Synthesis and Reactivity of Silylboranes

John D. Buynak* and Bolin Geng

Department of Chemistry, Southern Methodist University, Dallas, Texas 75275

Received January 31, 1995[⊗]

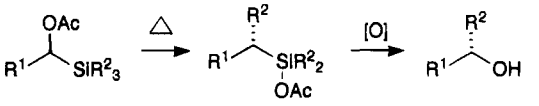
Summary: Several representative silylboranes, including B-(phenyldimethylsilyl)catecholborane (7), were prepared and their reactivity explored. The reaction of silylboranes with either vinyllithium or lithium acetylide generated the corresponding silylborates which rearrange upon treatment with I_2, producing the vinylsilane and silyl acetylide, respectively. The reaction of 7 with ethyl diazoacetate yielded ethyl (phenyldimethylsilyl)acetate upon hydrolysis.

Introduction

The first silylboranes were synthesized in 1960.[1] The preparation of compounds containing an Si–B bond has been briefly summarized.[2] Despite the relatively long history of silylboranes, few systematic studies of their reactivity are available. The most extensive studies were performed by Nöth, who prepared B–Si compounds which contain an (electronically shielding) B–N bond and described some of their chemistry.[3]

Silyl(mono)boranes are most commonly prepared by reaction of silyl anions with boron halides. However, the reaction is severely limited due to the ease with which the resultant silylboranes add an additional equivalent of the silicon nucleophile to form the corresponding anionic tetracoordinated borate. Strategies for overcoming this side reaction involve either sterically or electronically shielding the boron toward further reactivity. Very recently, a transition-metal-mediated instance of B–Si bond formation has been reported[4] as has the formation of a Bi–Si bond by the reaction of a phosphorus-complexed (and, therefore, electronically shielded) boryl anion with a silyl halide.[5]

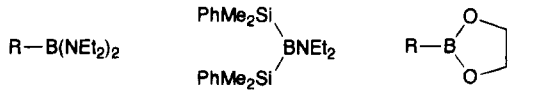
We recently reported studies on the thermal rearrangements of α-acyloxysilanes and the synthetic utility of such rearrangements in the preparation of chiral compounds.[6] Our ongoing research on the preparation and reactions of chiral organosilicon compounds[7] involved us in a search for new methods for the formation of the carbon–silicon bond. In our previous studies, C–Si bonds were usually formed by (a) reactions of carbanions with silyl halides or (b) reaction of silyl anions with organohalides. This methodology is inconvenient since both carbanions and silyl anions are relatively intolerant of other intramolecular functionality. Also, many silylmetallics can be difficult to prepare in high yield and deteriorate upon prolonged storage. Our experience with organoboron compounds led us to wonder if compounds with direct bonds between boron and silicon would react with typical organic functionality (such as C=O or C=C) leading to the formation of new carbon–silicon bonds. We thus decided to explore the potential of silylboranes as silyl-transfer reagents.



Results and Discussion

Synthesis. Our initial investigation into the preparation of silylboranes began with an attempt to react phenyldimethylsilyllithium with (+)-*B*-chlorodiisopinocampheylborane[8] (DIP chloride). While a reaction appeared to occur, the resultant solution, when reacted with benzaldehyde, produced only benzyl alcohol. Presumably this occurred from hydride transfer from the pinene ligand (analogous to the reaction of DIP–Cl itself with carbonyl compounds). The reaction mixture failed, however, to reduce acetophenone. Analysis of the crude reaction by ^{11}B NMR indicated the formation of a new compound with chemical shift of $\delta = 1.2$ ppm, more appropriate for a borate than the desired borane.

We then decided to employ the more established methods of Nöth in the preparation of these compounds. The reaction of $PhMe_2SiLi$ with $(Et_2N)_2BCl$[9] in cyclohexane afforded silylborane **1** in good yield. Similarly, silyl borane **2** was obtained when Et_3SiLi[10] was used. If Cl_2BNEt_2 was reacted with 2 equiv of $PhMe_2SiLi$, the bis(phenyldimethylsilyl)borane **3** was obtained. As observed by Nöth, compounds **1** and **2** are easily derivatized to compounds **4** and **5**, respectively, by reaction with ethylene glycol in CH_2Cl_2.



