71	452.74
crystal system	orthorhombic	orthorhombic	monoclinic
space group	$Aba2$	$P2_12_12_1$	$P2_1/n$
a, Å	21.704(4)	9.105(2)	14.110(3)
b, Å	17.575(3)	10.750(2)	11.228(15)
c, Å	11.997(4)	26.495	34.201(6)
β, deg			97.025(12)
V, Å^3	4576(2)	2593.3(8)	5377.4(16)
Z value	8	4	8
D_{calcd}, g cm^{-3}	1.131	1.083	1.118
$F(000)$	1632	869	1904
μ (cm^{-1})	0.160	0.148	0.144
λ(Mo Kα radiation) (Å)	3.5−50	3.5−50	1.91−22.50
scan type	ω	ω	ω
no. of reflns measd	2082	2581	7245
no. of obsd reflns $I > 2\sigma(I)$	1068	2028	6911
R	0.0822	0.0453	0.0458
R_w	0.2009	0.1115	0.1124
goodness of fit	1.013	1.019	1.018

strong Pt−Si bond strength, the Ni complex Ni(PEt₃)₄ was found to be a good catalyst for the dehydrogenative double silylation of aldehydes. The nickel-catalyzed double silylation can be carried out either by reacting **1** and the aldehyde in the presence of the Ni(PEt₃)₄ catalyst or by reacting **1** and the aldehyde in the presence of a catalytic amount of the cyclic bis(silyl)-nickel complex Me₂Si(o-C₂B₁₀H₁₀)SiMe₂Ni(PEt₃)₂ **2**.[9] Both procedures showed a high catalytic activity. However, the former procedure is preferred due to the easy accessibility of Ni(PEt₃)₄. The results are summarized in Table 2.

Isobutyraldehyde readily reacted at 80 °C with **1** in the presence of a catalytic amount of Ni(PEt₃)₄ to give 5,6-carboranylene-1,1,4,4-tetramethyl-2-oxa-3-isopropyl-1,4-disilacyclohexane **3** in 74% yield (eq 1). In a similar

$$ \text{(1)} $$

3	R = ^{i}C₃H₇	**4**	R = CMe₃
5	R = (CH₂)₄CH₃	**6**	R = Norbornene
7	R = Ph	**8**	R = C₆H₄-CN-4
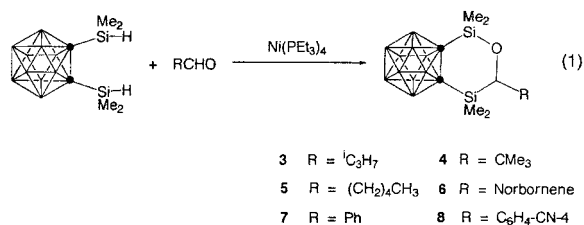
fashion, the nickel-catalyzed reaction of **1** with other aliphatic aldehydes such as trimethylacetaldehyde, 5-norbornene-2-carboxaldehyde, and hexanal yielded the corresponding six-membered cyclic insertion products. Benzaldehyde also underwent the 1,2-double silylation reaction under mild conditions. Experiments utilizing substituted aromatic aldehydes such as 4-cyanobenzaldehyde followed a similar course. These reactions of **1** with aromatic aldehydes were faster than those of aliphatic aldehydes. Such dehydrogenative 1,2-double silylation reactions have been reported using a platinum complex as the catalyst with o-bis(dimethyl-silyl)benzene.[8] The insertion of an aldehyde carbonyl group into the Si−Si bond promoted by fluoride ion was also noted.[10]

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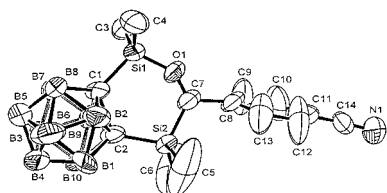(10) Hiyama, T.; Obayashi, M. *Tetrahedron Lett.* **1983**, *24*, 4109.

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

entry	reactns	products	yield (%)
1			74 %
2			66 %
3			38 %
4			83 %
5			85 %
6			92 %

To provide structural information for one of the newly prepared compounds, a single-crystal X-ray diffraction study of the 4-cyanobenzaldehyde addition product **8** was undertaken. The molecular structure of **8** is shown in Figure 1. A summary of cell constants and data collection parameters is included in Table 1. The X-ray crystal structure of **8** confirmed the presence of a six-membered ring comprising the two carboranylene carbon atoms, two silicon atoms, and a C−O fragment. The heterocyclic ring is best described as a flattened boat configuration. The Si(1)−O(1) bond length (1.621(7) Å) and O(1)−C(7) bond length (1.156(10) Å) are slightly shorter than those in 5,6-benzo-1,1,4,4-tetramethyl-3-(diphenylmethylidene)-1,4-disila-2-oxa-5-cyclohexene[6] and

