Organometallics **2001,** *20,* 937−944

Novel Nickel-Catalyzed Reactions of Nitriles with 1,2-Bis(dimethylsilyl)carborane

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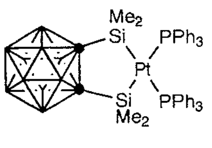
Received October 10, 2000

The nickel-catalyzed reaction of 1,2-bis(dimethylsilyl)carborane (**1**) with propionitrile afforded an *N*-silyl enamine. The dehydrogenative double silylation of nitriles without α-H such as isobutyronitrile, benzonitrile, *p*-tolunitrile, and 1-cyanonaphthalene yielded six-membered cyclic imines. In contrast, the reaction of **1** with 9-anthracenecarbonitrile under the same reaction conditions gave a five-membered *N*,*N*-bis(silyl) amine. Interestingly, the reaction of **1** with nitriles having an α-hydrogen such as benzyl cyanide, diphenylacetonitrile, and hydrocinnamonitrile afforded *N*,*N*-bis(silyl) enamines.

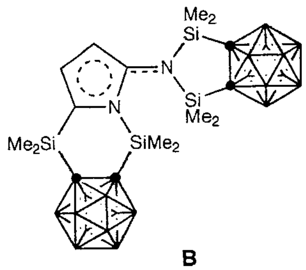
Introduction

Transition-metal-catalyzed double silylation of alkynes,[1] alkenes,[2] 1,3-dienes,[3] and carbonyl compounds[4] has been developed in the last 30 years. In contrast to the above well-developed reactions, little is known about double silylation of the carbon−nitrogen triple bond, because the cyano group has been believed to be inert. For example, rhodium-,[5] molybdenum-,[6] and cobalt-catalyzed[7] hydrosilylation and chemoselective[8] and photochemical[9] double silylation using a silyliron carbonyl complex have been developed as a method for the preparation of silyl-substituted nitriles.

Recently, we[10] reported the double-silylation reactions of a variety of unsaturated organic substrates with $(Ph_3P)_2Pt[o\text{-}(SiMe_2)_2C_2B_{10}H_{10}]$ (**A**), which contains an *o*-carboranylene unit. Interestingly, its reaction with fumaronitrile yielded the cyclization product **B**, which contains two types of disilyl moieties, an imine and *N*,*N*-bis(silyl)amine.



A



B

Tanaka and co-workers[11] reported that platinum-catalyzed double silylation of nitriles with *o*-bis(dimethylsilyl)benzene afforded *N*-silyl enamines and imines. The unusal reactivity of 1,2-bis(dimethylsilyl)carborane (**1**) has allowed novel transformations of some nitriles. In addition, the double silylation of nitriles by the cyclic bis(silyl)platinum complex **A** was a stoichiometric process and was quite limited. Accordingly, we have started a systematic study of the double silylation of nitriles catalyzed by a nickel complex. Here we report the double-silylation reactions of a variety of nitriles with 1,2-bis(dimethylsilyl)carborane.

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10.1021/om0008629 CCC: $20.00
Publication on Web 01/27/2001

Table 1. Crystal Data of Compounds 8 and 12

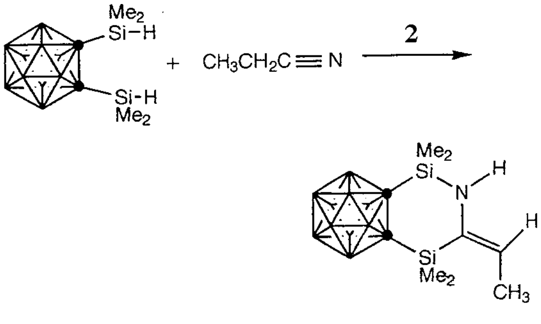
	8	**12**
empirical formula	$C_{21}H_{33}B_{10}NSi_2$	$C_{15}H_{28}B_{10}NSi_2$
mol wt	463.76	386.66
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a, Å	18.332(3)	11.7883(9)
b, Å	13.196(2)	14.4327(11)
c, Å	23.452(3)	13.8304(11)
α, deg	90	90
β, deg	107.414(10)	102.681(2)
γ, deg	90	90
V, Å^3	5413(1)	2295(3)
Z	8	4
D_{calcd}, g cm^{-3}	1.138	1.119
F(000)	1952	812
μ, cm^{-1})	0.143	0.156
scan type	ω	ω
no. of rflns measd	9733	14 807
no. of obsd rflns, $I > 2\sigma(I)$	3711	5520
R1	0.0856	0.0609
wR2^a	0.1897	0.1493
goodness of fit	1.103	1.008

[a] $wR2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.

Results and Discussion

Although the cyclic bis(silyl)platinum complex is not a catalyst for the double silylation of nitriles with 1,2-bis(dimethylsilyl)carborane (**1**), due to its strong Pt−Si bonds and the relative inertness of the cyano group, the cyclic bis(silyl)nickel complex **2**[12] was found to be a good catalyst for the dehydogenative double silylation of nitriles. The nickel-catalyzed double silylation can be carried out either by reacting **1** and the nitrile in the presence of $Ni(PEt_3)_4$ or by reacting **1** and the nitrile in the presence of a catalytic amount of the cyclic bis(silyl)-nickel complex **2**. Because the former procedure in some cases gave complex product mixtures, the latter procedure is preferred.

Propionitrile readily reacted with **1** in the presence of a catalytic amount of $(PEt_3)_2Ni[o\text{-}(SiMe_2)_2C_2B_{10}H_{10}]$[12] (**2**) in refluxing toluene to give the *N*-silyl enamine **3** (Table 2) in good yield (eq 1).



