Synthesis of 1-Substituted 1,2-Bis(trimethylsilyl)ethenes via Hydroboration of 1,2-Bis(trimethylsilyl)ethyne with Dialkylborane

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The reaction of 1,2-bis(trimethylsilyl)ethyne with a stoichiometric amount of dialkylborane proceeds to the monohydroboration stage, giving [(*Z*)-1,2-bis(trimethylsilyl)ethenyl]dialkylborane. In situ treatment of the above alkenylborane with iodine in the presence of aqueous sodium hydroxide provides highly pure (*E*)-1-alkyl-1,2-bis(trimethylsilyl)ethene whose alkyl group migrates from the boron atom. Successive treatment of [(*Z*)-1,2-bis(trimethylsilyl)ethenyl]dicyclohexylborane with copper(I) iodide, allyl bromide, and aqueous sodium hydroxide affords a cross-coupling product, (*Z*)-1,2-bis(trimethylsilyl)-1,4-pentadiene, stereoselectively. A similar cross-coupling reaction with 1-bromo-1-hexyne followed by UV irradiation affords (*E*)-1,2-bis(trimethylsilyl)-1-octen-3-yne stereoselectively.

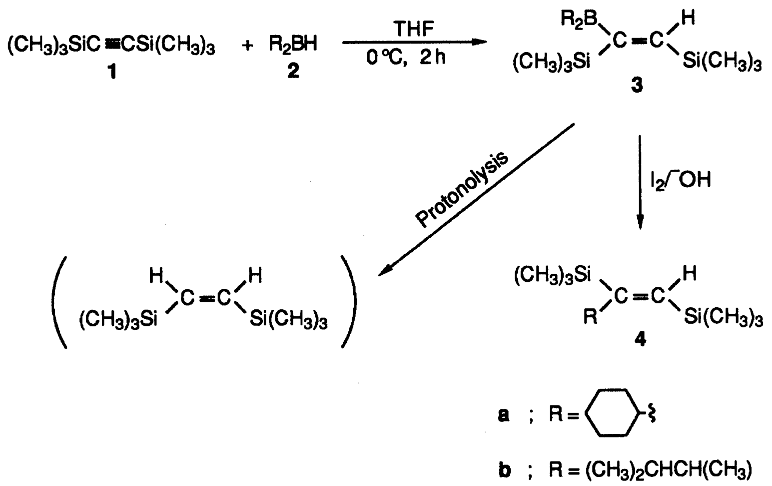
(1-Trimethylsilyl-1-alkenyl)dialkylborane[1)] and (2-trimethylsilyl-1-alkenyl)dialkylborane[2)] have been shown to be interesting intermediates for the regio- and stereoselective synthesis of substituted vinylsilanes which can be converted into a wide variety of organic compounds by reactions with electrophiles.[3)] In the course of our study on functionally substituted organoboranes[4)] we became interested in the hydroboration of 1,2-bis(trimethylsilyl)ethyne (**1**) with dialkylborane (**2**). The hydroboration is expected to give [(*Z*)-1,2-bis(trimethylsilyl)ethenyl]dialkylborane (**3**) which has both a [1-(trimethylsilyl)ethenyl]borane moiety and a [2-(trimethylsilyl)ethenyl]borane moiety in its molecule. Accordingly, the conversion of the carbon-boron bond of **3** into a carbon–carbon bond is expected to provide 1-substituted 1,2-bis(trimethylsilyl)ethene, a potential intermediate for trimethylsilylated compounds having a methoxymethyl, a formyl or an acetyl group.[5)] We now report stereoselective syntheses of three types of 1,2-bis(trimethylsilyl)ethene derivatives, (*E*)-1-alkyl-1,2-bis(trimethylsilyl)ethenes (**4**), (*Z*)-1,2-bis(trimethylsilyl)-1,4-pentadiene (**6**), and (*E*)-1,2-bis(trimethylsilyl)-1-octen-3-yne (**8**), from **1** via hydroboration followed by carbon–carbon bond formation reactions.