Figure 1. ORTEP drawing of **8** showing the atom-labeling scheme with 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Si(1)−O(1) 1.621(7), O(1)−C(7) 1.156(10), Si(2)−C(70) 1.825(10), Si(2)−C(2) 1.902(8), C(1)−C(2) 1.698(10), C(7)−C(8) 1.55(2), N(1)−C(14) 1.130(2), O(1)−Si(1)−C(1) 105.1(3), Si(1)−C(1)−C(2) 118.5(5), C(1)−C(2)−Si(2) 120.5(5), C(7)−Si(2)−C(2) 105.8-(4), Si(2)−C(7)−O(1) 125.8(8).

comparable to those of $Me_2SiOReO_3$[11] and bis[(8′-(di-methylamino)naphth-1′-yl)dimethylsilyl]ether.[12]

The ^{1}H, ^{13}C, and ^{29}Si NMR spectra and the mass spectra of compounds **3**−**8** were consistent with the structure determined for **8**. The ^{1}H NMR spectrum of **8** contained a distinguishing low-field methine resonance (δ 4.79) which was used to monitor its formation. Four singlets (δ 0.49, 0.44, 0.28, 0.03) in the ^{1}H NMR spectrum and four singlets (−0.64, −1.68, −2.04, −5.42 ppm) in the ^{13}C NMR spectrum of **8** could be assigned to the methyl groups on the silicon atoms which indicated that the methyl groups are not equivalent. The ^{29}Si NMR spectrum of **8** exhibited two resonances at 12.59 and 0.95 ppm arising from the nonequivalent silicon atoms. Similar nickel-catalyzed reactions of **1** with ketones such as acetone, acetophenone, and pina-colone afforded a complicated mixture of products which were difficult to separate in pure form.

Ishikawa,[13] Tanaka,[8] and their co-workers have suggested mechanistic pathways for the nickel- and plati-num-catalyzed reaction of 3,4-benzo-1,1,2,2-tetraethyl-1, 2-disilacyclobut-3-ene or *o*-bis(dimethylsilyl)benzene with carbonyl compounds. On the basis of their sugges-tions, a reasonable mechanism for the formation of **3**−**8** involves the initial formation of bis(silyl)nickel complex **2** as a key intermediate, a species which we had reported earlier.[9] Intermediate **2** then coordinates to a carbonyl group (**D**), followed by insertion of the carbonyl bond into a Ni−Si bond to give a seven-membered cyclic intermediate (**E**). Analogous reactions of a silyl-substi-tuted transition metal complex with carbonyl com-pounds have been reported previously.[8] Reductive elimi-nation of the nickel fragment from the latter intermediate then leads to the product (**F**).
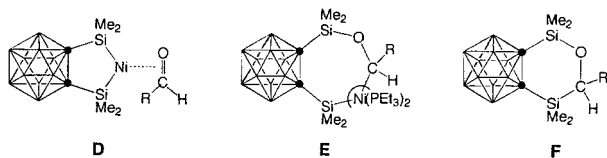

Nickel-Catalyzed Reaction with α,β-Unsaturated Aldehydes and Ketones. Since platinum complex catalyzed 1,4-double silylation of α,β-unsaturated car-bonyl compounds with disilanes is a known process,[8] we attempted the platinum complex catalyzed double

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Table 3. Nickel-Catalyzed Reactions of Enones with 1,2-Bis(dimethylsilyl)carborane

entry	reactns	products	yield (%)
7			56 %
8			28 %
9			88 %
10			53 %
11			80 %

silylation of prop-2-enal and methacrolein with 1,2-bis-(dimethylsilyl)carborane at high temperature. No reac-tion was observed in all cases when cyclic bis(silyl)-platinum complex was tried as the catalyst. However, α,β-unsaturated carbonyl compounds readily reacted with 1,2-bis(dimethylsilyl)carborane in the presence of a catalytic amount of $Ni(PEt_3)_4$ to give the 1,4-double silylating products. Thus, reaction of **1** with methac-rolein in the presence of a catalytic amount of $Ni(PEt_3)$ yielded 7,8-carboranylene-1,1,6,6-tetramethyl-4-methyl-2-oxa-1,6-disilacyclooct-3-ene (**9**) in 56% yield (eq 2). The