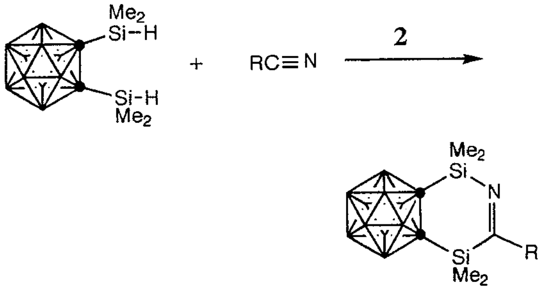
(1)

3

The ^1H, ^{13}C, and ^{29}Si NMR spectra and the mass spectrum of compound **3** were consistent with the proposed structure. A parent ion in the mass spectrum was observed at *m*/*z* 312. The ^1H NMR spectrum of **3** contained a broad N−H resonance (3.92 ppm) and an olefinic proton resonance (4.97 ppm). Two singlets (0.35 and 0.33 ppm) in the ^1H NMR spectrum and two singlets (−0.62 and −1.42 ppm) in the ^{13}C NMR spectrum of **3** could be assigned to the methyl groups on the silicon atoms. The ^{29}Si NMR spectrum of **3** exhibited two resonances at −12.4 and −8.8 ppm arising from the nonequivalent silicon atoms. We are tentatively assigned the *Z* configuration due to the steric hindrance. Such *N*-silyl enamines have been prepared using a platinum complex as the catalyst with *o*-bis(dimethylsilyl)benzene.[11]

The results of the nickel-complex-catalyzed reactions of **1** with nitriles that do not contain an α-hydrogen are presented in Table 2.

Reaction of benzonitrile and **1** in the presence of a catalytic amount of **2** in refluxing toluene afforded a six-membered cyclic imine (Table 2) in moderate yield (eq 2). In a similar fashion, the nickel-catalyzed reactions of **1** with other nitriles such as isobutyronitrile, *p*-tolunitrile, and 1-cyanonaphthalene in refluxing toluene yielded the respective six-membered cyclic insertion products. Such a nitrile insertion reaction has been reported using a platinum complex as catalyst and *o*-bis(dimethylsilyl)benzene.[11]



(2)

4 R = $^iC_3H_7$
5 R = C_6H_5
6 R = $C_6H_4CH_3$-*p*
7 R = β – naphthy

Compounds **4**−**7** were identified on the basis of their ^1H, ^{13}C, and ^{29}Si NMR spectra, their mass spectra, and elemental analyses. The ^1H NMR spectrum of **5** showed the phenyl and methyl resonances in the expected 5:12 ratio. In the ^{13}C NMR spectrum of **5**, a resonance at 141.81 ppm could be assigned to the imino carbon atom. The ^{29}Si NMR spectrum of **5** showed two resonances at −11.6 and −7.2 ppm.

In contrast to the double silylation of the above nitriles by **1**, when 9-anthracenecarbonitrile was employed in the reaction with **1** under the same reaction conditions (eq 3), the five-membered cyclic *N*,*N*-bis(silyl) amine **8** (Table 2) was isolated as colorless crystals in 76% yield.

A key feature in the ^1H NMR spectrum of **8** includes a singlet at 4.96 ppm assigned to the methylene protons. A high-frequency ^{13}C NMR resonance at 29.42 ppm provides evidence for a methylene carbon atom, in addition to a resonance at −2.64 ppm assigned to the methyl carbon. The value is close to that of the *N*,*N*-bis(silyl) amine reported by Tanaka and co-workers.[11] To confirm the structure of **8**, a single-crystal X-ray diffraction study was undertaken. The molecule structure of **8** is shown in Figure 1. A summary of cell

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

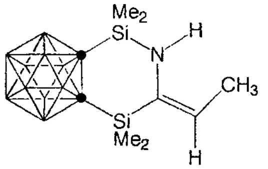
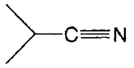
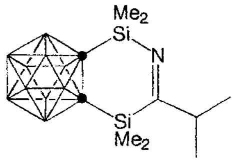
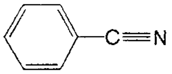
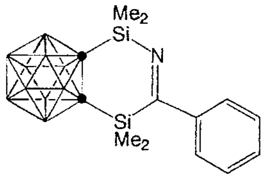
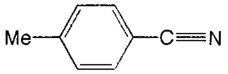
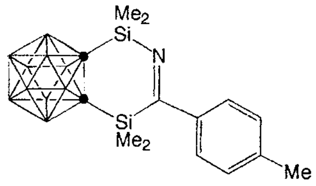
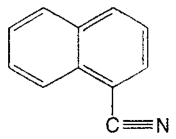
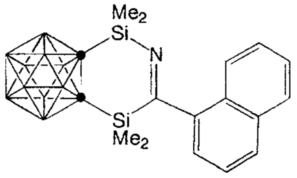
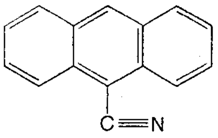
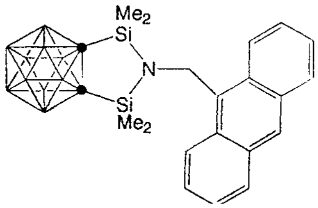
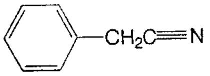
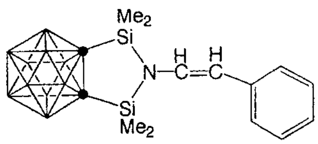
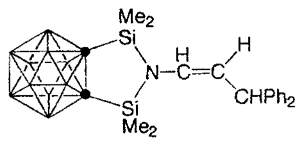
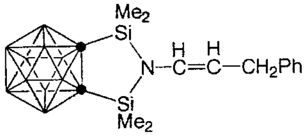
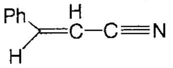
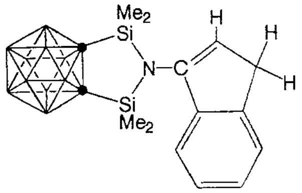
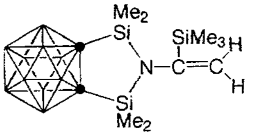
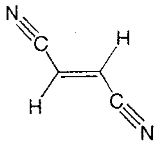
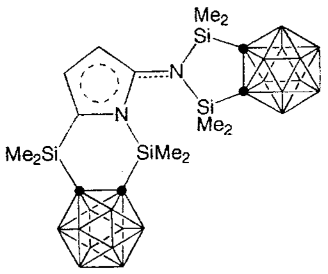
Reactant	Product	Compound number	yield (%)
$CH_3CH_2C\equiv N$		**3**	66
		**4**	66
		**5**	52
		**6**	74
		**7**	72
		**8**	76
		**9**	86
$Ph_2CHCH_2C\equiv N$		**10**	65
$PhCH_2CH_2C\equiv N$		**11**	71