1 R = $PhMe_2Si$
2 R = Et_3Si
3
4 R = $PhMe_2Si$
5 R = Et_3Si

The catechol derivatives of borane itself are known to have enhanced (hydroborating) reactivity relative to the analogous ethylene glycol derivatives.[11] We thus

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1995.

(1) (a) Seyferth, D.; Kogler, H. P. *J. Inorg. Nucl. Chem.* **1960**, *15*, 99. (b) Cowley, A. H.; Sisler, H. H.; Ryschkewitach, G. E. *J. Am. Chem. Soc.* **1960**, *82*, 501.

(2) Molloy, K. C. In *Inorganic Reactions and Methods*; Zuckerman, J. J., Hagan, A. P., Eds.; VCH Publishers, Inc.: 1989; Vol. 10, Section 5.3.7, pp 209–213.

(3) Biffar, W.; Nöth, H.; Schwerthoffer, R. *Liebigs Ann. Chem.* **1981**, 2067–2080.

(4) Jiang, Q.; Carroll, P. J.; Berry, D. H. *Organometallics* **1993**, *12*, 177.

(5) Blumenthal, A.; Bissinger, P.; Schmidaur, H. *J. Organomet. Chem.* **1993**, *462*, 107.

(6) Buynak, J. D.; Strickland, J. B.; Lamb, G. W.; Khasnis, D.; Modi, S.; Williams, D.; Zhang, H. *J. Org. Chem.* **1991**, *56*, 7076–7083.

(7) Buynak, J. D.; Geng, B.; Uang, S.; Strickland, J. B. *Tetrahedron Lett.* **1994**, *35*, 985–988.

(8) Chandrasekharan, J.; Ramachandran, P. V.; Brown, H. C. *J. Org. Chem.* **1985**, *50*, 5448.

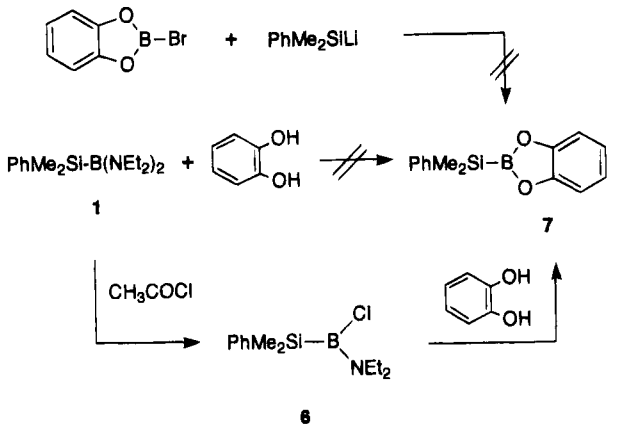
(9) Chavant, P. Y.; Vautier, M. *J. Organomet. Chem.* **1993**, *455*, 37.

(10) Vyazankin. N. S.; Razuvaev, G. A.; Gladyshev, E. N.; Korneva, S. P. *J. Organomet. Chem.* **1967**, *7*, 353.

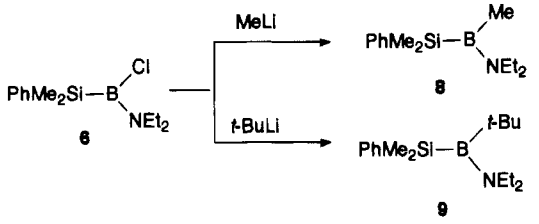
(11) (a) Brown, H. C. *Organic Synthesis via Boranes*; John Wiley and Sons: New York, 1975; p 44. (b) Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1971**, *93*, 1816.

0276-7333/95/2314-3112$09.00/0

Scheme 1



Scheme 2



decided to prepare the previously unknown catecholborosilane, **7**, and to explore its chemistry. The direct synthesis of silylcatecholborane **7** using phenyldimethylsilyllithium with *B*-bromocatecholborane was not successful, once again probably due to the formation of tetracoordinated borates. Attempted direct reaction of either **1** or **2** with catechol (under a variety of conditions) also did not produce catecholborane **7** (or its triethylsilyl analog). While searching for conditions to remove the organoamine from borane, it was discovered that reaction of **1** with acetyl chloride cleanly produces chloroborane **6**. Compound **6** was found to react with catechol to generate catecholborane **7** (see Scheme 1).