Results and Discussion

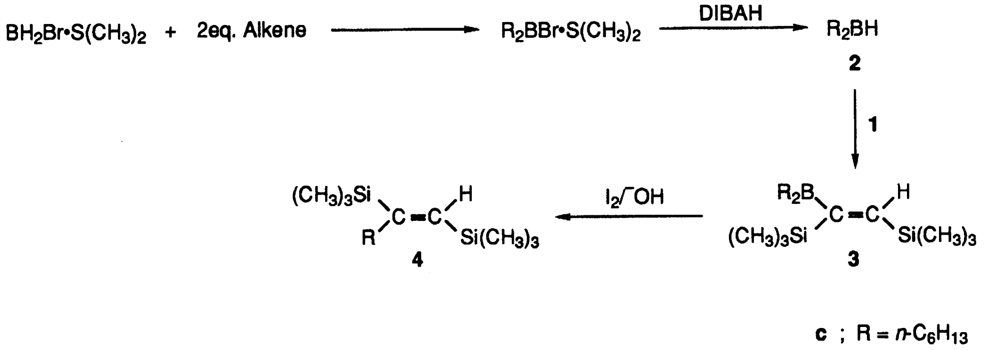
The hydroboration of **1** with an equimolar quantity of dicyclohexylborane (**2a**), prepared by the reaction of BH_3 in tetrahydrofuran (THF) with two equivalents of cyclohexene, was carried out at 0°C. After 2 h of the reaction neither residual **1** nor residual hydride of **2a** was detected by GLC or by hydrolysis of the reaction mixture, respectively. This fact indicated that the hydroboration had proceeded to the monohydroboration stage (Scheme 1). To clarify the stereochemistry of the hydroboration, the hydroboration mixture was treated with acetic acid which could convert the carbon–boron bond of alkenylborane into a carbon–hydrogen bond with retention of configuration.[6)] However, unfortunately, the protonolysis failed to give 1,2-bis(trimethylsilyl)ethene as a stable reaction product. A basic hydrolysis,[7)] which could achieve the same conversion, also failed to give the stable product. Similar results were obtained when bis(1,2-dimethylpropyl)borane (**2b**), derived from 2-methyl-2-butene, was employed as the hydroborating agent.

Accordingly, we examined the stereochemistry of the hydroboration indirectly employing stereospecific reactions characteristic of alkenylboranes. Zweifel's transfer reaction,[8)] where one of the two alkyl groups of alkenyldialkylborane was transferred from the dialkylboryl group to the α-alkenyl carbon atom with inversion of configuration, was applied to the hydroboration product. Thus, the hydroboration mixture obtained by the reaction of **1** with **2a** was treated with iodine in the presence of aqueous sodium hydroxide. After work-up (*E*)-1,2-bis(trimethylsilyl)-1-cyclohexylethene (**4a**) was isolated in 76% yield based on **1** and in >99% isomeric purity by column chromatography on basic aluminium oxide. Similarly, highly pure (*E*)-1,2-bis(trimethylsilyl)-3,4-dimethyl-1-pentene (**4b**) was obtained in 78% yield when **2b** was employed as the hydroborating agent. *E*-Configuration of both products was assigned by comparing their ^{1}H NMR spectra with those of (*Z*)-1,2-bis(trimethylsilyl)-1-alkene[9)] whose alkenyl proton appeared at lower field (δ=5.93 for **4a** and δ=5.95 for **4b**; δ=ca. 6.2 for *Z*-isomers[9b,9c)]). These results support the formation of **3** in the hydroboration of **1**. Further, they suggest that this transfer reaction of **3** provides a highly stereoselective method for the synthesis of (*E*)-1-alkyl-1,2-bis(trimethylsilyl)ethene (Scheme 1).

Several methods have been reported on the synthesis of 1-substituted 1,2-bis(trimethylsilyl)ethenes.[9,10)] However, there has been no stereoselective synthesis of (*E*)-1-alkyl-1,2-bis(trimethylsilyl)ethene except for the work of Hudrlik et al. who reported that hydrosilylation of 1-trimethylsilyl-1-octyne gave (*E*)-1,2-bis(trimethylsilyl)-1-octene (96%) accompanied by 1,1-bis(trimethylsilyl)-1-octene (4%).[10a)] Accordingly, the highly regio- and stereoselective formation of **4a** and **4b** led us to examine the present reaction further employing sterically



Scheme 1.

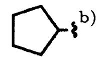
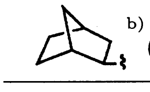


Scheme 2.

unhindered alkenes.

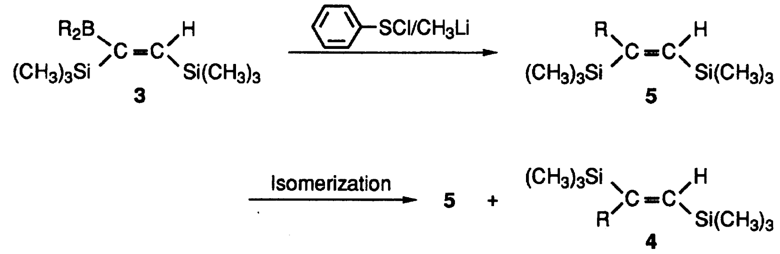
Since hydroboration of terminal or sterically unhindered internal alkenes with BH_3 (2 : 1) fails to give dialkylborane cleanly, a modified hydroboration procedure was employed. Thus, such an alkene was hydroborated with monobromoborane-dimethyl sulfide $[BH_2Br \cdot S(CH_3)_2]$[11] and the resulting dialkylbromoborane was treated with an equimolar quantity of diisobutylaluminium hydride (DIBAH) (Scheme 2). A stoichiometric hydroboration of **1** with dihexylborane (**2c**), thus obtained from 1-hexene as above, was carried out in a mixture of diethyl ether and hexanes at 0°C for 3 h and at room temperature for 2h. The hydroboration mixture was treated in a similar manner as above transfer reaction to provide isomerically pure (99%) (*E*)-1, 2-bis(trimethylsilyl)-1-octene (**4c**) in 61% yield based on **1**. The spectral datum agreed closely with that reported in the literature.[9c] Similar results were obtained when other dialkylboranes, derived from sterically unhindered alkene, were employed as the hydroborating agent. These results are shown in Table 1. The highly stereoselective manner in all cases examined demonstrated that the present reaction provided a general synthetic method for (*E*)-1-alkyl-1,2-bis(trimethylsilyl)-ethenes (**4**).