$$\quad (2)$$

9 R_1 = H, R_2 = Me, R_3 = H
10 R_1 = Ph, R_2 = H, R_3 = Me
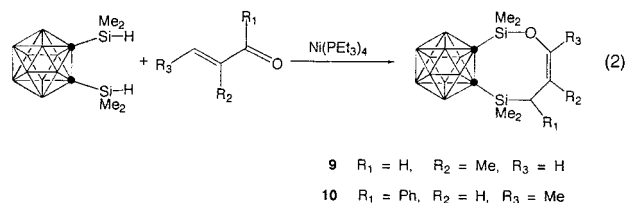
reaction of **1** with the more hindered *trans*-4-phenyl-3-buten-2-one afforded 7,8-carboranylene-1,1,6,6-tetrameth-yl-3-methyl-5-phenyl-2-oxa-1,6-disilacyclooct-3-ene **10** in 28% yield (Table 3). These products, **9** and **10**, could readily be isolated by preparative GLC. The ^{1}H NMR spectrum of **9** contains five resonances at 1.56, 0.42, 0.37, 0.35, and 0.33 ppm, assigned to the five kinds of methyl groups. The four resonances at 0.42, 0.37, 0.35, and 0.33 ppm were assigned to the methyl groups on the silicon atoms and the peak at 1.56 ppm to the methyl group on the olefinic carbon atom. In the olefinic region of the ^{13}C NMR spectrum of **9**, two resonances at 136.03 and 107.22 ppm are present. The ^{29}Si NMR spectrum of **9** shows two resonances at 16.42 and −1.36 ppm. The chemical shifts of **9** are in the range of those of the other eight-membered ring compounds. The structure of **10** was further indirectly confirmed by the
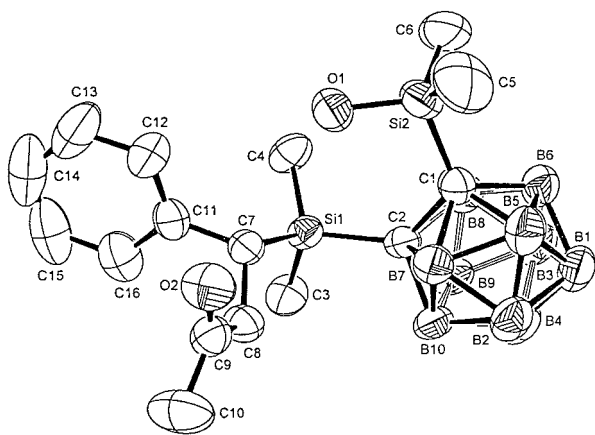
Figure 2. ORTEP drawing of **11** showing the atom-labeling scheme with 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Si(1)−C(7) 1.893(4), Si(1)−C(2) 1.939(4), C(7)−C(8) 1.529(6), C(8)−C(9) 1.501(6), C(9)−O(2) 1.205(5), C(9)−C(10) 1.488(8), Si(2)−O(1) 1.613(3), Si(2)−C(1) 1.912(4), C(1)−C(2) 1.724(5), C(1)−Si(2)−O(1) 104.18(18), Si(2)−C(1)−C(2) 123.9(2), C(2)−Si(1)−C(7) 109.43(16), Si(1)−C(7)−C(8) 113.8(3), C(7)−C(8)-C(9) 113.3(4), C(8)−C(9)−O(2) 121.0(4), O(2)−C(9)−C(10) 121.2(5).

crystal structure of **11**, the hydrolysis product of **10** (eq 3). Such 1,4-double silylation has been observed in the
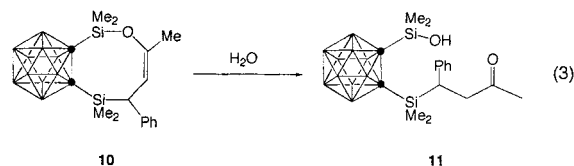
transition metal catalyzed double silylation of α,β-unsaturated ketones and aldehydes by Ito,[14] Kumada,[15] Ishkawa,[16] and their respective co-workers. The product **10** is sensitive to hydrolysis; when crystal growth of **10** was attempted, it was **11** which was isolated. In a subsequent experiment, treatment of **10** with 2 equiv of H_2O in benzene-d_6 was monitored by ^1H NMR spectroscopy. The disappearance of the olefinic hydrogen peak at 6.36 ppm and the formation of a new methylene signal at 2.55 ppm and a hydroxy signal at 2.16 ppm were noted. The ^1H NMR spectrum of the product exhibited four resonances at 0.32, 0.22, 0.21, and 0.07 ppm due to the methyl groups on silicon. The IR spectrum of the compound showed new absorptions due to the carbonyl stretch at 1683 cm^{-1} and ν_{OH} stretch at 3205 cm^{-1}, concomitant with the disappearance of the C−O stretching mode at 987 cm^{-1}. The mass spectrum of the product showed a molecular ion at m/z 422. The molecular structure of **11** as determined by a single-crystal X-ray diffraction study is shown in Figure 2. The crystallographic data are given in Table 1.