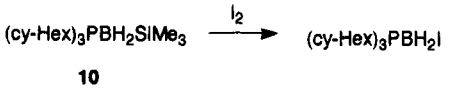
As shown in Scheme 2, compound **6** could be used to produce other *B*-silyl-*B*-(diethylamino)boranes by nucleophilic displacement of the chlorine. Unfortunately all attempts to remove the last diethylamine group from either **6**, **8**, or **9** failed.

We reasoned that the preparation of new members of this class of compounds would be made easier if we could generate a silylboron hydride, such as R_3SiBH_2, which could be used as a hydroborating agent. Attempts to prepare a silylboron hydride by ligand exchange of **1**, **3**, or **4** with borane dimethyl sulfide complex or direct reduction of these compounds with lithium aluminum hydride did not succeed. The major isolable product from such reactions was dimethylphenylsilane. No B–O or B–N bond reduced products were observed.

A recent report[12] of the preparation of tricyclohexylphosphine-complexed (trimethylsilyl)boron hydride **10** led us to prepare this compound and explore the potential for liberating the uncomplexed silylborane, Me_3SiBH_2. As described in the literature, the complexed silylborane is extremely stable, allowing its purification by column chromatography on silica gel.

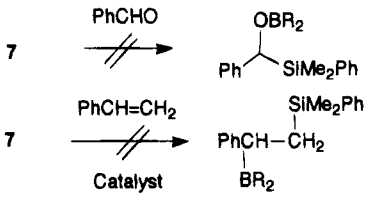
(12) Blumenthal, A.; Bissinger, P.; Schmidbaur, H. *J. Organomet. Chem.* **1993**, *462*, 107.

Scheme 3



Bestmann[13] has reported the removal of a boron-complexed triphenylphosphine by reaction with methyl iodide. However, no reaction occurred on treatment of **10** with either methyl iodide or methyl tosylate. In an attempt to thermally liberate Me_3SiBH_2, **10** was heated (under vacuum) with an external flame while trapping all volatiles. Instead of liberating the free silylborane, only trimethylsilane (Me_3SiH) was isolated. The Si–B bond was cleaved by iodine (Scheme 3), but **10** was inert toward reaction with nucleophiles such as tetrabutylammonium fluoride, vinyllithium, and triethylamine as well as toward electrophilic organic functionalities, such as aldehydes.

Reactivity. We had initially hoped that silylboranes would have enhanced reactivity (relative to alkylboranes, for example) leading to facile transfer of silicon to organic molecules. We had in particular hoped that such compounds would react with aldehydes and ketones (as shown below)



leading to (after hydrolysis) secondary and tertiary α-hydroxysilanes. Unfortunately, both compounds **4** and **7** were inert in the presence of aldehydes and ketones, even at elevated temperatures. Secondly, we had hopes that catecholsilylborane **7** would undergo borosilylation of double bonds, either by itself or in the presence of catalysts. Once again, we were impressed by the inert nature of this compound in the presence of alkenes and alkynes, even in the presence of catalysts such as Wilkinson's catalyst.

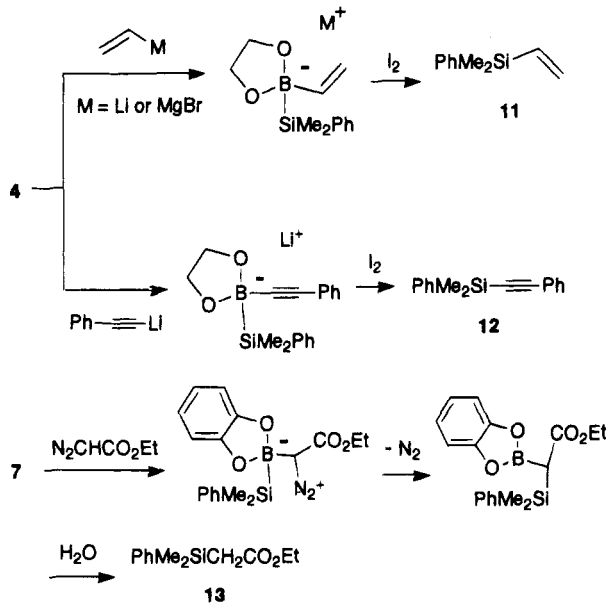
Many extremely useful transformations of boron-carbon bonds involve rearrangements of deliberately formed four-coordinate anionic organoborates.[14] In a suitable substituted organoborate, a 1,2-intramolecular migration can be induced by the presence or generation of an electron-deficient center α to the boron. As a further extension of the analogy between B–Si and B–C, we desired to know if a similar transformation (with migration of silicon) was possible for silylborates.

