Articles

Synthesis and Double-Silylation Reactions of a P_2PtSi_2 Complex Containing an *o*-Carboranylene

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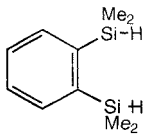
The reaction of the 1,2-bis(dimethylsilyl)carborane **1** with $Pt(CH_2{=}CH_2)(PPh_3)_2$ yielded the cyclic bis(silyl)platinum complex **2**, which was found to be a good precursor for the double-silylation reaction. Thus, the reaction of **2** with RC≡CR′ in refluxing toluene yielded the six-membered disilyl ring compounds $B_{10}H_{10}C_2(SiMe_2)_2(RC{=}CR')$ (R = Ph, R′ = Ph (**3**); R = Ph, R′ = H (**4**); R = Et, R′ = Et (**5**); R = Me, R′ = Me (**6**); R = CO_2Me, R′ = CO_2Me (**7**)). In contrast, the reaction of **1** with 1-hexyne under the same reaction conditions yielded the five-membered disilyl ring compound $B_{10}H_{10}C_2(SiMe_2)_2(C{=}C(C_4H_9)H)$ (**8**). Thermolysis of **2** with *trans*-cinnamaldehyde afforded the insertion compound **9**, formed through the di-insertion of two carbonyl ligands into the C−Si bond of **2**. The structure of the nine-membered-ring compound **9** was determined by single-crystal X-ray crystallography. The reaction of **2** with fumaronitrile yielded the cyclization product **14**, which contains two types of disilyl moieties, an imino and an *N*,*N*-bis(silyl)amino group.

Introduction

Organosilicon compounds have attracted considerable interest because of their potential applications in organic synthesis as well as in material science.[1] The double-silylation reaction, pioneered by Kumada and coworkers,[2] is a convenient synthetic route to obtain compounds in which two Si−C bonds are created by the addition of two silicon units to unsaturated organic substrates such as alkynes,[3] alkenes,[4] and 1,3-dienes.[5] Platinum complexes, in particular, are excellent catalysts for the transformation of silicon-containing linear compounds[6] and for hydrosilylation.[7] Bis(silyl)platinum complexes have been implicated as key intermediates in the platinum-catalyzed double silylation of alkynes, alkenes, 1,3-dienes, nitriles,[8] and aldehydes.[9] Eaborn et al.,[10] Tanaka et al.,[11] and Fink[12] reported that the reaction of 1,2-bis(dimethylsilyl)benzene **A** with $Pt(CH_2{=}CH_2)(PPh_3)_2$ afforded the cyclic bis (silyl)platinum complex **B**.



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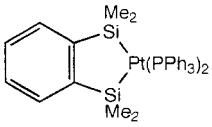

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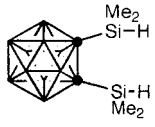

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(1) *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley-Interscience: Chichester, U.K., 1989.

(2) (a) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 9263. (b) Kiso, Y.; Tamao, K.; Kumada, M. *J. Organomet. Chem*. **1974**, *76*, 105. (c) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Organomet. Chem*. **1975**, *86*, C27.

(3) (a) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1975**, *97*, 931. (b) Tamao, K.; Hayashi, T.; Kumada, M. *J. Organomet. Chem*. **1976**, *114*, c19. (c) Watanabe, H.; Kobayashi, M,; Higuchi, K.; Nagai, Y. *J. Organomet. Chem*. **1980**, *186*, 51. (d) Watanabe, H.; Kobayashi, M.; Saito, M.; Nagai, Y. *J. Organomet. Chem*. **1981**, *216*, 149. (e) Matsumoto, H.; Matsubara, I.; Kato, T.; Shono, K.; Watanabe, H.; Nagai, Y. *J. Organomet. Chem*. **1980**, *199*, 43. (f) Seyferth, D.; Goldman, E. W.; Escudié, J. *J. Organomet. Chem*. **1984**, *271*, 337. (g) Naka, A.; Okazaki, S.; Hayashi, M.; Ishikawa, M. *J. Organomet. Chem*. **1995**, *499*, 35.

(4) (a) Hayashi, T.; Kobayashi, T.; Kawamoto, A. M.; Yamashita, H.; Tanaka, M. *Organometallics* **1990**, *9*, 280. (b) Murakami, M.; Anderson, P. G.; Suginome, M.; Ito, Y. *J. Am. Chem. Soc.* **1991**, *113*, 3987. (c) Ozawa, F.; Sugawara, M.; Hayashi, T. *Organometallics* **1994**, *13*, 3237. (d) Ishikawa, M.; Naka, A.; Ohshita. J. *Organometallics* **1993**, *12*, 4987.

(5) (a) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *Chem. Lett*. **1975**, 887. (b) Carlson, C. W.; West, R. *Organometallics* **1983**, *2*, 1801. (c) Tsuji, Y.; Largo, R. M.; Tomohiro, S.; Tsuneishi, H. *Organometallics* **1992**, *11*, 2353. (d) Obora, Y.; Tsuji, Y.; Kawamura, T. *Organometallics* **1993**, *12*, 2853. (e) Tamao, K.; Okazaki, S.; Kumada, M. *J. Organomet. Chem*. **1978**, *146*, 87. (f) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *Chem. Lett*. **1975**, 887.

(6) (a) Yamashita, H.; Kobayashi, T.; Hayashi, T.; Tanaka, M. *Chem. Lett*. **1990**, 1447. (b) Yamashita, H.; Catellani, M.; Tanaka, M. *Chem. Lett*. **1991**, 241.

(7) (a) Tanaka, M.; Uchimaru, Y.; Lautenschlager, H.-J. *J. Organomet. Chem*. **1992**, *428*, 1. (b) Tanaka, M.; Uchimaru, Y.; Lautenschlager, H.-J. *Organometallics* **1991**, *10*, 16.

(8) Reddy, N. P.; Uchimaru, Y.; Lautenschlager, H.-J.; Tanaka, M. *Chem. Lett*. **1992**, 45.

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

(10) Eaborn, C.; Metham, T. N.; Pidcock, A. *J. Organomet. Chem*. **1973**, *63*, 107.

(11) Tanaka. M.; Uchimaru, Y. *Bull. Soc. Chim. Fr*. **1992**, *129*, 667.

(12) Fink, W. *Helv. Chim. Acta* **1976**, *59*, 60.

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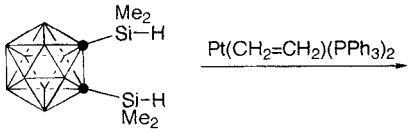
Although disilane **A** has been used extensively in double-silylation reactions, many variants of this compound remain virtually unexplored. One such variant, 1,2-bis(dimethylsilyl)carborane **1**, has received little attention.[13]

o-Carborane has attracted much interest due to the ease of its preparation and derivatization, its thermal stability, steric bulk, and electronic property.[14] The properties of moderate reactivity and ease of preparation make **1** a good choice for the double-silylation reaction. Accordingly, we have started an investigation of the synthesis of bis(silyl)platinum complexes bearing a bulky *o*-carborane unit that might confer some additional stability on the Si−Pt bonds. Here we report the general synthesis of such bis(silyl)platinum complexes. This study includes the first crystal structure of a cyclic bis(silyl)platinum compound and a variety of double-silylation reactions with unsaturated organic compounds. Early results of this study have been communicated.[15]

Results and Discussion

Synthesis of $PtSi_2P_2$ Complex 2. Initially, we attempted the double-silylation reaction of 1,2-bis(dimethylsilyl)carborane and diphenylacetylene in the presence of a catalytic amount of $Pt(CH_2{=}CH_2)(PPh_3)_2$ at 60−80 °C. After careful workup, the product was found to be a cyclic bis(silyl)platinum complex rather than a double-silylation derivative. Thus, when a mixture of $Pt(CH_2{=}CH_2)(PPh_3)_2$ (0.05 mmol) and 1,2-bis(dimethylsilyl)carborane **1** (0.07 mmol) was heated in a sealed NMR tube (80 °C, 6 h), the solution changed from red to yellow, concomitant with the evolution of gas (eq 1). The yellow product **2** was a crystalline solid that was relatively stable in air and to brief heating to 120−130 °C.