The 1,4-double silylation reactions are quite sensitive to the substituents on the C=O group. In contrast to the 1,4-double silylation reactions of **1** with methac-

rolein, when α-methyl-*trans*-cinnamaldehyde was employed in the reaction of **1** under the same conditions, the insertion product, **12**, of a carbonyl group into each of the C−Si bonds was obtained as a colorless solid in 88% yield (eq 4). A key feature in the ^1H NMR spectrum
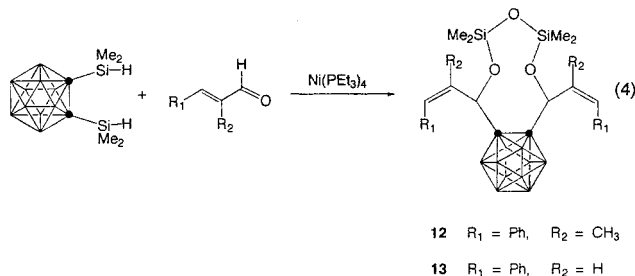

of **12** includes a singlet at 5.46 ppm assigned to the methine, concomitant with the disappearance of the aldehyde hydrogen peak. *trans*-Cinnamaldehyde reacted similarly to give **13**. As noted in the Introduction, platinum complex **A** had been found[6] to react with *trans*-cinnamaldehyde to give a product (**B**) in which a C=O bond had inserted into both of the C−Si bonds. The spectral data for **13** were identical to those we had observed for compound **A**. It is of interest that in the case of compound **A** it had been proven that the oxygen atom of the disiloxane unit was derived from the aldehyde.[6] Similar insertion was observed in the reactions of (CO)FeSiMe$_2$CH$_2$CH$_2$SiMe$_2$,[17] (CO)$_5$MnSiMe$_3$,[18] and MeEt$_2$SiCo(CO)$_3$L[19] with benzaldehyde and of 3,4-benzo-1,1,2,2-tetraethyldisilacyclobut-3-ene with benzophenone in cyclohexene.

Such an insertion of the carbonyl functionality into the *o*-carborane C−H bond was observed in Yamamoto's work on the chemoselective addition of *o*-carborane to aldehyde groups[20] or in the fluoride-promoted reaction of *o*-carborane with aldehydes.[21]

Diphenylketene also underwent dehydrogenative double silylation with **1** (eq 5) and the product, 1,2-
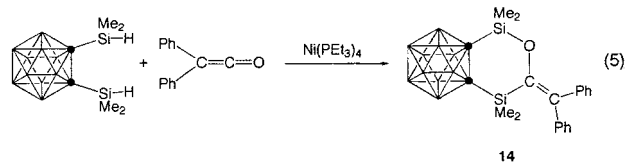
adduct to the carbonyl group, was obtained in 80% yield. The initial indication of the cyclization to form **14** was given by the observation of a parent ion in the mass spectrum at m/z 468. Although the ^1H and ^{13}C NMR spectra of **14** supported the proposed structure, unambiguous confirmation was provided by an X-ray crystallographic analysis. The molecular structure of **14** is shown in Figure 3. The molecule contains one C$_2$Si$_2$CO six-membered ring comprising two carboranylene car-

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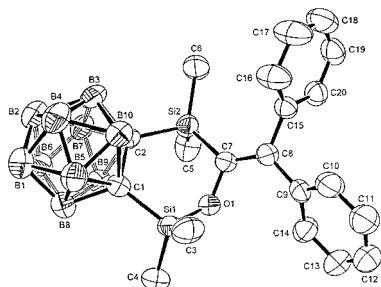
Figure 3. ORTEP drawing of **14** showing the atom-labeling scheme with 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Si(1)−O(1) 1.641(2), O(1)−C(7) 1.414(3), C(7)−Si(2) 1.875(3), Si(2)−C(2) 1.919(3), C(1)−C(2) 1.700(3), C(1)−Si(1) 1.908(3), C(7)−C(8) 1.335(4), C(7)−O(1)−Si(1) 122.3(2), O(1)−Si(1)−C(1) 105.11(11), Si(1)−C(1)−C(2) 118.18(18), C(1)−C(2)−Si(2) 120.39(17), C(2)−Si(2)-C(7) 103.80(11), Si(2)−C(7)−O(1) 107.46(18), C(7)−O(1)−Si(1) 122.29(16), Si(2)−C(7)−C(8) 132.5(2), C(7)−C(8)−C(15) 119.6(2), C(9)−C(8)−C915 115.8(2).

bon atoms, two silicon atoms, and a saturated C−O fragment. The C_2Si_2CO ring is described as a tilted boat configuration. The C7−C8 bond length (1.335(4) Å) is slightly longer than the typical value for the carbon−carbon double bond (1.317 Å) and comparable to that in 5,6-carboranylene-1,1,4,4-tetramethyl-2,3-diphenyl-1,4-disilacyclohex-2-ene (1.33(1) Å). The bond lengthening of C7−C8 may be related to the wideness of the Si(2)−C(7)−C(8) bond angle (132.5(2)°), resulting in a diminishing of the s character of the C7 atom. The two phenyl rings attached to C8 are nearly perpendicular to one another with a dihedral angle of 86.9°.

In conclusion, the cyclic bis(silyl)nickel complex was found to be a good catalyst for the double silylation of a variety of carbonyl compounds. Thus, the nickel-catalyzed reactions of 1,2-bis(dimethylsilyl)carborane with aldehydes such as isobutyraldehyde, trimethylacetaldehyde, hexanal, and benzaldehyde afforded 5,6-carboranylene-2-oxa-1,4-disilacyclohexane.