As shown below, the silylborane **4** was treated with either vinyllithium or vinylmagnesium bromide to form the corresponding silyl borate. This borate was then reacted with iodine to form dimethylphenylvinylsilane, **11**. Similarly, the reaction of **4** with lithium phenylacetylide, and subsequent treatment with iodine, produced dimethylphenylsilylphenylacetylide **12**. Silylborane **7** reacted with ethyl diazoacetate yielding silyl substituted acetate **13** (Scheme 4). The intermediate borate formed by the reaction of **4** and lithium phenyl-

(13) Bestmann, H. J.; Roder, T.; Suhs, K. *Chem. Ber.* **1988**, *121*, 1509.

(14) Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*; Academic Press: New York, 1988.

Scheme 4



acetylide did not react with other electrophiles such as MeI, Me_3SiCl, Me_3SnCl, Bu_3SnCl, CH_3COCl, $(MeO)_2SO_2$, PhSeCl, and MeOTf.

Conclusion

The chemistry of the Si–B bond of silylboranes and silylborates is most closely analogous to the chemistry of the C–B bond of organoboranes. No (silylboration) process analogous to hydroboration (of either alkenes or carbonyls) was discovered. Like the alkyl groups of organoborates, the silicon of silylborates can migrate to an adjacent electron-deficient center.

Experimental Section

General Procedures. All reactions were performed under an atmosphere of argon using standard vacuum line techniques. ^1H, ^{13}C, and ^{11}B NMR spectra were obtained on a Bruker WP200SY spectrometer. Mass spectral data were obtained by the EI technique from Midwest Center for Mass Spectrometry at the University of Nebraska–Lincoln. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, NY. TLC was performed on Merck 0.2-mm Kieselgel 60 F254 silica-coated plates. The compounds were identified in one of the following manners: UV (254 nm) and phosphomolybdic acid spray reagent. Flash chromatography was performed in thick-walled glass columns using Merck 0.040–0.063-mm Kieselgel 60 silica gel. The glassware used in the reactions described below was oven- or flame-dried and was cooled under argon. The chromatography solvents were distilled from CaH_2 before use. All additional solvents were obtained from Aldrich in Sure-Seal bottles. Anhydrous reagents were used as received from Aldrich unless otherwise noted.

$PhMe_2SiB(NEt_2)_2$ (1). To a solution of bis(diethylamino)-boron chloride[15] (17.6 g, 92 mmol) in 100 mL of cyclohexane was added a solution of phenyldimethylsilyllithium in THF (0.8 M, 115 mL) at 0 °C via cannula (leaving behind most excess lithium). After addition, the brown reaction mixture was stirred overnight at room temperature. The precipitate was filtered under argon, and the yellow solution was concentrated *in vacuo*. Vacuum distillation of the residue produced 24.5 g (92%) of **1** as a slightly yellow liquid: bp 105–110 °C/0.2 mm Hg. ^1H NMR ($CDCl_3$): δ 0.33 (s, 6H), 0.99 (t, J = 7.0 Hz, 12 H), 3.01 (q, J = 7.0 Hz, 8 H), 7.4–7.7 (m, 5 H). ^{13}C NMR (C_6D_6): δ 1.40 (q), 16.93 (q), 43.17 (t), 135.78, 132.71, 129.62, 126.48. ^{11}B NMR (C_6D_6): δ 36.5. Anal. Calcd for $C_{16}H_{31}BN_2Si$: C, 66.20; H, 10.76; N, 9.65. Found: C, 66.25; H, 10.58; N, 9.47.