Table 2 (Continued)

Reactant	Product	Compound number	yield (%)
		**12**	68
$Me_3SiCH_2C{\equiv}N$		**13**	75
		**14**	75

constants and data collection parameters is included in Table 1. A five-membered ring containing a carboranyl unit, two silicon atoms, and an amine fragment was shown to be present. There are two crystallographically independent molecules in an asymmetric unit. This is why the unit cell has a *Z* value of 8. These two molecules are essentially identical within experimental error. The anthracene group is almost perpendicular to the molecule plane defined by the two silicon atoms, the two carborane carbon atoms, and the nitrogen atom with dihedral angles of 88.1(1)°. The N(1)–C(7) bond distance (1.478(7) Å) is typical of the nitrogen–carbon single bond (1.47 Å).[13] The N(1)–C(7)–C(8) bond angle (116.0(5)°) is slightly wider than the usual value for an sp^3 carbon center due to the steric hindrance of the anthracene group.

The formation of **8** is interesting, because the sequential hydrosilylation of the carbon–nitrogen triple bond by the Si–H bond in **1** must have occurred during the course of the reaction. A similar hydrosilylation has been observed in the rhodium[5]- and platinum-catalyzed[11] double silylation of nitriles with a bis(hydrosilane).

A preliminary study of the reactivity of cyclic bis-

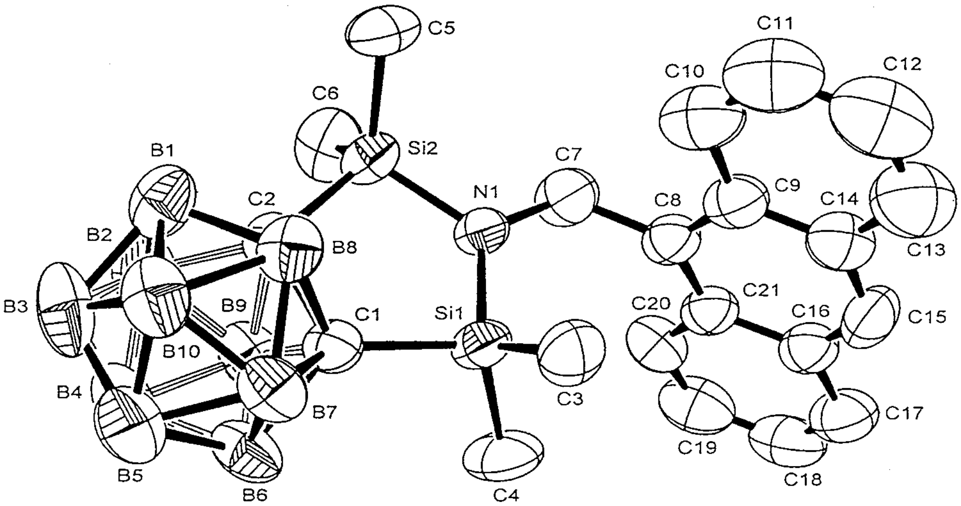
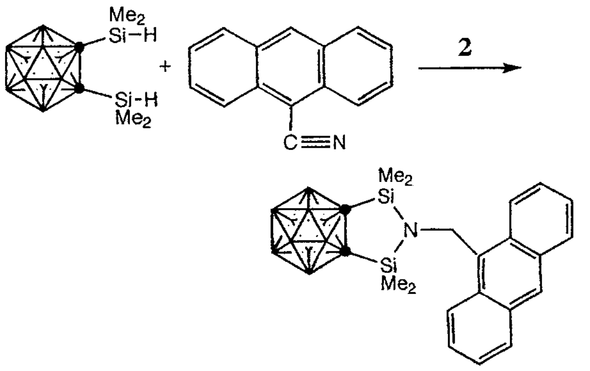


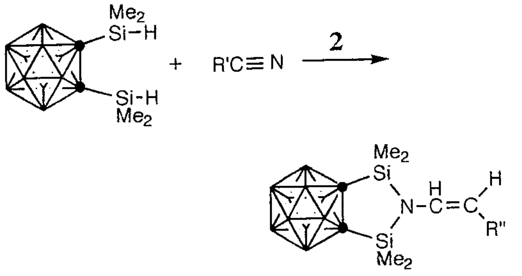
Figure 1. ORTEP drawing of **8** showing the atom-labeling scheme with 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Si(1)–N(1) = 1.730(7), Si(1)–C(1) = 1.909(6), Si(2)–N(1) = 1.734(4), Si(2)–C(2) = 1.894(6), N(1)–C(7) = 1.478(7); N(1)–Si(1)–C(B) = 98.5(2), N(1)–Si(2)–C(2) = 99.4(2), Si(1)–N(1)–Si(2) = 120.6(3), C(2)–C(1)–Si(1) = 111.1(4), C(1)–C(2)–Si(2) = 110.3(4), N(1)–C(7)–C(8) = 116.0(5), C(7)–N(1)–Si(1) = 124.7(4), C(7)–N(1)–Si(2) = 114.4(3).