The 1,4-double silylation of α,β-unsaturated carbonyl compounds such as methacrolein and *trans*-4-phenyl-3-buten-2-one gave the 1,4-double silylated products. In contrast, the double silylation reaction of **1** with α-methyl-*trans*-cinnamaldehyde and *trans*-cinnamaldehyde yielded products formed by insertion of a carbonyl group into each of the C−Si bonds of **2**. Thus, the cyclic bis(silyl)nickel complex as a catalyst has been further exploited in a series of novel chemical transformations.

Experimental Section

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques. Benzene, toluene, and THF were distilled from sodium benzophenone. Dichloromethane and hexane were distilled over CaH_2. EtOH was distilled over Linde type 4 Å molecular sieves. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 spectrometer operating at 200.1 and 50.3 MHz, respectively. ^{29}Si NMR spectra were recorded on a JEOL model EX-270 spectrometer. Chemical shifts were referenced relative to TMS. IR spectra were recorded on a Biorad FTS-165 spectrometer. Mass spectra were recorded on a Shimadzu model QP-1000 spectrometer, and elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA 1108 analyzer.

Carborane was purchased from the Callery Chemical Co. and used without purification. The starting materials, Ni-$(COD)_2$, PEt_3, and $ClSiMe_2H$, were purchased from Strem Chemicals. All the aldehydes were purchased from Aldrich. 1,2-Bis(dimethylsilyl)carborane and Ni$(PEt_3)_4$[22] were prepared according to previous described procedures.

Nickel-Catalyzed Reaction of 1 with Various Aldehydes. General Procedure. Compounds **3−14** were prepared by the reaction of **1** with the corresponding aldehydes in the presence of a catalytic amount of Ni$(PEt_3)_4$. In a typical synthesis, a mixture of isobutyraldehyde (0.04 mL, 0.43 mmol), **1** (0.09 g, 0.36 mmol), and Ni$(PEt_3)_4$ (0.005 g, 0.018 mmol) in toluene (15 mL) was heated to 80 °C for 12 h. The mixture was passed through a short silica gel column to remove the nickel species from the reaction mixture. The solution was chromatographed using benzene/hexane (1:4) as eluent. Recrystallization from ethanol at −10 °C afforded 5,6-carboranylene-1,1,4,4-tetramethyl-3-isopropyl-2-oxa-1,4-disilacyclohexane **3** in 74% yield: mp 82 °C; ^1H NMR $(CDCl_3)$ δ 3.14 (d, 1H, J_{HH} = 8.4 Hz, OCH), 1.79 (d, sept, 1H, J_{HH} = 8.2 Hz, CH), 0.93 (d, 6H, J_{HH} = 8.2 Hz, CCH_3), 0.36 (s, 3H, SiCH_3), 0.33 (s, 3H, SiCH_3), 0.31 (s, 3H, SiCH_3), 0.28 (s, 3H, SiCH_3); $^{13}C\{^1H\}$ NMR $(CDCl_3)$ δ 70.78, 31.86, 19.77, −0.97, −1.10, −3.30, −5.09; ^{29}Si NMR $(CDCl_3)$ δ 11.94, −0.56; MS m/z 330 [M⁺]; IR (KBr pellet; cm⁻¹) 2968 (m), 2908 (w), 2602 (s), 1471 (m), 1416 (w), 1382 (w), 1361 (w), 1288 (w), 1258 (s), 1218 (w), 1092 (m), 1076 (m), 1043 (s), 982 (w), 942 (w), 878 (m), 820 (m), 801 (m), 692 (m), 662 (w). Anal. Calcd for $C_{10}H_{30}B_{10}OSi_2$: C, 36.32; H, 9.15. Found: C, 35.94; H, 8.86.

4 from the Reaction with Trimethylacetaldehyde. Compound **4** was prepared by using the same procedure as described for **3** in 66% yield. It was purified by sublimation: mp 123 °C; ^1H NMR $(CDCl_3)$ δ 3.32 (s, 1H, OCH), 0.90 (s, 9H, CCH_3), 0.38 (s, 3H, SiCH_3), 0.37 (s, 3H, SiCH_3), 0.35 (s, 3H, SiCH_3), 0.33 (s, 3H, SiCH_3); $^{13}C\{^1H\}$ NMR $(CDCl_3)$ δ 74.88, 29.38, 21.45, −0.26, −0.48, −0.92, −1.80; ^{29}Si NMR $(CDCl_3)$ δ 11.36, 0.35 ; MS m/z 344 [M⁺]; IR (KBr pellet; cm⁻¹) 2972 (m), 2911 (w), 2880 (w), 2602 (s), 1476 (w), 1462 (w), 1415 (w), 1400 (w), 1365 (w), 1258 (m), 1202 (w), 1160 (w), 1090 (m), 1076 (m), 1032 (m), 984 (w), 942 (w), 881 (m), 862 (m), 850 (m), 822 (m), 804 (w), 736 (w), 722 (w), 696 (w), 688 (w), 660 (w). Anal. Calcd for $C_{11}H_{32}B_{10}OSi_2$: C, 38.33; H, 9.35. Found: C, 37.94; H, 9.06.