$Et_3SiB(NEt_2)_2$ (2). This compound was prepared as described for **1** using triethylsilyllithium[16] (84%): bp 89–92 °C/0.2 mm Hg. ^1H NMR (C_6D_6): δ 0.81 (q, J = 7.9 Hz, 6 H), 1.01 (t, J = 7.9 Hz, 12 H), 1.16 (t, J = 7.9 Hz, 9 H), 3.03 (q, J = 7.9 Hz, 8 H). ^{13}C NMR ($CDCl_3$): δ 5.71, 8.66, 15.62, 42.30. ^{11}B NMR ($CDCl_3$): δ 36.7. Anal. Calcd for $C_{14}H_{35}BN_2Si$: C, 62.21; H, 13.04; N, 10.36. Found: C, 62.11; H, 12.91; N, 10.06.

$(PhMe_2Si)_2BNEt_2$ (3). This compound was prepared as described for **1** using 2 equiv of phenyldimethylsilyllithium and (diethylamino)boron dichloride (22%).[17] ^1H NMR (C_6D_6): δ 0.45 (s, 12 H), 0.85 (t, J = 7.0 Hz, 6 H), 3.20 (q, J = 7.0 Hz, 4 H), 7.2–7.8 (m, 10 H). ^{13}C NMR (C_6D_6): δ 0.32, 16.86, 50.35, 128.27, 133.32, 134.33, 143.17. ^{11}B NMR (C_6D_6): δ 55.7.

$PhMe_2SiB(OCH_2-)_2$ (4): To a solution of **1** (8.74 g, 30.1 mmol) in 50 mL of CH_2Cl_2 was added ethylene glycol (1.87 g, 30.1 mmol) slowly by syringe at room temperature. After addition, the slightly yellow solution was stirred for 1 h. Concentration and distillation gave 4.3 g of **4** (69%): bp 95–100 °C/0.5 mm Hg. ^1H NMR (C_6D_6): δ 0.48 (s, 6 H), 3.53 (s, 4 H), 7.2–7.9 (m, 5 H). ^{11}B NMR (C_6D_6): δ 34.3. HRMS. Calcd for $C_9H_{12}BO_2Si$ (M – CH_3) 191.0700, found 191.0703.

$Et_3SiB(OCH_2-)_2$ (5). This compound was prepared as described for **4** using **2** (47%). ^1H NMR (C_6D_6): δ 0.80 (q, J = 7.8 Hz, 6 H), 1.15 (t, J = 7.8 Hz, 9 H), 3.65 (s, 4 H). ^{11}B NMR (C_6D_6): δ 34.5.

$PhMe_2SiBCl(NEt_2)$ (6). To a solution of **1** (15.1 g, 52 mmol) in 60 mL of diethyl ether was added acetyl chloride (5.2 g, 67 mmol) at 0 °C. After addition, the clear solution was stirred for 30 min at room temperature. Concentration and vacuum distillation produced 11.4 g of **6** (86%): bp 108–110 °C/1.0 mm Hg. ^1H NMR (C_6D_6): δ 0.55 (d, J = 0.5 Hz, 6 H), 0.75 (t, J = 7.0 Hz, 3 H), 0.97 (t, J = 7.0 Hz, 3 H), 2.90 (q, J = 7.0 Hz, 2 H), 3.15 (q, J = 7.0 Hz, 2 H), 7.2–7.5 (m, 5 H). ^{13}C NMR (C_6D_6): δ –1.8, 15.2, 15.9, 43.0, 46.0, 128.1, 128.8, 134.2, 140.0. ^{11}B NMR (C_6D_6): δ 40.7. Anal. Calcd for $C_{12}H_{21}BClNSi$: C, 56.83; H, 8.34; N, 5.52. Found: C, 56.70; H, 8.29; N, 5.71.