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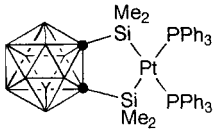


(1)

2

The unusually high thermal stability of **2** is attributed to the advantageous properties of the carborane moiety, including electronic and steric effects, and the strengthening of the Pt−Si bond. Compound **2** is moderately soluble in toluene, chloroform, and THF. The structure of **2**, unambiguously established by single-crystal X-ray analysis, is shown in Figure 1. Crystallographic data and processing parameters are given in Table 1. Complex **2** has a slightly distorted square-planar geometry. The five Si, P, and Pt atoms comprising the central

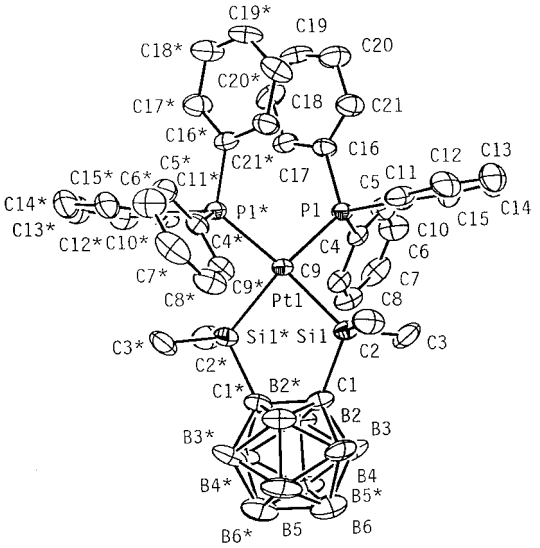


Figure 1. X-ray crystal structure of **2** with 50% probability thermal ellipsoids depicted. Selected bond lengths (Å) and angles (deg): Pt(1)−Si(1) = 2.369(2), Pt(1)−P(1) = 2.357(2), Si(1)−C(1) = 1.946(8), C(1)−C(1*) = 1.65(2); Si(1)−Pt(1)−Si(1*) = 85.4(1), P(1)−Pt(1)−P(1*) = 103.59(9), Pt(1)−Si(1)−C(1) = 113.7(2), Si(1)−C(1)−C(1*) = 113.6(2).

skeleton of the molecule are all nearly coplanar with a dihedral angle of 3.4° between the two planes defined by Si(1), Pt(1), Si(1*) and P(1), Pt(1), P(1*). The Pt−Si bond length (2.369(2) Å) is within known values of Pt−Si bond lengths in analogous complexes.[16]

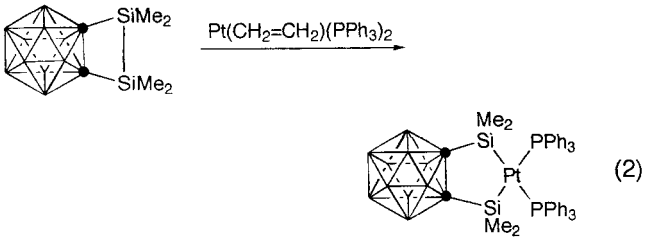
The ^{1}H, ^{13}C, ^{31}P, and ^{29}Si NMR spectra of **2** were consistent with the structure determined by X-ray crystallography. ^{1}H NMR signals ascribable to the Pt−$SiMe_2$ moiety were observed at 0.32 (d, $^3J_{PtH}$ = 14 Hz) ppm. In particular, the ^{31}P NMR signal had cleanly shifted from 32.0 ($^1J_{PtP}$ = 3500 Hz) ppm for $Pt(CH_2{=}CH_2)(PPh_3)_2$[17] to 92.2 ppm with a rather small coupling constant of $^1J_{PtP}$ (1732 Hz), which is consistent with the cis configuration of **2**.[18] The ^{29}Si NMR spectrum of **2** shows the expected pattern of a doublet of doublets ($^1J_{Pt-Si}$ = 1281.6 Hz, $^2J_{SiP(trans)}$ = 148.8 Hz, $^2J_{SiP(cis)}$ = 12.8 Hz) from coupling to two different ^{31}P nuclei, along with satellites arising from coupling to ^{195}Pt. The ^{29}Si NMR chemical shift of 39.6 ppm as a doublet of doublets strongly resembles the literature values for the *cis*-$PtSi_2P_2$ complexes.[20]

We have also carried out the reaction of $Pt(CH_2{=}CH_2)(PPh_3)_2$ with 2,3-(1,1,4,4-tetramethyldisilanediyl)-carborane[19] in benzene at room temperature in an alternate synthesis of complex **2**, which was isolated as yellow crystals in 92% yield (eq 2). A similar cyclic bis(silyl)platinum complex has been prepared by the reaction of 1,2-bis(dimethylsilyl)benzene with $Pt(CH_2{=}CH_2)(PPh_3)_2$.[10−12]

(13) Kang, Y.; Lee, J.; Kong, Y. K.; Kang, S. O.; Ko, J. *Chem. Commun*. **1998**, 2343.
(14) Beall, H. In *Boron Hydride Chemistry*; Muetterties, E., Ed.; Academic Press: New York, 1975; Chapter 9.
(15) Kang. Y.; Kang, S. O.; Ko, J. *Organometallics* **1999**, *18*, 1818.
(16) Aylett, B. J. *Adv. Inorg. Chem. Radiochem*. **1982**, *25*, 1. (b) Chang, L. S.; Johnson, M. P.; Fink, M. J. *Organometallics* **1991**, *10*, 1219. (c) Ozawa, F.; Kamite, J. *Organometallics* **1998**, *17*, 5630.
(17) Head, R. A. *J. Chem. Soc., Dalton Trans*. **1982**, 1637.
(18) (a) Kobayashi, T.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett*. **1988**, 1411. (b) Yamashita, H.; Tanaka, M.; Goto, M. *Organometallics* **1992**, *11*, 3227. (c) Holmes-Smith, R. D.; Stobart, S. R.; Cameron, T. S.; Jochem, K. *J. Chem. Soc., Chem. Commun*. **1981**, 937.
(19) de Rege, F. M.; Kassebaum, J. D.; Scott, B. L.; Abney, K. D.; Balaich, G. J. *Inorg. Chem*. **1999**, *38*, 486.
(20) (a) Pham, E. K.; West, R. *Organometallics* **1990**, *9*, 1517. (b) Schubert, U.; Müller, C. *J. Organomet. Chem*. **1991**, *418*, C6.

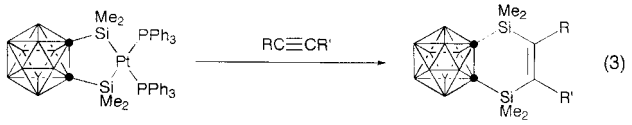
Table 1. Crystal Data of 2, 3, 9, and 14

	2	3	9	14
empirical formula	$C_{46}H_{64}P_2PtSi_2$	$C_{20}H_{32}B_{10}Si_2$	$C_{24}H_{38}B_{10}O_3Si_2$	$C_{16}H_{46}B_{20}N_2Si_4$
mol wt	1054.32	436.74	538.83	595.09
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	$P2_1/c$	$P2_1/m$	$P2_1/m$
a (Å)	22.435(1)	9.6765(5)	10.711(1)	9.322(1)
b (Å)	15.855(2)	15.064(1)	24.060(1)	22.191(2)
c (Å)	14.859(2)	17.693(2)	12.654(1)	17.580(1)
β (deg)	114.544(5)	91.277(6)	97.978(8)	99.449(8)
V, Å^3	4807.8(7)	2578.5(3)	3229.3(4)	3587.2(5)
Z	4	4	2	4
D(calcd) (g cm^{-3})	1.456	1.125	1.108	1.102
F(000)	2136.00	920.00	1136.00	1248.00
μ (cm^{-1})	3.059	0.145	0.134	0.181
λ(Mo Kα radiation) (Å)	0.7107	0.7107	0.7107	0.7107
monochromator	graphite	graphite	graphite	graphite
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
no. of rflns measd	8553	4670	6809	7461
no. of obsd rflns ($I > 3.00\sigma(I)$)	3210	1190	2808	5056
R	0.0377	0.0617	0.1130	0.0444
R_w	0.0456	0.0483	0.1403	0.0568
goodness of fit	1.695	1.676	4.967	2.253