(3)

8

(silyl)nickel complex **2** showed that its catalytic reactions with nitriles that have an α-hydrogen produce *N*,*N*-bis(silyl) enamines (Table 1), providing easy access to a variety of *N*,*N*-bis(silyl) enamines, which recently were shown to be precusors of substituted 2-aza-1,3-butadienes.[14] Thus, treatment of **1** with 4 equiv of benzyl cyanide in the presence of a catalytic amount of **2** in refluxing toluene-d_8 resulted in the diminishment of the methylene peak and new signals at 6.53 and 5.82 ppm grew in (eq 4). The ^{1}H NMR spectrum of the isolated product **9** exhibited two olefinic proton resonances at 6.53 and 5.82 ppm (both doublets). The IR spectrum of compound **9** showed a new absorption due to the $\nu_{C=C}$ stretch at 1592 cm^{-1}, concomitant with the disappearance of the original strong absorption at 2240 cm^{-1}, assigned to the cyano group of the ligand. The ^{29}Si NMR spectrum of **9** showed two resonances at 2.4 and −3.2 ppm, indicative of the presence of two chemically nonequivalent silicon atoms. The chemical shifts in the ^{29}Si NMR spectrum of **9** are in the range of those of the other five-membered-ring compounds.[15] Such selective conversion of nitriles into *N*,*N*-bis(silyl) enamines has been observed previously in the iron-catalyzed double silylation.[15]



(4)

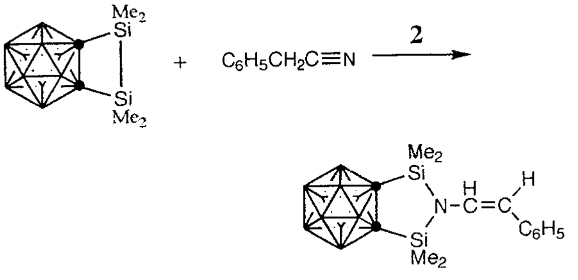
9 R' = $CH_2C_6H_5$; R" = C_6H_5

10 R' = Ph_2CHCH_2 ; R" = $CHPh_2$

11 R' = $PhCH_2CH_2$; R" = CH_2Ph

On the basis of our results and some other related results,[15] a plausible reaction pathway for the present reaction (**9**−**11**) may be proposed (Scheme 1). In the first stage, insertion of the cyano group into one Ni−Si bond gives a seven-membered intermediate (**C**). The migration of the other silicon atom to the nitrogen affords the carbene intermediate **D**. The σ-vinyl complex **E** can be obtained via a migration of one hydrogen atom α to the cyano group of the nitrile to the carbon α to the nitrogen atom. The *N*,*N*-bis(silyl) enamine is then formed in a reductive elimination step.

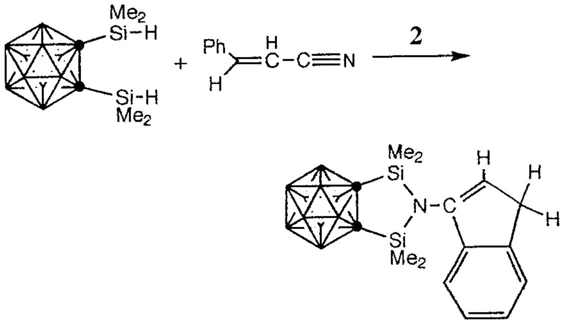
To further prove the above proposed mechanism, we have carried out the reaction of 2,3-(1,1,4,4-tetramethyldisilanediyl)carborane with 3 equiv of benzyl cyanide in the presence of a catalytic amount of **2** in toluene at 60−70 °C. It gave compound **9** in 76% yield (eq 5). This is additional evidence for the mechanism proposed above.



(5)

9

Surprisingly, when cinnamonitrile was employed in the catalytic reaction with **2**, a five-membered cyclopentanone enamine (Table 2) was isolated as colorless crystals in 68% yield (eq 6). A key feature in the ^{1}H NMR spectrum of **12** includes a doublet at 3.34 ppm assigned to the methylene and a triplet at 5.98 ppm assigned to the vinyl proton. A characteric high-field ^{13}C NMR resonance at 35.89 ppm provides evidence for formation of a methylene group. The structure of the product was not deduced on the basis of spectroscopic data; therefore, a single-crystal X-ray diffraction study was undertaken. The molecular structure of **12** is shown in Figure 2. Crystallographic data are given in Table 1. To our surprise, the X-ray study of **12** showed it to be the cyclic enamine. The C(1)−C(9) bond length (1.393(5) Å) in the ring is in the range of a double bond, demonstrating the presence of an enamine. Such a transformation of nitrile to enamine has been observed in the photochemical reaction of iron with 4-cyanobut-1-ene.[16]



(6)

12

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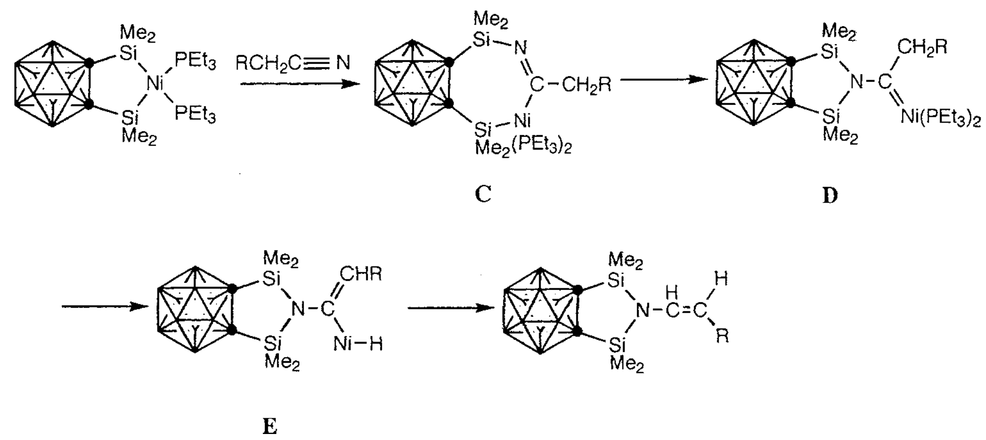
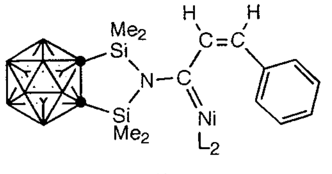
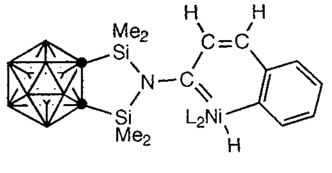
Scheme 1