$PhMe_2SiBMe(NEt_2)$ (8). To a solution of **6** (3.3 g, 13.0 mmol) in 20 mL of diethyl ether was added methylmagnesium chloride (3 M, 6.5 mL, 19.5 mmol) at room temperature. After 24 h of stirring, the suspension was centrifuged (3000 RPM). Concentration and distillation of the supernatant gave **8** (1.7 g, 58%) as a colorless oil: bp 95 °C/1.0 mm Hg. ^1H NMR (C_6D_6): δ 0.46 (s, 6 H), 0.64 (s, 3 H), 0.85 (t, J = 7.0 Hz, 3 H) 0.90 (t, J = 7.0 Hz, 3 H), 2.9 (q, J = 7.0 Hz, 2 H), 3.1 (q, J = 7.0 Hz, 2 H), 7.2–7.8 (m, 5 H). ^{13}C NMR ($CDCl_3$): δ –1.33, 15.96, 16.51, 42.68, 48.36, 127.54, 133.05, 133.94, 142.78. ^{11}B NMR (C_6D_6): δ 49.1. Anal. Calcd for $C_{13}H_{24}BNSi$: C, 66.95; H, 10.37; N, 6.01. Found: C, 66.84; H, 10.24; N, 5.83.

$PhMe_2SiB(NEt_2)$-*t*-Bu (9). To an ice-cooled solution of **6** (2.1 g, 8.3 mmol) in 10 mL of cyclohexane was added *tert*-butyllithium (1.7 M, 6.0 mL, 10.2 mmol). After 24 h of stirring at room temperature, the suspension was centrifuged (3000 RPM). Concentration and distillation of the supernatant gave **9** (1.53 g, 67%) as a colorless oil: bp 125 °C/0.9 mm Hg. ^1H NMR (C_6D_6): δ 0.55 (s, 6 H), 0.76 (t, J = 7.0 Hz, 3 H), 0.95 (t, J = 7.0 Hz, 3 H), 1.25 (s, 9 H), 3.1 (m, 4 H), 7.1–7.7 (m, 5 H); ^{13}C NMR (C_6D_6): δ 2.89, 16.27, 30.48, 42.93, 48.45, 126.91, 128.23, 133.98, 144.80. ^{11}B NMR (C_6D_6): δ 50.0. Anal. Calcd for $C_{16}H_{30}BNSi$: C, 69.80; H, 10.98; N, 5.09. Found: C, 69.80; H, 10.93; N, 4.89.

(15) Nöth, H. In *Progress in Boron Chemistry*; Pergamon Press: Oxford, U.K., 1970; Vol. 3, p 281.

(16) Vyazankin. N. S.; Razuvaev, G. A.; Gladyshev, E. N.; Korneva, S. P. *J. Organomet. Chem.* **1967**, *7*, 353.

(17) Bestmann, H. J.; Roder, T.; Suhs, K. *Chem. Ber.* **1988**, *121*, 1509.

***B*-(Phenyldimethylsilyl)catecholborane (7).** To a solution of **1** (7.32 g, 25.2 mmol) in 45 mL of cyclohexane was added dropwise acetyl chloride (1.98 g, 25.2 mmol) slowly at room temperature. After 20 min of stirring, the cloudy solution became clear (slightly yellow). NMR showed the silylborane chloride **6** was formed quantitatively after 1 h. Solid catechol (2.77 g, 25.2 mmol) was added under stream of argon, and then the reaction was stirred for 3 h at room temperature. The reaction mixture was transferred to a large, dry, septum-capped test tube and centrifuged at 3000 RPM for 5 min to separate the diethylamine · HCl salt. The supernatant was transferred to a flask. After concentration and distillation, 4.4 g of **7** was obtained as an oil (69%): bp 115–120 °C/0.4 mm Hg. ^{1}H NMR (C_6D_6): δ 0.50 (s, 6 H), 6.8–7.8 (m, 9 H). ^{11}B NMR (C_6D_6): δ 34.4. Anal. Calcd for $C_{14}H_{15}BO_2Si$: C, 66.16; H, 5.95. Found: C, 66.07; H, 6.04.