5 from the Reaction with Hexanal. Compound **5** was prepared by using the same procedure as described for **3** as a liquid in 38% yield: ^1H NMR $(CDCl_3)$ δ 3.46 (t, 1H, J_{HH} = 6.6 Hz, OCH), 1.62−1.22 (m, 8H, CH_2), 0.89 (t, 3H, J_{HH} = 4.3 Hz, CH_3), 0.37 (s, 3H, SiCH_3), 0.30 (s, 3H, SiCH_3), 0.22 (s, 3H, SiCH_3), 014 (s, 3H, SiCH_3); $^{13}C\{^1H\}$ NMR $(CDCl_3)$ δ 77.23, 38.24, 31.82, 28.16, 22.68, 11.14, −0.12, −0.98, −3.10, −6.19; ^{29}Si NMR $(CDCl_3)$ δ 13.08, 0.22; MS m/z 358 [M⁺]. Anal. Calcd for $C_{12}H_{34}B_{10}OSi_2$: C, 40.19; H, 9.55. Found: C, 39.79; H, 9.22.

6 from the Reaction with 5-Norbornene-2-carboxaldehyde. Compound **6** was prepared by using the same procedure as described for **3** in 83% yield: mp 168 °C; ^1H NMR $(CDCl_3)$ δ 6.18 (dd, 1H, J_{HH} = 8.40 Hz, J_{HH} = 1.04 Hz), 5.83 (dd, 1H, J_{HH} = 8.40 Hz, J_{HH} = 1.04 Hz), 3.41 (d, 1H, J_{HH} = 4.08 Hz, OCH), 2.17 (s, 2H, CH_2), 1.94−1.05 (m, 5H), 0.33 (s, 9H, SiCH_3), 0.31 (s, 3H, SiCH_3), 0.28 (s, 3H, SiCH_3), 0.25 (s, 3H, SiCH_3); $^{13}C\{^1H\}$ NMR $(CDCl_3)$ δ 138.42, 131.95 (C=CH), 77.03 (OCH), 52.68, 43.51, 41.92, 39.27, 36.77, −0.97 (Si−CH₃), −1.39 (Si−CH₃), −3.06 (Si−CH₃), −5.76 (Si−CH₃); MS m/z 380 [M⁺]; IR (KBr pellet; cm⁻¹) 3072 (m), 2954 (s), 2877 (m), 2598 (s), 1448 (w), 1402 (w), 1257 (s), 1087 (m), 1022 (s,br), 983 (w), 942 (w), 908 (w), 870 (m), 822 (s), 802 (w), 744 (w), 682 (w). Anal. Calcd for $C_{14}H_{32}B_{10}OSi_2$: C, 44.20; H, 8.41. Found: C, 43.94; H, 8.22.

7 from the reaction with benzaldehyde: mp 146 °C; ^1H NMR $(CDCl_3)$ δ 7.37−7.12 (m, 5H, *Ph*), 4.74 (s, 1H, OCH), 0.47

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

(s, 3H, SiCH_3), 0.43 (s, 3H, SiCH_3), 0.25 (s, 3H, SiCH_3), 0.06 (s, 3H, SiCH_3); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 139.61, 128.91, 127.85, 126.89, 126.73, 124.61, 67.86, -0.91, -2.78, -3.78, -6.48; ^{29}Si NMR (CDCl$_3$) δ 10.46, -0.72; MS m/z 364 [M$^+$]; IR (KBr pellet; cm^{-1}) 30 (62 (w), 3035 (w), 2924 (m), 2852 (w), 2602 (s), 1494 (w), 1450 (w), 1402 (w), 1258 (s), 1162 (w), 1086 (m), 1078 (m), 1040 (m), 1022 (m), 982 (w), 962 (w), 918 (w), 878 (m), 870 (m), 838 (m), 820 (m), 792 (w), 770 (w), 721 (w), 629 (w), 662 (w). Anal. Calcd for C$_{13}$H$_{28}$B$_{10}$OSi$_2$: C, 42.85; H, 7.68. Found: C, 42.41; H, 7.88.

8 from the reaction with 4-cyanobenzaldehyde: mp 173 °C; ^{1}H NMR (CDCl$_3$) δ 7.64$-$7.23 (m, 4H, *Ph*), 4.79 (s, 1H, OCH), 0.49 (s, 3H, SiCH_3), 0.44 (s, 3H, SiCH_3), 0.28 (s, 3H, SiCH_3), 0.03 (s, 3H, SiCH_3); ^{13}C{^{1}H} (NMR (CDCl$_3$) δ 217.74, 137.27, 129.32, 128.77, 127.45, 127.04, 126.82, 68.04, -0.64, -1.68, -2.04, -5.42; ^{29}Si NMR (CDCl$_3$) δ 12.59, 0.95; MS m/z 390 [M$^+$]; IR (KBr pellet; cm^{-1}) 3046 (w), 2968 (w), 2918 (w), 2852 (w), 2596 (s), 2238 (m), 1604 (m), 1498 (m), 1408 (w), 1335 (w), 1258 (s), 1204 (w), 1108 (w), 1084 (m), 1061 (s), 1020 (w), 982 (w), 882 (s), 863 (s), 832 (s), 805 (w), 764 (m), 722 (w), 682 (w), 664 (w), 652 (w), 562 (m). Anal. Calcd for C$_{14}$H$_{27}$B$_{10}$NOSi$_2$: C, 43.18; H, 6.93. Found: C, 43.52; H, 7.08.