(2)

Reaction of 2 with Alkynes. Attempts were made to insert a variety of alkynes into the Pt−Si bond of **2**. As expected, **2** was found to be a good reactant in the double-silylation reaction. Thus, thermolysis of a toluene solution of **2** and diphenylacetylene in a 1:8 molar ratio at 120 °C for 12 h, followed by chromatographic workup, afforded 5,6-carboranylene-1,1,4,4-tetramethyl-2,3-diphenyl-1,4-disilacyclohex-2-ene **3** as colorless crystals in 92% yield (eq 3). In similar fashion, reaction of **2** with



(3)

2

3 R = R' = Ph
4 R = Ph R' = H
5 R = R' = Et
6 R = R' = Me
7 R = R' = COOMe

other alkynes such as phenylacetylene, 3-hexyne, 2-butyne, and dimethyl acetylenedicarboxylate in refluxing toluene yielded the six-membered cyclic insertion products. Such acetylene insertion reactions have been effected using palladium and platinum complexes as catalysts with *o*-(dimethylsilyl)benzene.[7]

To provide structural information for one of the new compounds prepared, a single-crystal X-ray diffraction study of the diphenylactylene insertion product **3** was undertaken. The molecular structure of **3** is shown in Figure 2. A summary of cell constants and data collection parameters is included in Table 1.

The X-ray crystal structure of **3** confirmed the presence of a six-membered ring comprising an *o*-carboranylene, two silicon atoms, and an unsaturated hydrocarbon fragment containing a C=C bond. The C=C bond length (1.33(1) Å) is slightly longer than the typical value for the carbon−carbon double bond (1.317 Å)[21] and is comparable to that of the tricyclic product formed in the reaction between diphenylacetylene and tetrakis(dimethylsilyl)benzene.[22] The Si1−C3−C4 bond angle is slightly wider (125.4(8)°) than the usual values for sp^2 carbon centers.

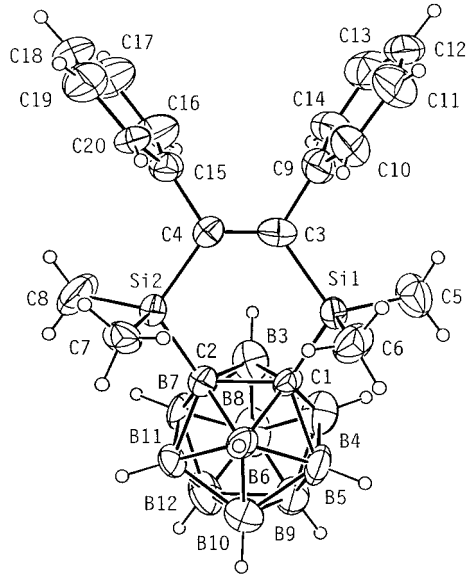


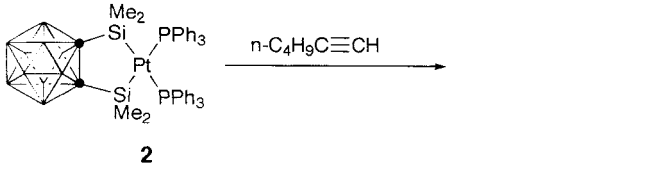
Figure 2. X-ray crystal structure of **3** with 50% probability thermal ellipsoids depicted. Selected bond lengths (Å) and angles (deg): Si(1)−C(1) = 1.906(8), Si(1)−C(4) = 1.902(9), C(3)−C(4) = 1.33(1), Si(2)−C(3) = 1.875(10), Si(2)−C(2) = 1.898(8); C(1)−Si(1)−C(3) = 107.2(4), Si(1)−C(1)−C(2) = 120.7(6), Si(1)−C(3)−C(4) = 125.4(8), C(2)−Si(2)−C(4) = 108.6(4).

The ^{1}H, ^{13}C, and ^{29}Si NMR spectra, the mass spectra, and elemental analyses of compounds **3**−**7** were consistent with the structure determined for **3**. The ^{1}H NMR spectrum of **4** showed the phenyl and methyl

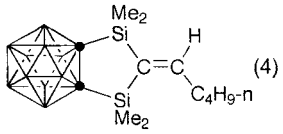
(21) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans.* **1987**, *1*, 51.
(22) Uchimaru, Y.; Brandl, P.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1993**, 744.

resonances in the expected 5:12 ratio. In addition, a low-field resonance due to the olefinic proton was detected at 6.41 ppm. In the olefinic region of the ^{13}C NMR spectrum of **4**, two resonances of equal intensity at 158.5 and 142.6 ppm were present. The ^{29}Si NMR spectrum of **4** showed two singlet resonances of equal intensity at −8.94 and −13.58 ppm arising from the nonequivalent silicon atoms present. The mass spectrum of **4** showed a molecular ion at *m*/*z* 354.

In contrast to the double-silylation reaction of **2** with the above alkynes, when 1-hexyne was employed in the reaction with **2** under the same reaction conditions, the five-membered disila ring compound **8** was isolated as a colorless oil in 54% yield (eq 4). A key feature in the



2



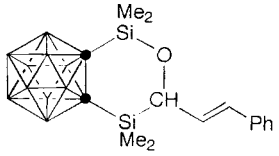
(4)

8

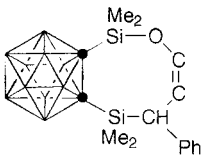
^1H NMR spectrum of **8** includes a singlet at 6.24 ppm assigned to the vinyl proton. A characteristic high-frequency ^{13}C NMR resonance at 138.50 ppm provides evidence for a tethered sp^2 carbon atom between the two silicon atoms, in addition to a low-frequency resonance at 160.4 ppm assigned to the terminal olefinic carbon. The values are close to those of 4,5-benzo-1,1,3,3-tetraethyl-2-(*n*-pentylidene)-1,3-disilacyclopent-4-ene, reported by Ishikawa and co-workers.[23] The ^{29}Si NMR spectrum of **8** showed two resonances at 4.42 and 0.92 ppm, indicative of the presence of two chemically nonequivalent silicon atoms. The formation of **8** is of interest because a 1,2-hydrogen shift must have occurred during the course of the reaction. A similar 1,2-shift in the alkynes coordinated to a transition metal has been observed in the reaction of chloro(triisopropylphosphine)rhodium(I) with trimethylsilyl-substituted alkynes.[24]

Reaction of 2 with *trans*-Cinnamaldehyde. As platinum-complex-catalyzed 1,2-double silylation of the carbonyl groups with disilanes has been well-established,[25] we attempted the double silylation of carbonyl compounds such as benzaldehyde, heptanal, acetone, and acetophenone with *o*-bis(dimethylsilyl)carborane at 100−110 °C. However, no reaction was observed in all cases in the presence of platinum complex **2**. In stoichiometric reactions of **2** with carbonyl compounds such as benzaldehyde and ketones, only decomposition occurred. However, *trans*-cinnamaldehyde readily reacted with **2** to give the disilylation product in 56% yield.

Treatment of **2** with 3 equiv of *trans*-cinnamaldehyde in refluxing toluene-d_8 while the reaction progress was monitored by ^1H NMR spectroscopy resulted in the disappearance of the aldehyde hydrogen peak and the formation of a new methine signal (δ 1.56). The ^1H NMR spectrum of the product exhibited two resonances at 6.88 and 6.74 ppm as a doublet of doublets due to olefinic protons. The IR spectrum of the compound showed a new absorption due to the ν_{CO} stretch at 997 cm^{-1}, concomitant with the disappearance of the original strong absorption at 1675 cm^{-1}, assigned to the carbonyl peak of the ligand. Obvious candidates for the product were the 1,2-adduct **C** and the 1,4-adduct **D**.