Reaction of 4 with Vinylmagnesium Bromide. To a solution of **4** (1.0 g, 4.85 mmol) in 5 mL of THF at 0 °C was added dropwise vinylmagnesium bromide (6.0 mL, 1 M, 6.0 mmol). After 15 h of stirring at room temperature, a solution of I_2 (2.46 g, 9.7 mmol) in 5 mL of THF was added and then stirred for 6 h. The crude reaction mixture was diluted into 50 mL of pentane and washed with saturated $Na_2S_2O_3$ (2 × 20 mL) and water (3 × 30 mL). The combined organic layers were dried (Na_2SO_4) and concentrated. The colorless oil was purified by flash chromatography using pentane as eluant (R_f = 0.8). A 250 mg amount of colorless volatile oil **11**[18] was obtained (33%). ^{1}H NMR (C_6D_6): δ 0.31 (s, 6 H), 5.6–6.4 (ABX, 12 lines, 3 H), 7.2–7.7 (m, 5 H). ^{13}C NMR ($CDCl_3$): δ −2.87, 127.76, 128.99, 132.79, 133.82, 137.96, 138.38. IR (CCl_4): 1595, 1547, 1248, 1111, 1090 cm^{-1}. The ^{1}H NMR, ^{13}C NMR, and IR were identical with material we independently prepared by the direct addition of vinylmagnesium bromide to phenyldimethylchlorosilane. This reaction could also be performed by using silylborane **4** and vinyllithium.

Reaction of 4 with Lithium Phenylacetylide. To a solution of **4** (1.0 g, 4.85 mmol) in 10 mL of THF was added dropwise lithium phenylacetylide (4.85 mL, 1 M in THF, 4.85 mmol) at 0 °C. After 2.5 h of stirring, the reaction was treated with a solution of I_2 (1.23 g, 4.85 mmol) in 5 mL of THF. The stirring was continued for 1 h, and then the reaction mixture was diluted with 50 mL of diethyl ether and washed with saturated $NaHSO_3$ solution (2 × 30 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Preparative TLC using pure hexane as eluent (R_f = 0.6) produced 720 mg (63%) of dimethylphenylsilyl phenyl acetylene **12**.[19] ^{1}H NMR (C_6D_6): δ 0.52 (s, 6 H), 6.8–7.9 (m, 10 H). ^{13}C NMR ($CDCl_3$): δ −0.78, 91.98, 106.88, 122.93, 127.88, 128.14, 128.61, 129.38, 131.94, 133.65, 136.85. IR (liquid film) 2156.4, 1589.7, 1483.9, 1425.8, 1250.5, 1108.8 cm^{-1}. The ^{1}H NMR, ^{13}C NMR, and IR are identical with that of dimethylphenylsilyl phenyl acetylene prepared by the direct addition of lithium phenylacetylide to phenyldimethylchlorosilane.

Reaction of 7 with Ethyl Diazoacetate. To a solution of **7** (117 mg, 0.46 mmol) in 11 mL of THF was added dropwise ethyl diazoacetate (48 μL, 0.46 mmol) at 0 °C. After 3 h of stirring, 5 mL of water was added and the reaction was stirred for 30 min. Then the product was extracted with pentane. The organic layer was dried (Na_2SO_4) and concentrated *in vacuo*. After preparative TLC separation using ether–hexane (9:1) as eluent, 61 mg (60%) of ethyl dimethylphenylsilylacetate,[20] **13**, was obtained. ^{1}H NMR (C_6D_6): δ 0.33 (s, 6 H), 0.93 (t, J = 7.6 Hz, 3 H), 2.03 (s, 2 H), 3.96 (q, J = 7.6 Hz, 2 H), 7.1–7.6 (m, 5 H). ^{13}C NMR ($CDCl_3$): δ −2.78, 14.34, 26.29, 59.93, 127.84, 129.42, 133.48, 136.93, 172.49.

Acknowledgment. We thank the Robert A. Welch Foundation for the support of this work. We are also indebted to the Chemistry Department of Southern Methodist University for providing use of the high-field NMR and on-line literature searching.

OM950079U

(18) Fleming, I.; Newton, T. W.; Roessler, F. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2527.

(19) Jun, C. H.; Crabtree, R. H. *J. Organomet. Chem.* **1993**, *447*, 177.

(20) Danilkina, L. P.; Dorokhova, O. V.; Slobodin, Ya. M. *Zh. Obshch. Khim.* **1975**, *45*, 2677; *Russ. J. Gen. Chem. (Engl. Transl.)* **1975**, 2640.