A reasonable mechanism for the formation of **12** involves the initial insertion of the cyano group into one of the nickel−silicon bonds, leading to the seven-membered intermediate **C**. The migration of the silicon atom to the nitrogen atom in our case then would afford



F



G

an amine and the carbene **F**. The intramolecular aromatic C−H activation would occur to give the nickel hydride intermediate **G**. The nickelacyclohexene thus formed can liberate the cyclic enamine by reductive elimination with extrusion of $Ni(PEt_3)_2$. Such a formation of a nickel carbene intermediate is supported by the isolation of iron carbene complexes as reported by Gladysz and co-workers.[17]

The reaction of (trimethylsilyl)acetonitrile gave the acylsilane enamine **13**. Two characteristic doublets at 5.52 and 5.46 ppm in the ^{1}H NMR spectrum of **13** were assigned to the vicinal olefinic protons. Such a formation of an enamine due to the migration of a trimethylsilyl group has been observed previously.[18]

In earlier work,[10] we attempted the stoichiometric reaction of the cyclic bis(silyl)platinum complex with fumaronitrile. An X-ray study revealed the product to be a cyclization product, **B**, which contained two types of disilyl moieties, imine and *N*,*N*-bis(silyl) amine. To determine whether the nickel-catalyzed double silylation of fumaronitrile proceeds in a similar direction, we attempted the double silylation under the same reaction conditions.

Fumaronitrile was found to react with **1** in the

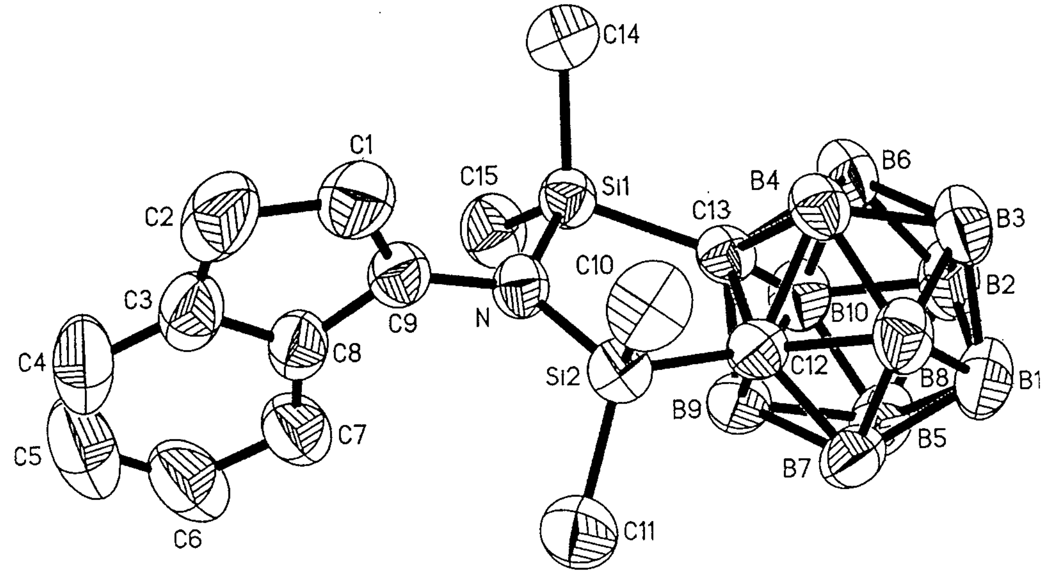


Figure 2. ORTEP drawing of **12** showing the atom-labeling scheme with 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (deg): C(1)−C(9) = 1.393(5), C(1)−C(2) = 1.494(5), C(2)−C(3) = 1.489(6), C(3)−C(8) = 1.393(5), C(9)−C(9) = 1.471(4), C(12)−C(13) = 1.681(4), N−C(9) = 1.430(4), Si(1)−N = 1.740(2), Si(1)−C(13) = 1.903(3), Si(2)−C(12) = 1.901(3); Si(1)−N−Si(2) = 121.60(14), Si(1)−N−C(9) = 118.55(18), N−C(9)−C(1) = 127.4(3), C(9)−C(1)−C(2) = 111.4(4).

presence of a catalytic amount of **2** to afford the cyclization product **14**. Four singlets (0.29, 0.35, 0.44, and 0.63 ppm) in the ^{1}H NMR spectrum and four singlets (−0.03, 0.40, 0.93, and 2.20 ppm) in the ^{13}C NMR spectrum of **14** could be assigned to the methyl groups, which indicated that the four methyl groups are not equivalent. The spectral data for **14** were identical with those of the authentic sample obtained in the reaction of the platinum complex with fumaronitrile.

In summary, the nickel-catalyzed double silylation of nitriles allowed easy access to bis(silyl)carboranyl products. The disilanickela complex **2** is an effective catalyst for the selective conversion of nitriles to bis(silyl) products. The reactions are quite sensitive to the substituent of the nitriles. The present reaction provides a new route to a novel class of heterocyclic compounds.

Experimental Section

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques. Toluene, benzene, and diethyl ether were freshly distilled from sodium benzophenone. Hexane was dried and distilled from CaH_2. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Varian Gemini 300 spectrometer operating at 300.00, 75.44, and 59.60 MHz, respectively. Chemical shifts are referenced relative to TMS. IR spectra were recorded on a Biorad FTS-165 spectrometer. Mass spectra were recorded on a Shimadzu Model QP-1000 spectrophotometer, and elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA 1108 analyzer.

o-Carborane was purchased from Callery Chemical Co. and used without purification. The starting materials $Ni(COD)_2$, PEt_3, and $SiMe_2HCl$ were purchased from Strem Chemicals. The nitriles were purchased from Aldrich. 1,2-Bis(dimethylsilyl)carborane,[12] $Ni(PEt_3)_4$,[19] and $(PEt_3)_2Ni[$*o*$\text{-}(SiMe_2)_2\text{-}C_2B_{10}H_{10}]$[12] were prepared according to the known procedures.