C



D

Recently, Tanaka et al.[9] reported that the $Pt(CH_2{=}CH_2)(PPh_3)_2$-catalyzed double silylation of but-3-en-2-one gave the 1,2- and 1,4-adducts. Ito,[26] Kumada,[27] and Ishikawa[28] and their respective co-workers also reported that α,*β*-unsaturated ketones undergo double silylation to give 1,4-adducts. However, the ^{29}Si NMR of our product exhibited a single resonance at 17.4 ppm. The mass spectrum of the product showed a molecular ion at *m*/*z* 538. On the basis of these data, structures **C** and **D** obviously are ruled out. The next possibility would be the insertion of the *trans*-cinnamaldehyde ligand into the carbon−silicon bond of **2**. As the structure of the product was not deduced on the basis of spectroscopic data, a single-crystal X-ray diffraction study was undertaken. The molecular structure of **9** is shown in Figure 3. Crystallographic data are given in Table 1, selected bond lengths and angles in Table 2. To our surprise, the X-ray study of **9** showed it to be the insertion product of two carbonyl ligands into the C−Si bond of **2** (eq 5).

The molecule contains a $C_4Si_2O_3$ nine-membered ring. Such an insertion of the carbonyl functionality into *o*-carborane has been observed in Yamamoto's work on the chemoselective addition of *o*-carborane to aldehyde groups in a palladium-catalyzed[29] or fluoride-promoted reaction.[30]

The formation of compound **9** raises the following question: What is the source of a siloxane oxygen atom, and by which mechanism does the reaction proceed? To confirm whether the siloxane oxygen atom originated from a carbonyl group of *trans*-cinnamaldehyde, we carried out the reaction of **2** with *trans*-cinnamaldehyde in cyclohexene in an attempt to trap a possible carbene species generated in the deoxygenation of the

(23) Naka, A.; Hayashi, M.; Okazaki, S.; Kunai, A.; Ishikawa, M. *Organometallics* **1996**, *15*, 1101.
(24) (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.
(25) Uchimaru, Y.; Lautenschlager, H.-J.; Wynd, A. J.; Tanaka, M.; Goto, M. *Organometallics* **1992**, *11*, 2639.
(26) Tamao, K.; Okazaki, S.; Kumada, M. *J. Organomet. Chem.* **1978**, *146*, 87.
(27) (a) Hayashi, T.; Matsumoto, Y.; Ito, Y. *Tetrahedron Lett.* **1988**, *29*, 4147. (b) Hayashi, T.; Matsumoto, Y.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 5579.
(28) Ishikawa, M.; Sakamoto, H. Tabuchi, T. *Organometallics* **1991**, *10*, 3173.
(29) Nakamura, H.; Aoyagi, K.; Yamamoto, Y. *J. Org. Chem.* **1997**, *62*, 780.
(30) Cai, J.; Nemoto, H.; Nakamura, H.; Singaram, B.; Yamamoto, Y. *Chem. Lett.* **1996**, 792.

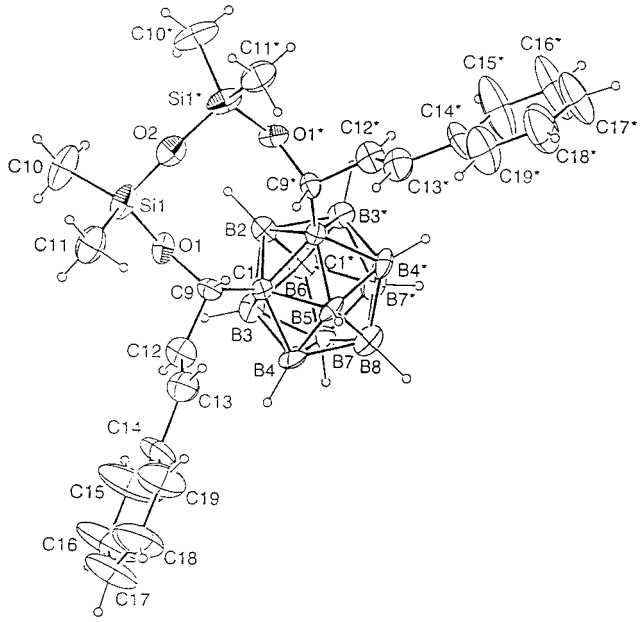
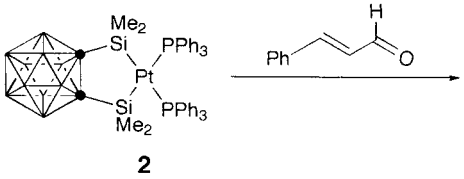


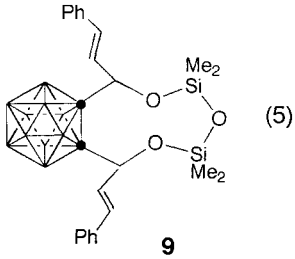
Figure 3. Crystal structure of **9** with 50% probability thermal ellipsoids.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 9

C(1)−C(1*)	1.71(2)	C(1)−C(9)	1.58(1)
C(9)−O(1)	1.421(10)	Si(1)−O(1)	1.648(6)
Si(0)−O(2)	1.625(4)	C(9)−C(12)	1.50(1)
C(12)−C(13)	1.29(1)	C(13)−C(14)	1.51(1)
Si(1)−O(2)−Si(1*)	144.4(7)	O(1)−Si(1)−O(2)	108.3(4)
Si(1)−O(1)−C(9)	123.5(5)	O(1)−C(9)−C(1)	107.6(7)
C(1*)−C(1)−C(9)	118.1(4)	O(1)−C(9)−C(12)	105.7(8)
C(9)−C(12)−C(13)	121.7(10)	C(12)−C(13)−C(14)	126(1)

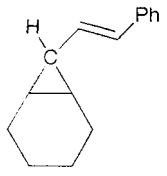


2

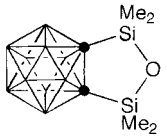


9 (5)

aldehyde. Thus, when a mixture of **2** and *trans*-cinnamaldehyde in 1:8 molar ratio was heated at reflux in cyclohexene (72 h), 7-(*β*-styrenyl)norcarane (**10**) was obtained in 14% yield, together with compound **9** (18%).



10

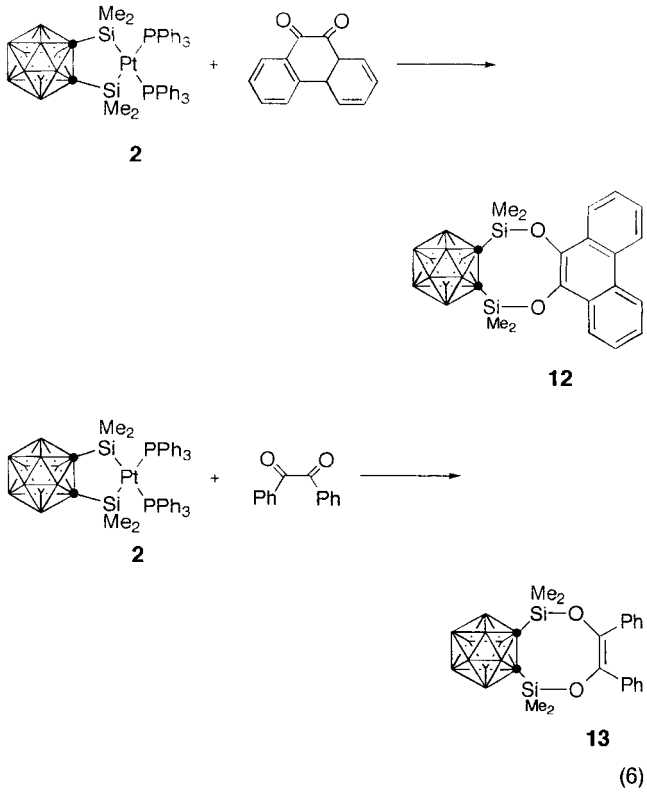


11

The formation of **10** clearly indicates that the oxygen atom in **9** was derived from the *trans*-cinnamaldehyde. Similar results were observed in the reaction of $(OC)_4FeSiMe_2CH_2CH_2SiMe_2$ with benzaldehyde[31a] and of 3,4-benzo-1,1,2,2-tetraethyldisilacyclobut-3-ene with benzophenone in cyclohexene.[31b]

In an attempt to understand the insertion process, we carried out the reaction of 4,5-carboranylene-1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane[32] (**11**) with *trans*-cinnamaldehyde. However, only decomposition was observed. This result suggests that the insertion of carbonyl groups into Si−C bonds proceeds with the Pt−Si bonds intact.