9 from the reaction with methacrolein: ^{1}H NMR (CDCl$_3$) δ 6.01 (t, 1H, J_{HH} = 2.4 Hz, OCH), 1.65 (d, 2H, J_{HH} = 2.4 Hz, CH_2), 1.56 (s, 3H, CCH_3), 0.42 (s, 3H, SiCH_3), 0.37 (s, 3H, SiCH_3), 0.35 (s, 3H, SiCH_3), 0.33 (s, 3H, SiCH_3); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 136.03, 107.22, 22.70, 18.38, -0.64, -1.09, -2.54, -2.94; ^{29}Si NMR (CDCl$_3$) δ 16.42, -1.36; MS m/z 328 [M$^+$]; IR (KBr pellet; cm^{-1}) 2968 (m), 2938 (w), 2855 (w), 2602 (s), 1678 (w), 1455 (w), 1258 (s), 1172 (s), 1136 (w), 1082 (s), 1072 (w), 1042 (s), 864 (w), 850 (w), 822 (br), 802 (s). Anal. Calcd for C$_{10}$H$_{28}$B$_{10}$OSi$_2$: C, 36.58; H, 8.53. Found: C, 36.32; H, 8.38.

10 from the reaction with *trans*-4-phenyl-3-butyn-2-one: mp 145 °C; ^{1}H NMR (CDCl$_3$) δ 7.43$-$7.18 (m, 5H, *Ph*), 6.36 (d, 1H, J_{HH} = 9.6 Hz, =CH), 2.11 (d, 1H, J_{HH} = 9.6 Hz, CHPh), 1.53 (s, 3H, CCH_3), 0.45 (s, 3H, SiCH_3), 0.43 (s, 3H, SiCH_3), 0.33 (s, 3H, SiCH_3), 0.25 (s, 3H, SiCH_3); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 207.17, 136.99, 134.51, 128.87, 128.55, 127.68, 126.75, 126.48, 71.65, 29.93, 26.03, 1.76, 1.25, 0.58, -2.17; ^{29}Si NMR (CDCl$_3$) δ 24.72, 6.24; MS m/z 404 [M$^+$]; IR (KBr pellet; cm^{-1}) 3026 (w), 2971 (m), 2932 (s), 2854 (s), 2602 (s), 1598 (w), 1492 (w), 1462 (m), 1442 (w), 1260 (m), 1182 (m), 1104 (m), 1092 (m), 1036 (w), 987 (s), 962 (m), 862 (m), 823 (m), 722 (m). Anal. Calcd for C$_{16}$H$_{32}$B$_{10}$O Si$_2$: C, 47.51; H, 7.91. Found: C, 47.34; H, 7.68.

Preparation of Carboranylene-1-dimethyl(hydroxy)-silyl-2-(1-phenyl-butan-3-one)dimethylsilane (11). To a stirred toluene solution (10 mL) of **10** (0.18 g, 0.43 mmol) was added H$_2$O (0.02 g, 1.11 mmol) at room temperature. The solution was stirred for 36 h at that temperature. The product was isolated by chromatography using benzene/hexane (1:8) as eluent in 92% yield: mp 139 °C; ^{1}H NMR (CDCl$_3$) δ 7.36$-$7.08 (m, 5H, *Ph*), 2.55 (d, 2H, J_{HH} = 6.8 Hz, CH_2), 2.35 (t, 1H, J_{HH} = 6.8 Hz, CH), 2.16 (s, 1H, OH), 1.25 (s, 3H, CH_3), 0.32 (s, 3H, SiCH_3), 0.22 (s, 3H, SiCH_3), 0.21 (s, 3H, SiCH_3), 0.07 (s, 3H, SiCH_3); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 207.06, 128.73, 128.64, 128.07, 127.87, 127.63, 127.04, 31.02, 29.44, 14.20, 2.42, 1.10, 0.59, -0.13; ^{29}Si NMR (CDCl$_3$) δ 19.22, -2.36; MS m/z 422 [M$^+$]; IR (KBr pellet; cm^{-1}) 3205 (m), 2968 (s), 2601 (s), 1683 (m), 1462 (m), 1384 (w), 1364 (w), 1261 (s), 1082 (m), 1052 (m), 1036 (m), 1017 (m), 910 (w), 864 (w), 855 (w), 804 (s). Anal. Calcd for: C$_{16}$H$_{34}$B$_{10}$O$_2$Si$_2$: C, 45.49; H, 8.05. Found: C, 45.18; H, 7.86.