Nickel-Catalyzed Reaction of 1 with Various Nitriles. General Procedure. Compounds **3**−**14** were prepared by the reaction of **1** with the corresponding nitriles in the presence of a catalytic amount of **2**. In a typical synthesis, a mixture of propionitrile (0.27 mL, 6.35 mmol), **1** (0.1 g, 0.38 mmol), and **2** (0.01 g, 0.018 mmol) in toluene (15 mL) was heated at reflux for 12 h. The solvent was removed in vacuo. The solid residue was extracted with three portions (10 mL) of hexane. The pure product (**3**) was obtained by sublimation as air-sensitive colorless crystals in 66% yield. Mp: 88−92 °C. ^{1}H NMR ($CDCl_3$): δ 4.97 (q, 1H, $J_{HH} = 6.60$ Hz, C*H*), 3.92 (br, 1H, N*H*), 1.54 (d, 3H, $J_{HH} = 6.60$ Hz, C*H*$_3$), 0.35 (s, 6H, Si−C*H*$_3$), 0.33 (s, 6H, Si−C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 116.15 (N*C*), 97.00 (*C*CH$_3$), 10.52 (C*C*H$_3$), −0.62 (2C, Si−*C*H$_3$), −1.42 (2C, Si−*C*H$_3$). ^{29}Si NMR ($CDCl_3$): δ −8.8, −12.4. MS: *m*/*z* 312 [M$^+$]. IR (KBr pellet; cm^{-1}): 3329 (w), 3052 (w), 2961 (s), 2599 (s), 1607 (w), 1425 (w), 1335 (m), 1258 (s), 1145 (m), 1090 (s), 1078 (m), 1012 (sh), 878 (m), 815 (s), 722 (w), 680 (m), 583 (m), 542 (w), 492 (w), 422 (m). Anal. Calcd for $C_9H_{26}B_{10}NSi_2$: C, 34.61; H, 8.32. Found: C, 34.16; H, 8.04.

Compound 4 from the Reaction with Isobutyronitrile. Compound **4** was prepared using the same procedure as described for **3**, except isobutyronitrile was used instead of propionitrile. Pure **4** was obtained by sublimation in 66% yield. Mp: 92−95 °C. ^{1}H NMR ($CDCl_3$): δ 2.91 (sept, 1H, $J_{HH} = 7.02$ Hz, C*H*), 0.94 (d, 6H, $J_{HH} = 7.02$ Hz, C*H*$_3$), 0.43 (s, 6H, Si−C*H*$_3$), 0.41 (s, 6H, Si−C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 107.83 (*C*N), 41.25 (*C*HMe$_2$), 19.14 (CH*C*H$_3$), −1.40 (2C, Si−*C*H$_3$), −2.24 (2C, Si−*C*H$_3$). ^{29}Si NMR ($CDCl_3$): δ −7.6, −12.8. MS: *m*/*z* 328 [M$^+$]. IR (KBr pellet; cm^{-1}): 3068 (m), 2963 (m), 2592 (s), 2576 (s), 1658 (w), 1545 (w), 1261 (s), 1208 (w), 1095 (s), 1020 (s), 982 (w), 932 (w), 803 (s), 716 (w), 583 (w). Anal. Calcd for $C_{10}H_{29}B_{10}NSi_2$: C, 36.69; H, 8.86. Found: C, 36.22; H, 8.52.

Compound 5 from the Reaction with Benzonitrile. Compound **5** was prepared using the same procedure as described for **3.** The pure yellow product **5** was obtained by repeated recrystallization from hexane at −30 to −40 °C in 52% yield. Mp: 96−98 °C. ^{1}H NMR ($CDCl_3$): δ 7.62−7.32 (m, 5H, *Ph*), 0.60 (s, 6H, Si−C*H*$_3$), 0.54 (s, 6H, Si−C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 141.81, 129.48, 127.11, 124.95, 102.76, −1.84, −2.79. ^{29}Si NMR ($CDCl_3$): δ −7.2, −11.6. MS: *m*/*z* 362 [M$^+$]. IR (KBr pellet; cm^{-1}): 3084 (w), 3064 (w), 3036 (w), 2966 (m), 2595 (s), 2561 (s), 1616 (s), 1591 (m), 1579 (m), 1447 (w), 1403 (w), 1311 (w), 1257 (s), 1203 (m). 1172 (m), 1087 (s), 1072 (w), 1024 (w), 1001 (w), 983 (m), 932 (m), 868 (s), 820 (s), 789 (s), 688 (m), 666 (m), 627 (m), 588 (w), 452 (m). Anal. Calcd for $C_{13}H_{27}B_{10}NSi_2$: C, 43.20; H, 7.47. Found: C, 42.89; H, 7.22.

Compound 6 from the Reaction with *p*-Tolunitrile. Compound **6** was prepared using the same procedure as described for **3.** The pure product **6** was isolated by chromatographic workup (eluent benzene/hexane (1/4), $R_f = 0.58$) in 74% yield. Mp: 102−104 °C. ^{1}H NMR ($CDCl_3$): δ 7.26−7.06 (m, 4H, *Ph*), 2.17 (s, 3H, C*H*$_3$), 0.17 (s, 12H, Si−C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 137.27, 129.27, 127.94, 123.87, 96.98, 30.93, −1.28. MS: *m*/*z* 376 [M$^+$]. IR (KBr pellet; cm^{-1}): 3038 (w), 2957 (w), 2926 (w), 2858 (w), 2600 (s), 2578 (s), 1641 (w), 1512 (w), 1405 (w), 1361 (w), 1258 (s), 1089 (m), 1067 (s), 1027 (w), 987 (w), 943 (w), 904 (w), 880 (m), 820 (s), 786 (m), 722 (w), 697 (w), 668 (w), 515 (w), 473 (w). Anal. Calcd for $C_{14}H_{29}B_{10}NSi_2$: C, 44.79; H, 7.73. Found: C, 44.92; H, 7.58.