Reaction of 2 with 1,2-Diones. The insertion of 1,2-diones into **2** readily proceeds to give eight-membered-ring compounds with 1,2-vinylenedioxy groups in high yield (eq 6). The identity of compounds **12** and **13** was



2 **12** **2** **13** (6)

confirmed by their ^1H and ^{13}C NMR and mass spectra and by elemental analysis. Such an insertion of a carbonyl group into the Si−Si bond had been observed in the Pd-catalyzed reactions of hexamethyldisilane with 1,2-diones.[33]

Reaction of 2 with Fumaronitrile. The rhodium- and platinum-catalyzed double silylation of nitriles with bis(hydrosilane) species[8,34] and the photochemical reactions of bis(silyl)iron carbonyl complexes with nitriles[35]

(31) (a) Nakazawa, H.; Johnson, D. L.; Gladysz, J. A. *Organometallics* **1983**, *2*, 1846. (b) Ishikawa, M.; Naka, A.; Okazaki, S.; Sakamoto, H. *Organometallics* **1993**, *12*, 87.
(32) Papetti, S.; Heying, T. L. *Inorg. Chem.* **1963**, 1405.
(33) (a) Yamashita, H.; Reddy, N. P.; Tanaka, M. *Macromolecules* **1993**, *26*, 2143. (b) Yamashita, H.; Reddy, N. P.; Tanaka, M. *Chem. Lett.* **1993**, 315. (c) Yamashita, H.; Reddy, N. P.; Tanaka, M. *Organometallics* **1997**, *16*, 5223.
(34) Corriu, R. J. P.; Moreau, J. J. E.; Padaud-Sat, M. *J. Organomet. Chem.* **1982**, *228*, 301.
(35) (a) Corriu, R. J. P.; Moreau, J. J. E. *J. Chem. Soc., Chem. Commun.* **1980**, 278. (b) Carré, F. H.; Moreau, J. J. E. *Inorg. Chem.* **1982**, *21*, 3099.

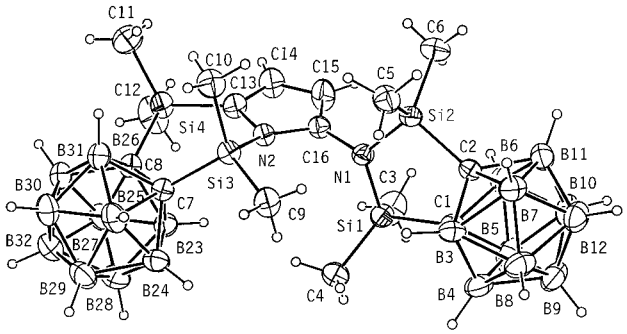


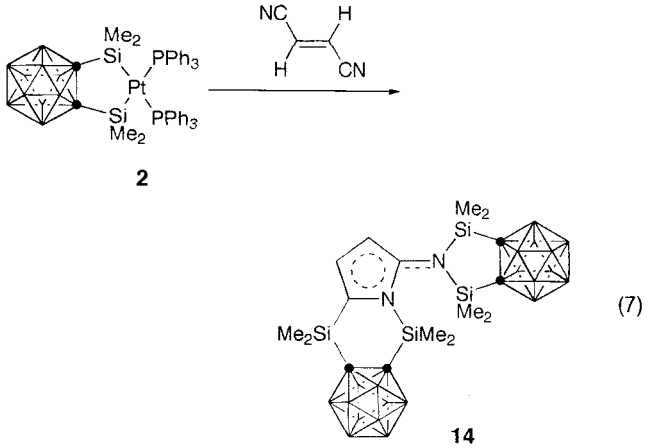
Figure 4. Crystal structure of **14** with 50% probability thermal ellipsoids.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for 14

Si(1*)−N(2)	1.749(2)	Si(1*)−C(1*)	1.869(2)
C(1*)−C(2*)	1.674(3)	Si(2*)−N(2*)	1.750(2)
Si(2*)−C(2*)	1.899(3)	N(2)−C(20)	1.422(3)
N(1)−C(20)	1.393(3)	N(1)−C(13)	1.419(3)
C(13)−C(18)	1.363(4)	C(18)−C(19)	1.398(4)
Si(2)−N(1)	1.764(2)	Si(2)−C(2)	1.904(3)
C(1)−C(2)	1.671(3)	Si(1)−C(1)	1.901(3)
Si(1)−C(13)	1.850(3)		

N(2)−Si(1*)−C(1*)	98.43(10)	Si(1*)−C(1*)−C(2*)	111.2(1)
C(1*)−C(2*)−Si(2*)	110.9(2)	N(2)−Si(2*)−C(2*)	98.4(1)
Si(1*)−N(2)−Si(2*)	120.5(1)	N(1)−C(20)−N(2)	122.9(2)
N(1)−C(20)−C(19)	108.6(2)	N(2)−C(20)−C(19)	128.3(2)
C(18)−C(19)−C(20)	107.4(2)	C(13)−C(18)−C(19)	109.7(2)
N(1)−C(13)−C(18)	106.7(2)	Si(1)−C(13)−N(1)	129.1(2)
C(1)−Si(1)−C(13)	106.1(1)	Si(1)−C(1)−C(2)	117.0(2)
Si(2)−C(2)−C(1)	120.1(2)		

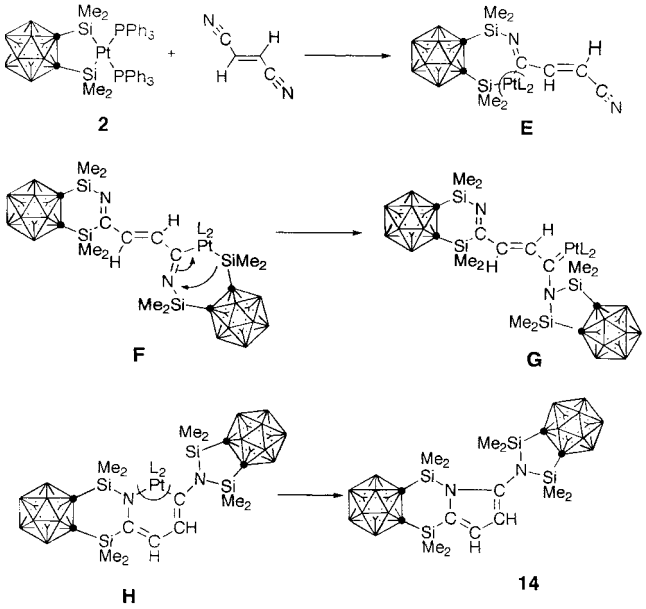
are well-established. Accordingly, we attempted analogous reactions of **2** with nitriles such as benzonitrile and propionitrile, but these nitriles did not react, even on extended heating in refluxing toluene solution. However, **2** readily reacted with fumaronitrile to give a cyclization product. Its reaction with 4 equiv of fumaronitrile in refluxing toluene for 8 h gave the product **14** as colorless crystals in 75% yield (eq 7).