12 from the reaction with α-Methyl-*trans*-cinnamaldehyde. Compound **12** was prepared by using the same

procedure as described for **3**. The product was isolated by chromatography using benzene/hexane (1:9) as eluent in 88% yield: mp 158 °C; ^{1}H NMR (CDCl$_3$) δ 7.47$-$7.18 (m, 10H, *Ph*), 6.54 (d, 2H, J_{HH} = 1.4 Hz, CH=), 5.46 (d, 1H, J_{HH} = 1.4 Hz, CHO), 1.96 (s, 6H, =CCH_3), 0.27 (s, 6H, Si$-$CH_3), 0.08 (s, 6H, Si$-$CH_3); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 136.82, 136.59, 131.80, 129.22, 129.15, 128.45, 127.41, 71.22, 14.58, 1.17, -0.67; ^{29}Si NMR (CDCl$_3$) δ 13.6; MS(EI) m/z 566 [M$^+$]; IR (KBr pellet; cm^{-1}) 3088 (w), 3055 (w), 3042 (w), 2968 (m), 2625 (s), 1598 (w), 1479 (w), 1442 (w), 1365 (m), 1261 (s), 1182 (w), 1092 (s), 1048 (s), 1030 (s), 954 (w), 918 (m), 892 (m), 808 (s), 782 (m), 722 (m), 666 (w). Anal. Calcd for C$_{26}$H$_{42}$B$_{10}$O$_3$Si$_2$: C, 55.12; H, 7.41. Found: C, 54.88; H, 7.28.

13 from the Reaction with *trans*-Cinnamaldehyde. Compound **13** was prepared by using the same procedure as described for **3**. The product was isolated by chromatography using benzene/hexane (1:9) as eluent in 53% yield: mp 56 °C; ^{1}H NMR (CDCl$_3$) δ 7.52$-$6.18 (m, 10H, *Ph*), 6.88 (dd, 2H, J_{HH} = 12.3 Hz, J_{HH} = 5.8 Hz, =CH), 6.74 (dd, 2H, J_{HH} = 12.3 Hz, J_{HH} = 4.4 Hz, =CH), 4.89 (dd, 2H, J_{HH} = 5.8 Hz, J_{HH} = 4.4 Hz, CH), 0.23 (s, 6H, Si$-$CH_3), 0.11 (s, 6H, Si$-$CH_3); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 162.2, 156.6, 137.4, 133.6, 132.1, 129.1, 128.7, 31.1, -0.46 (Si$-$CH_3), -0.68 (Si$-$CH_3); ^{29}Si NMR (CDCl$_3$) δ 17.4; MS(EI) m/z 538 [M$^+$]; Anal. Calcd for C$_{24}$H$_{38}$B$_{10}$O$_3$Si$_2$: C, 53.52; H, 7.05. Found: C, 53.22; H, 6.83.

14 from the Reaction with Diphenylketene. Compound **14** was prepared by using the same procedure as described for **3**. The product was isolated by chromatography using benzene/hexane (1:1) as eluent in 80% yield: mp 98 °C; ^{1}H NMR (CDCl$_3$) δ 7.44$-$7.12 (m, 10H, *Ph*), 0.19 (s, 6H, Si$-$CH_3), -0.02 (s, 6H, Si$-$CH_3); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 143.28, 141.18, 136.25, 130.57, 129.24, 128.45, 128.36, 128.25, 127.95, 127.68, 127.43, 127.28, 71.53, $-1/26$, -1.53; ^{29}Si NMR (CDCl$_3$) δ 11.97, -6.47; MS(EI) m/z 468 [M$^+$]; IR (KBr pellet; cm^{-1}) 3001 (w), 2950 (w), 2925 (m), 2600 (s), 1460 (m), 1260 (s), 1080 (m), 950 (m), 860 (m), 710 (w). Anal. Calcd for C$_{20}$H$_{32}$B$_{10}$OSi$_2$: C, 53.09; H, 5.90. Found: C, 52.86; H, 5.72.

X-ray Crystallography. Details of the crystal data and a summary of intensity data collection parameters for **8**, **11**, and **14** are given in Table 1. Crystals of **8**, **11**, and **14** were grown from hexane at -5 °C. Crystals of **8**, **11**, and **14** were mounted in thin-walled glass capillaries and sealed under argon. The data sets of three crystals were collected on an Enraf CAD4 automated diffractometer. Mo Kα radiation (λ = 0.7107 Å) was used for all structure. Each structure was solved by the application of direct methods using the SHELX-96 program and least-squares refinement using SHELX-97. All non-hydrogen atoms in compounds **8**, **11**, and **14** were refined anisotropically. All other hydrogen atoms were included in calculated positions.

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 **8**, **11**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.