Compound 7 from the Reaction with 1-Cyanonaphthalene. Compound **7** was prepared using the same prodedure as described for **6**, except 1-cyanonaphthalene was used instead of *p*-tolunitrile. Pure **7** was isolated by chromatographic workup (eluent benzene/hexane (1/4), $R_f = 0.52$). Yield: 72%. Mp: 104−106 °C. ^{1}H NMR ($CDCl_3$): δ 8.08−7.16 (m, 7H, naphthyl), 0.34 (s, 6H, Si−C*H*$_3$), 0.33 (s, 6H, Si−C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 134.05, 131.52, 130.01, 129.23, 127.50, 127.28, 126.43, 126.39, 124.87, 124.39, 1.99, 0.60. MS: *m*/*z* 412 [M$^+$]. IR (KBr pellet; cm^{-1}): 3153 (w), 3072 (w), 2960 (s), 2927 (w), 2864 (w), 2594 (s), 1467 (w), 1382 (w), 1261 (s), 1091 (s), 1039 (w), 908 (s), 804 (m), 734 (s), 651 (w), 543 (m), 449 (m), 423 (m). Anal. Calcd for $C_{17}H_{29}B_{10}NSi_2$: C, 49.63; H, 7.05. Found: C, 49.28; H, 6.87.

Compound 8 from the Reaction with 9-Anthracenecarbonitrile. Compound **8** was prepared using the same procedure as described for **3**. Pure **8** was isolated by chromatographic workup (benzene/hexane (1/1), $R_f = 0.62$) in 76% yield. Mp: 269−271 °C. ^{1}H NMR ($CDCl_3$): δ 8.49−7.52 (m, 9H, anthracene), 4.96 (s, 2H, C*H*$_2$), −0.09 (s, 12H, Si−C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 127.80, 127.38, 127.04, 124.93, 124.76, 123.72, 122.60, 118.24, 29.42, −2.64 (Si-*C*H$_3$). ^{29}Si NMR ($CDCl_3$): δ −11.6. MS: *m*/*z* 464 [M$^+$]. IR (KBr pellet; cm^{-1}): 3056 (w), 2973 (w), 2882 (w), 2579 (s), 1626 (w), 1525 (w), 1496 (w), 1473 (w), 1446 (m), 1404 (m), 1368 (m), 1343 (m), 1258 (s), 1181 (w), 1160 (m), 1073 (s), 1039 (s), 978 (m), 950 (s), 898 (w), 882 (s), 876 (s), 831 (w), 817 (s), 784 (s), 732 (s), 700 (m), 670 (m), 649 (w), 564 (w), 514 (w), 408 (m). Anal. Calcd for $C_{21}H_{33}B_{10}NSi_2$: C, 54.42; H, 7.12. Found: C, 53.95; H, 6.84.

Compound 9 from the Reaction with Benzyl Cyanide. A mixture of 0.11 g (0.25 mmol) of **2** and 0.117 g (1 mmol) of benzyl cyanide in toluene (10 mL) was heated at reflux for 6 h. The solvent was removed in vacuo and chromatographed using hexane/benzene (4/1) as eluent. Recrystallization from hexane (10 mL) at −20 °C afforded **9** as colorless crystals in 86% yield. Mp: 103 °C. ^{1}H NMR ($CDCl_3$): δ 7.27−7.14 (m,

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5H, *Ph*), 6.53 (d, 1H, $J_{\mathrm{HH}} = 14.4$ Hz, ═C*H*), 5.82 (d, 1H, $J_{\mathrm{HH}} = 14.4$ Hz, ═C*H*), 0.48 (s, 12H, Si−C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 130.49, 128.67, 128.22, 126.10, 124.77, 124.52, 114.67, 97.21, −1.40. ^{29}Si NMR (CDCl$_3$): δ 2.4, −3.2. MS: *m*/*z* 376 [M$^+$]. IR (KBr pellet; cm^{-1}): 3031 (w), 2960 (w), 2587 (s), 1597 (w), 1592 (m), 1401 (w), 1335 (w), 1259 (m), 1227 (m), 1158 (s), 1089 (s), 987 (w), 958 (s), 930 (m), 883 (m), 848 (m), 822 (s), 788 (w), 749 (w), 695 (w), 674 (w), 647 (w), 545 (w). Anal. Calcd for $C_{14}H_{29}B_{10}NSi_2$: C, 44.79; H, 7.73. Found: C, 44.42; H, 7.52.

Compound 10 from the Reaction with Diphenylacetonitrile. Compound **10** was prepared using the same procedure as described for **9**, except diphenylacetonitrile was used intead of benzyl cyanide. Pure **10** was isolated by chromatographic workup (eluent hexane/benzene (3.5/1), $R_f = 0.48$). Yield: 65%. Mp: 106 °C. ^{1}H NMR (CDCl$_3$): δ 7.36−7.10 (m, 10H, *Ph*), 6.48 (d, 1H, $J_{\mathrm{HH}} = 2.3$ Hz, *H*C═), 4.77 (dd, 1H, $J_{\mathrm{HH}} = 2.3$ and 6.6 Hz, ═C*H*), 0.96 (d, 1H, $J_{\mathrm{HH}} = 6.6$ Hz, C*H*). 0.32 (s, 12H, Si−C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 145.60, 128.66, 127.44, 126.92, 126.04, 125.38, 29.85, −2.03. ^{29}Si NMR (CDCl$_3$): δ 8.8, −1.4. MS: *m*/*e* 452 [M$^+$]. IR (KBr pellet; cm^{-1}): 3064 (w), 3028 (w), 2974 (m), 2594 (s), 1596 (m), 1490 (s), 1454 (s), 1411 (w), 1259 (s), 1149 (s), 1076 (m), 1035 (m), 914 (m), 777 (m), 748 (s), 698 (s), 650 (m), 628 (w), 538 (m), 453 (m). Anal. Calcd for $C_{21}H_{35}B_{10}NSi_2$: C, 54.19; H, 7.52. Found: C, 53.76; H, 7.38.