(7)

The molecular structure of **14** is shown in Figure 4. Crystallographic data are given in Table 1 and selected bond lengths and angles in Table 3. The X-ray study revealed **14** to be a cyclization product which contains two types of disilyl moieties, imino and *N*,*N*-bis(silyl)-amino, which are connected by a five-membered ring. The five-membered ring (C_4N) is nearly planar, with the largest deviation of the ring atoms from the mean plane

Scheme 1



at N(1) equal to 0.003 Å. The C−C bond lengths (1.363−1.398 Å) and C−N bond lengths (1.393−1.422 Å) in the ring fall between a single and double bond,[36] demonstrating the presence of a delocalized ring system. Such a transformation of nitriles to imines or *N*,*N*-bis(silyl) enamines has been observed during photochemical reaction[37] or the platinum-catalyzed reaction of 1,2-bis-(dimethylsilyl)benzene with nitriles.[8] Compound **14** was characterized by its ^{1}H, ^{13}C, and ^{29}Si NMR and IR spectra and elemental analysis. Four singlets (δ 0.29, 0.35, 0.44, 0.63) in the ^{1}H NMR spectrum and four singlets (δ −0.03, 0.40, 0.93, 2.20) in the ^{13}C NMR spectrum of **14** could be assigned to the methyl groups on the silicon atoms, which indicated that the four dimethylsilyl groups are not equivalent. The ^{29}Si NMR spectrum of **14** exhibits four resonances at δ 12.53, 4.36, 4.28, and −6.51. The IR spectrum of **14** failed to show a new signal for a terminal CN.

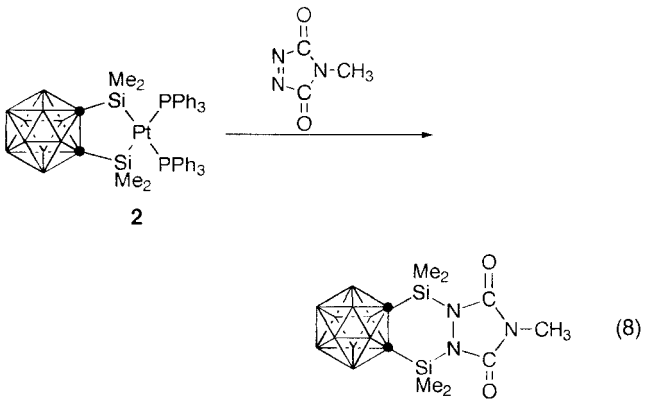
A reasonable mechanism for the formation of **14** (Scheme 1) involves the initial insertion of the cyano group into one of the platinum−silicon bonds, leading to seven-membered intermediate **E**, followed by cyclization to imine **F** and concomitant with another insertion of the cyano group into the remaining Pt−Si bond. It had been well-established that, in the platinum-catalyzed reaction with 1,2-bis(dimethylsilyl)benzene, nitriles not having an α-hydrogen such as cyanoarenes were converted into imines of type **F**.[8] The migration of the silicon atom to the nitrogen atom in our case then would afford the carbene complex **G**. This lends some credence to the notion that the nucleophilic attack of the imine is at the platinum carbene intermediate **H**. The cyclization product **14** then is formed in a reductive elimination process with the extrusion of PtL_2.

Reaction of 2 with Triazolinedione. The reaction of triazolinedione with **2** in toluene at room temperature

(36) Huheey, J. E. *Inorgnic Chemistry*, 3rd ed.; Harper & Row: New York, 1983; p 258.

(37) (a) Corriu, R. J. P.; Huynh, V.; Moreau, J. J. E.; Pataud-Sat, M. *J. Organomet. Chem.* **1983**, *255*, 359. (b) Walter, W.; Luke, H. W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 535. (c) Corriu, R. J. P.; Moreau, J. J. E.; Padaud-Sat, M. *Organometallics* **1985**, *4*, 623.

afforded the cyclization compound **15** with extrusion of the $Pt(PPh_3)_2$ fragment (eq 8). The resulting colorless



(8)

compound was isolated as an air-stable solid in 74% yield. It is soluble in benzene, toluene, and THF. The initial indication of a cyclization formulation for **15** stemmed from the observation of a parent ion in the mass spectrum at *m/z* 371. The ^1H and ^{13}C NMR spectra of **15** support the proposed structure. Both the ^1H and ^{13}C NMR spectra of **15** exhibited two CH_3 resonances due to the methyl groups on the silicon and nitrogen atoms.

Conclusions

We have prepared a cyclic bis(silyl)platinum complex of the type $PtSi_2P_2$ with *o*-carboranylene unit. The complex was an effective reactant in the double-silylation reaction. The cyclic bis(silyl)platinum complex reacts with a variety of unsaturated organic substrates such as alkynes, 1,2-diones, an enone, and a fumaronitrile, generating new classes of heterocycles incorporating alkenes, diolates, ketonate, imine, and amine. In contrast to the similar $PtSi_2P_2$ compounds, complex **2** is relatively robust, probably due to the presence of a carboranylene unit, and is not as readily attacked by unsaturated organic substrates. Complex **2** also exhibits unusual reactivities. For example, the reaction of **2** with an enone such as *trans*-cinnamaldehyde afforded the insertion product of two carbonyl ligands into the C−Si bond in **2**. The reaction of **2** with fumaronitrile also afforded an unusual cyclization product which contains both imino and *N*,*N*-bis(silyl)amino units. Thus, the cyclic bis(silyl)platinum complex **2** with a relatively strong Pt−Si bond has been further exploited in a series of novel chemical transformations.

Experimental Section

General Considerations. All experiments were performed under a dry nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques. Benzene, diehyl ether, toluene, and THF were freshly distilled from sodium benzophenone. Dichloromethane and hexane were dried and distilled from CaH_2. Gas chromatographic separations were carried out by using a column packed with 30% SE−30 silicon on Chromosorb P. ^1H, ^{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 were referenced relative to TMS (^1H), benzene-d_6 (^1H, δ 7.156; $^{13}C\{^1H\}$, δ 128.00), and 85% H_3PO_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, 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, K_2PtCl_4 and Me_2SiHCl, were purchased from Strem Chemicals. All the alkynes, *trans*-cinnamaldehyde, fumaronitrile, and 9,10-phenanthroquinone were purchased from Aldrich. $Pt(CH_2{=}CH_2)(PPh_3)_2$ was prepared according to the literature.[38]

1,2-Bis(dimethylsilyl)carborane 1. To a stirred THF solution (20 mL) of the *o*-carborane (1 g, 6.93 mmol) was added a solution of *n*-butyllithium in hexane (9.5 mL, 1.6 M, 15.26 mmol) at 0 °C. The reaction mixture was warmed to ambient temperature and stirred for 13−14 h. The reaction mixture was cooled to 0 °C, and a solution of Me_2SiHCl (1.73 mL, 15.26 mmol) in THF (4 mL) was added to the reaction mixture at that temperature. The reaction mixture was refluxed overnight. All volatiles were removed under reduced pressure, followed by extraction of the residues with *n*-hexane (20 mL × 3). The extracts were concentrated to 2 mL and cooled to −20 °C to furnish 0.87 g (50.5%) of a waxy powder. ^1H NMR (C_6D_6): δ 4.01 (sept, 2H, ^3J = 3.6 Hz, Si*H*), −0.03 (d, 12H, ^3J = 3.6 Hz, SiCH_3). IR (KBr pellet; cm^{-1}): ν(BH), 2512 (s); ν(SiH), 2154 (s). MS (EI): *m/z* 260 [M^+]. Anal. Calcd for $C_6H_{24}B_{10}Si_2$: C, 27.63; H, 9.21. Found: C, 27.32; H, 9.04.

$Me_2Si(1,2\text{-}C_2B_{10}H_{10})SiMe_2Pt(PPh_3)_2$ (2). To a solution of $Pt(CH_2{=}CH_2)(PPh_3)_2$ (0.32 g, 0.428 mmol) in benzene (20 mL) was added 1,2-bis(dimethylsilyl)carborane (0.13 g, 0.514 mmol) at room temperature. After the mixture was stirred for 1 h at the same temperature, the reaction mixture was warmed to 60−80 °C and stirred for 12 h to give a yellow precipitate, which was filtered. The yellow product was washed with hexane (20 mL). Recrystallization from a mixture of CH_2Cl_2 and *n*-hexane gave the title compound (0.36 g, 82%) as yellow crystals. Mp: 175−180 °C dec. ^1H NMR ($CDCl_3$): δ 7.26−6.78 (m, 30H, *Ph*), 0.32 (d, 12H, $^3J_{PtH}$ = 14 Hz, SiCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 134.4, 134.3, 134.1, 133.6, 130.1, 128.2, 128.0, 127.9 (*Ph*) 6.1 (d, 2C, $^2J_{PtC}$ = 104.6 Hz, Si*C*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 92.2 (d, $^1J_{PtP}$ = 1732 Hz). ^{29}Si NMR ($CDCl_3$): δ 39.6 (dd, $^1J_{PtSi}$ = 1281.6 Hz, $^2J_{PSi(trans)}$ = 148.8 Hz, $^2J_{PSi(cis)}$ = 12.8 Hz). Anal. Calcd for $C_{46}H_{64}B_{10}P_2PtSi_2$: C, 53.23; H, 6.16. Found: C, 52.96; H, 6.02.

Thermolysis of 2 with Diphenylacetylene. A mixture of 0.15 g (0.153 mmol) of **2** and 0.22 g (1.226 mmol) of diphenylacetylene in toluene (30 mL) was refluxed for 12 h. The solvent was then removed in vacuo, and the residue was chromatographed using benzene/hexane (1:1) as eluent (R_f = 0.85−0.9). The first band was crystallized from hexane at −10 °C to give 5,6-carboranylene-1,1,4,4-tetramethyl-2,3-diphenyl-1,4-disilacyclohex-2-ene (**3**) as colorless crystals in 92% yield. Mp: 50 °C. ^1H NMR ($CDCl_3$): δ 7.03−6.71 (m, 10H, *Ph*), 0.28 (s, 12H, SiCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 162.1 (Si*C*=), 141.0, 127.9, 127.7, 125.9 (*Ph*), 67.8 (carborane *C*), −1.4 (Si*C*H_3). ^{29}Si NMR ($CDCl_3$): δ −8.15. MS *m/z* 436 [M^+]. Anal. Calcd for $C_{20}H_{32}B_{10}Si_2$: C, 55.03; H, 7.33. Found: C, 54.87; H, 7.08.

Thermolysis of 2 with Phenylacetylene. A mixture of 0.025 g (0.025 mmol) of **2** and 0.02 mL (0.2 mmol) of phenylacetylene in toluene (10 mL) was refluxed for 20 h. The solvent was removed in vacuo and the residue chromatographed using hexane as eluent (R_f = 0.8). The first band was crystallized from hexane at −15 °C to give 5,6-carboranylene-1,1,4,4-tetramethyl-2-phenyl-1,4-disilacyclohex-2-ene (**4**) as white crystals in 95% yield. Mp: 48 °C. ^1H NMR ($CDCl_3$): δ 7.26−6.96 (m, 5H, *Ph*), 6.41 (s, 1H, C*H*), 0.38 (s, 6H, SiCH_3),

(38) Hartley, F. R. *Organomet. Chem. Rev., Sect. A* **1970**, *6*, 119.

0.35 (s, 6H, SiCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 158.5 (C=*C*Ph), 142.6 (C=*C*H), 128.5, 127.3, 126.3 (*Ph*). ^{29}Si NMR ($CDCl_3$): δ −8.94, −13.58. MS: *m/z* 354 [M^+]. Anal. Calcd for $C_{14}H_{28}B_{10}Si_2$: C, 45.30; H, 7.87. Found: C, 45.58; H, 7.68.

Thermolysis of 2 with 3-Hexyne. A mixture of 0.25 g (0.255 mmol) of **2** and 0.67 g (2 mmol) of 3-hexyne in toluene (30 mL) was refluxed overnight. GLC analysis of the reaction mixture showed the presence of 5,6-carboranylene-1,1,4,4-tetramethyl-2,3-dimethyl-1,4-disilacyclohex-2-ene (**5**). Pure **5** was isolated by chromatographic workup (eluent hexane, R_f = 0.55) in 88% yield. Mp: 75 °C. ^1H NMR ($CDCl_3$): δ 2.24 (q, 4H, J_{HH} = 7.6 Hz, CH_2), 0.96 (t, 6H, J_{HH} = 7.6 Hz, CH_3), 0.33 (s, 12H, SiCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 151.8 (*C*=C), 24.3 (*C*H_2), 14.6 (*C*H_3), −0.8 (Si*C*H_3). ^{29}Si NMR ($CDCl_3$): δ −8.51. 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.

Thermolysis of 2 with 2-Butyne. The same procedure was used as described for **5**, except 2-butyne was used instead of 3-hexyne. GLC analysis of the reaction mixture showed the presence of 5,6-carboranylene-1,1,4,4,-tetramethyl-2,3-dimethyl-1,4-disilacyclohex-2-ene (**6**). Pure **6** was isolated by chromatographic workup (eluent hexane, R_f = 0.6) in 92% yield. mp 146−148 °C. ^1H NMR ($CDCl_3$): δ 1.77 (s, 6H, CCH_3), 0.30 (s, 12H, Si − CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 144.9 (C=*C*), 17.5 (*C*CH_3), −2.1 (Si*C*H_3). ^{29}Si NMR ($CDCl_3$): δ −8.64. MS: *m/z* 312 [M^+]. Anal. Calcd for $C_{10}H_{28}B_{10}Si_2$: C, 38.44; H, 8.36. Found: C, 38.06; H, 8.20.

Thermolysis of 2 with Dimethyl Acetylenedicarboxylate. The same procedure was used as described for **5**, except dimethyl acetylenedicarboxylate was used instead of 3-hexyne. GC-MS analysis of the reaction mixture showed the presence of 5,6-carboranylenylene-1,1,4,4-tetramethyl-2,3-dicarbomethoxy-1,4-disilacyclohex-2-ene (**7**). Pure **7** was isolated by chromatographic workup (eluent ethyl acetate/hexane (1:1), R_f = 0.7, 90% yield) as a colorless, waxy solid. ^1H NMR ($CDCl_3$): δ 3.77 (s, 6H, OCH_3), 0.46 (s, 12H, SiCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 169.9 (*C*OO), 153.9 (=*C*CO_2CH_3), 53.4 (O*C*H_3), 0.2 (Si*C*H_3). ^{29}Si NMR ($CDCl_3$): δ −4.47. MS: *m/z* 400 [M^+]. Anal. Calcd for $C_{12}H_{28}O_4B_{10}Si_2$: C, 35.99; H, 6.99. Found: C, 35.62; H, 6.78.

Thermolysis of 2 with 1-Hexyne. The same procedure was used as described for **5**, except 1-hexyne was used instead of 3-hexyne. GC-MS analysis of the reaction mixture showed the presence of 4,5-carboranylene-1,1,3,3-tetramethyl-2-(*n*-butylmethylene)-1,3-disilacyclopentane (**8**). Pure **8** was isolated by chromatographic workup (eluent hexane, R_f = 0.55, second band, 54% yield). ^1H NMR ($CDCl_3$): δ 6.24 (s, 1H, =C*H*), 2.17 (t, 2H, J_{HH} = 9.4 Hz, CCH_2), 1.57−1.24 (m, 4H, −CH_2), 0.92 (t, 3H, J_{HH} = 4.4 Hz, CH_3), 0.33 (s, 6H, SiCH_3), 0.29 (s, 6H, SiCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 160.4 (=*C*H), 138.5 (Si*C*=), 40.1, 31.7, 23.3, 14.9 (*Bu*), −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.