Compound 11 from the Reaction with Hydrocinnamonitrile. Compound **11** was prepared using the same procedure as described for **9**. Yield: 71%. Mp: 139 °C. ^{1}H NMR (CDCl$_3$): δ 7.36−7.21 (m, 5H, *Ph*), 5.85 (d, 1H, $J_{\mathrm{HH}} = 13.8$ Hz, ═C*H*), 5.02 (dt, 1H, $J_{\mathrm{HH}} = 13.8$ Hz, $J_{\mathrm{HH}} = 6.9$ Hz, ═C*H*), 3.24 (d, 2H, $J_{\mathrm{HH}} = 6.9$ Hz, C*H*$_2$), 0.38 (s, 12H, Si−C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 138.06, 137.84, 128.86, 128.26, 127.22, 127.04, 126.84, 126.52, 31.54, 5.70, 1.03. MS: *m*/*z* 390 [M$^+$]. IR (KBr pellet; cm^{-1}): 3075 (w), 3042 (w), 2964 (s), 2948 (m), 2906 (w), 2618 (s), 2578 (s), 1952 (w), 1675 (w), 1610 (m), 1509 (w), 1462 (s), 1418 (w), 1265 (s), 1092 (m), 1078 (m), 1032 (w), 918 (m), 805 (s), 784 (w), 756 (m), 725 (s), 698 (m), 472 (m), 447 (w). Anal. Calcd for $C_{15}H_{31}B_{10}NSi_2$: C, 46.26; H, 7.96. Found: C, 45.84; H, 7.68.

Compound 12 from the Reaction with Cinnamonitrile. Compound **12** was prepared using the same procedure as described for **9**. Yield: 68%. Mp: 124 °C. ^{1}H NMR (CDCl$_3$): δ 7.44−7.19 (m, 4H, *Ph*), 5.98 (t, 1H, $J_{\mathrm{HH}} = 3.82$ Hz, ═C*H*), 3.34 (d, 2H, $J_{\mathrm{HH}} = 3.8$ Hz, C*H*$_2$), 0.29 (s, 6H, Si−C*H*$_3$), 0.27 (s, 6H, Si−C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 138.42, 129.28, 128.34, 127.51, 126.34, 125.57, 124.20, 119.21, 35.89, 1.16, −0.98. ^{29}Si NMR (CDCl$_3$): δ 11.05. MS: *m*/*e* 338 [M$^+$]. IR (KBr pellet; cm^{-1}): 3146 (w), 2997 (w), 2934 (w), 2592 (s), 2566 (s), 1976 (m), 1665 (w), 1594 (m), 1537 (w), 1455 (w), 1404 (w), 1266 (s), 1076 (w), 1055 (m), 1044 (m), 943 (w), 922 (w), 895 (m), 834 (s), 807 (m), 754 (w), 742 (w), 724 (s), 487 (w), 468 (w). Anal. Calcd for $C_{15}H_{29}B_{10}NSi_2$: C, 46.50; H, 7.49. Found: C, 46.26; H, 7.24.

Compound 13 from the Reaction with (Trimethylsilyl)acetonitrile. A mixture of (trimethylsilyl)acetonitrile (0.16 mL, 1.19 mmol), **1** (4.15 mL, 1.08 mmol), and **2** (0.03 g, 0.054 mmol) in toluene (20 mL) was heated at 60−80 °C for 12 h. The volatiles were removed in vacuo. The product was extracted with hexane (30 mL). The pure product **13** was obtained by crystallization from pentane at −20 °C in 75% yield. Mp: 134−136 °C. ^{1}H NMR (CDCl$_3$): δ 5.52 (d, 1H, $J_{\mathrm{HH}} = 2.42$ Hz, ═C*H*), 5.46 (d, 1H, $J_{\mathrm{HH}} = 2.42$ Hz, ═C*H*), 0.27 (s, 12H, Si−C*H*$_3$), 0.12 (s, 9H, Si−(C*H*$_3$)$_3$). ^{13}C NMR (CDCl$_3$): δ 129.05, 128.99, 0.45 (s, Si−*C*H$_3$), −0.95 (s, Si−(*C*H$_3$)$_3$). ^{29}Si NMR (CDCl$_3$): δ 8.6, 1.4, −4.9. MS: *m*/*e* 372 [M$^+$]. IR (KBr pellet; cm^{-1}): 3075 (w), 2960 (m), 2900 (w), 2599 (s), 2578 (s), 2080 (w), 1549 (s), 1450 (w), 1400 (w), 1260 (s), 1175 (m), 1090 (m), 1078 (m), 1006 (s), 960 (m), 905 (s), 880 (m), 805 (s), 780 (m), 750 (w), 695 (m), 680 (m), 450 (w), 430 (w). Anal. Calcd for $C_{11}H_{33}B_{10}NSi_3$: C, 35.57; H, 8.88. Found: C, 35.08; H, 8.61.

Compound 14 from the Reaction with Fumaronitrile. A mixture of fumaronitrile (0.126 g, 1.6 mmol), **1** (4.15 mL, 1.08 mmol), and **2** (0.03 g, 0.054 mmol) was heated at 60−80 °C 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 pentane at −20 °C in 75% yield. Mp: 158−162 °C. All spectral data for product **14** were identical with those of an authentic sample.[2e]

X-ray Crystallography. Details of the crystal data and a summary of intensity data collection parameters for **8** and **12** are given in Table 1. Crystals of **8** and **12** were grown from hexane at −20 °C, mounted in thin-walled glass capillaries, and sealed under argon. The data sets of **8** and **12** were collected on a Siemens P4 diffractometer equipped with a Mo X-ray tube and a graphite crystal monochromator. Mo Kα radiation ($\lambda = 0.7107$ Å) was used for all structures. Each structure was solved by the application of direct methods using the SHELX-96 program. All non-hydrogen atoms in compounds **8** and **12** were refined anisotropically. All other hydrogen atoms were included in calculated positions.

Acknowledgment. We wish to acknowledge the financial support of the Korean Research Foundation made in the program year of 2000 (2000-015-DP0296).

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** and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0008629