Thermolysis of 2 with *trans*-Cinnamaldehyde. A mixture of **2** (0.2 g, 0.2 mmol) and *trans*-cinnamaldehyde (0.21 g, 1.6 mmol) in toluene (15 mL) was heated under reflux for 16 h, and volatiles were removed under vacuum. The remaining oil was purified by chromatography over silica gel, with benzene and hexane (1:1) as eluent. The residue, in hexane, was left to crystallize at −15 °C to yield 0.06 g (56%) of colorless crystals. Mp: 56 °C. ^1H NMR ($CDCl_3$): δ 7.52−6.18 (m, 10H, *Ph*), 6.88 (dd, 1H, J_{HH} = 12.3 Hz, J_{HH} = 5.8 Hz, =C*H*), 6.74 (dd, 1H, J_{HH} = 12.3 Hz, J_{HH} = 4.4 Hz, =C*H*), 1.56 (dd. 1H, J_{HH} = 5.8 Hz, J_{HH} = 4.4 Hz, C*H*), 0.84 (s, 12H, SiCH_3). ^{13}C NMR ($CDCl_3$): δ 162.2, 156.6, 137.4, 133.6, 132.1, 129.1, 128.7, 31.5 (s, *C*H), 14.0 (s, Si*C*H_3). ^{29}Si NMR ($CDCl_3$): δ 17.4. MS (EI): *m/z* 538 [M^+]. Anal. Calcd for $C_{24}H_{38}B_{10}O_3Si_2$: C, 53.52; H, 7.05. Found: C, 53.20; H, 6.78.

Reaction of 2 with *trans*-Cinnamaldehyde in Cyclohexene. A mixture of **2** (0.1 g, 0.1 mmol) and *trans*-cinnamaldehyde (0.10 g, 0.78 mmol) in cyclohexene (8 mL) was heated at reflux for 72 h. GLC analysis of the reaction mixture showed the presence of 7-(β-styrenyl)norcarane (**10**; 14% yield) and **11** (18% yield). The volatiles were removed under vacuum. The product **10** was purified by chromatography over silica gel, with benzene and hexane (1.5:1) as eluent. ^1H NMR ($CDCl_3$): δ 7.48−6.22 (m, 5H, *Ph*), 6.76 (d, 1H, J_{HH} = 11.6 Hz, =C*H*), 6.62 (dd, 1H, J_{HH} = 11.6 Hz, J_{HH} = 4.8 Hz, =C*H*), 2.02−0.64 (m, 11H, C*H*). ^{13}C NMR ($CDCl_3$): δ 156.7, 154.9, 138.7, 136.1, 132.4, 130.0, 129.3, 128.8, 34.6, 25.3, 25.1, 22.6, 21.8, 21.2. MS (EI): *m/z* 198 [M^+]. Anal. Calcd for $C_{15}H_{18}$: C, 90.91; H, 9.09. Found C, 90.74; H, 8.96.

Reaction of 2 with Phenanthrenequinone. To a stirred toluene solution (10 mL) of **2** (0.3 g, 0.306 mmol) was added a solution of phenanthrenequinone (0.127 g, 0.613 mmol) in toluene (5 mL) at 25 °C. The color immediately changed from yellow to brown. The reaction mixture was stirred overnight at 25 °C. The solvent was removed in vacuo, and the residue was chromatographed using benzene/hexane (1:1) as eluent (R_f = 0.81). Recrystallization from hexane at 4 °C afforded 7,8-carboranylene-1,1,6,6-tetramethyl-2,5-dioxa-3,4-phenanthrene-1,6-disilacyclooctane (**12**) as brown crystals in 76% yield. Mp: 190−192 °C. ^1H NMR ($CDCl_3$): δ 8.67−8.62 (m, 2H, *Ph*), 8.02−7.98 (m, 2H, *Ph*), 7.66−7.59 (m, 4H, *Ph*), 0.49 (s, 12H, SiCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 135.4, 127.9, 127.2, 125.9, 122.8, 122.2, 121.6, 70.8 (carborane *C*), −0.3(Si-*C*H_3). MS: *m/z* 466 [M^+]. Anal. Calcd for $C_{20}H_{30}B_{10}O_2Si_2$: C, 51.49; H, 6.43. Found: C, 51.32; H, 6.22.

Reaction of 2 with Benzil. The same procedure was used as described for **12**, except that benzil was instead of phenanthrenequinone; yield 85%. Mp: 148−149 °C. ^1H NMR ($CDCl_3$): δ 7.20−7.13 (m, 10H, *Ph*), 0.43 (s, 12H, SiCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 139.3 (*C*=C), 128.4, 128.2, 128.1, 127.8 (*Ph*), 71.6 (carborane *C*), 0.1 (SiCH_3). MS: *m/z* 468 [M^+]. Anal. Calcd for $C_{20}H_{32}B_{10}O_2Si_2$: C, 51.27; H, 6.83. Found: C, 50.92; H, 6.64.

Thermolysis of 2 with Fumaronitrile. A mixture of 0.198 (0.2 mmol) of **2** and 0.126 g (1.6 mmol) of fumaronirile in toluene (15 mL) was refluxed for 8 h. The solvent was removed in vacuo. The crude product was chromatographed, with benzene and hexane (1:1) as eluent, and recrystallized from hexane in 75% yield. Mp: 158−162 °C. ^1H NMR ($CDCl_3$): δ 6.51 (d, 1H, J_{HH} = 5.1 Hz, C*H*), 5.67 (d, 1H, J_{HH} = 5.1 Hz, C*H*), 0.63 (s, 6H, SiCH_3), 0.44 (s, 6H, SiCH_3), 0.35 (s, 6H, SiCH_3), 0.29 (s, 6H, SiCH_3). ^{13}C NMR ($CDCl_3$): δ 128.6, 128.2, 125.4, 124.9 (Si*C*N), 2.20 (s, Si*C*H_3), 0.93 (s, Si*C*H_3), 0.40 (s, Si*C*H_3), −0.03 (s, Si*C*H_3). ^{29}Si NMR ($CDCl_3$): δ 12.53, 4.36, 4.28, −6.51. Anal. Calcd for $C_{16}H_{46}B_{20}N_2Si_4$: C, 32.26; H, 7.73. Found: C, 32.02; H, 7.56.

Reaction of 2 with Triazolinedione. A mixture of 0.4 g (0.407 mmol) of **2** and 0.18 g (1.635 mmol) of triazolinedione in toluene (20 mL) was stirred overnight at room temperature. The solvent was removed in vacuo and chromatographed using ethyl acetate/hexane (2:1) as eluent. Recrystallization from hexane afforded 5,6-carboranylene-1,1,4,4-tetramethyl-2,3-triazolinedione (**15**) as colorless crystals in 74% yield. Mp: 144 °C. ^1H NMR ($CDCl_3$): δ 3.03 (s, 3H, N−CH_3), 0.68 (s, 12H, SiCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 161.8 (*C*=O), 25.4 (N*C*H_3), −1.51 (Si*C*H_3). IR (KBr pellet; cm^{-1}): 3056 (w), 2980 (w), 2583 (s), 1695 (s), 1500 (m), 1259 (m), 1086 (m), 980 (s), 881 (m), 825 (s), 676 (w), 614 (w). MS: *m/z* 371 [M^+]. Anal. Calcd for $C_9H_{25}B_{10}N_3O_2Si_2$: C, 29.10; H, 6.73. Found: C, 28.88; H, 6.54.

X-ray Crystallography. Details of the crystal data and a summary of intensity data collection parameters for **2**, **3**, **9**, and **14** are given in Table 1. Crystalline **2** was grown from CH_2Cl_2/hexane, and crystals of **3**, **9**, and **14** were grown from hexane solution stored at −10 to −20 °C. Crystals of **2**, **3**, **9**, and **14** were mounted in thin-walled glass capillaries and sealed under argon. The data sets of four crystals were collected on an Enraf CAD4 automated diffractometer. Mo Kα

radiation (λ = 0.7107 Å) was used for all structures. Each structure was solved by the application of direct methods using the SHELX-96 program and least-squares refinement using SHELXL-97. All non-hydrogen atoms in compounds **2**, **3**, **9**, and **14** were refined anisotropically. All other hydrogen atoms were included in calculated positions.

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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**, **3**, **9**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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