Table 1. Synthesis of (*E*)-1-Alkyl-1,2-bis(trimethylsilyl)ethenes (**4**) by Successive Reaction of 1,2-Bis-(trimethylsilyl)ethyne (**1**) with Dialkylborane (**2**), Aqueous Sodium Hydroxide, and Iodine

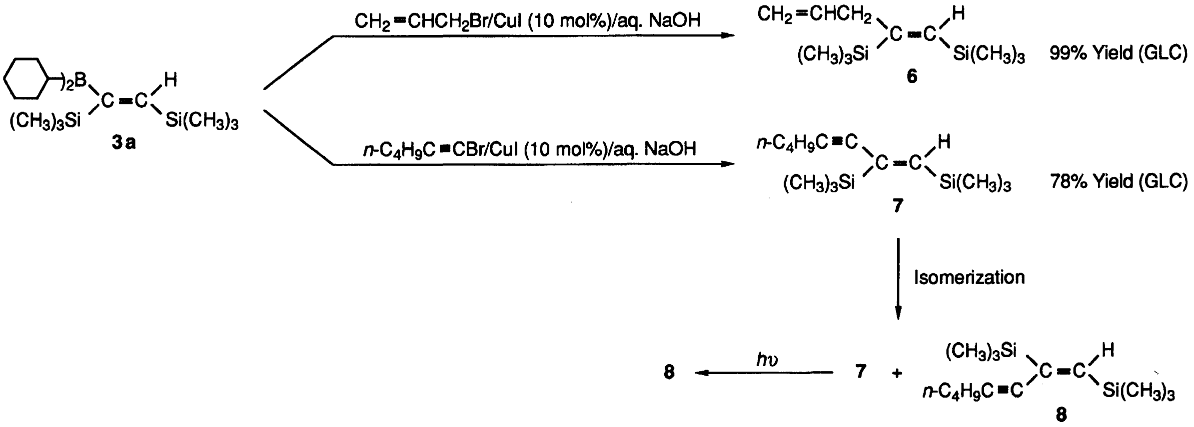
R of R_2BH (**2**)		Yield of **4**/%[a)]	Isomeric purity
	a	76	>99
$(CH_3)_2CHCH(CH_3)$	b	78	>99
n-C_6H_{13}[b)]	c	61	99
n-$C_3H_7CH(CH_3)CH_2$[b)]	d	71	>99
 $-CH(CH_3)CH_2$[b)]	e	62	≒100
	f	71	≒100
 (*exo*-)	g	60	>99

a) Isolated yields and based on **1** employed. b) Prepared by hydridation of R_2BBr with DIBAH.

Then our attention was put on to the synthesis of the *Z*-isomer of **4** by using a method for the migration of the alkyl group of 1-alkenyldialkylborane onto the α-alkenyl carbon atom with retention of configuration.[12] Thus, [(*Z*)-1,2-bis(trimethylsilyl)ethenyl]dicyclohexylborane (**3a**) was treated successively with equimolar



Scheme 3.



Scheme 4.

quantities of methyllithium and benzenesulfenyl chloride.

GLC and GC-MS analyses of the reaction mixture demonstrated that isomerically almost pure (*Z*)-1,2-bis(trimethylsilyl)-1-cyclohexylethene (**5a**) was formed in 92% yield (Scheme 3). Although **5a** was stable in the reaction mixture, it isomerized to **4a** during column chromatography (using either an acidic or a neutral aluminium oxide column), giving a mixture of **4a** and **5a** (ca 1:1) (Scheme 3). Similar results were obtained when other dialkylboranes were employed as the hydroborating agent. Although this procedure seemed to provide a method for the preparation of (*Z*)-1-alkyl-1,2-bis(trimethylsilyl)ethene (**5**),[13] an application of this compound to an intermediate has to be made in situ without isolation procedure.

By the way, we have reported that a cross-coupling reaction of [(*Z*)-1-trimethylsilyl-1-alkenyl]dicyclohexylborane with allyl bromide or 1-bromo-1-alkyne in the presence of aqueous sodium hydroxide and 10 mol% of copper(I) iodide proceeded with retention of configuration to provide the corresponding [(*Z*)-1-allyl- or (*Z*)-1-alkynyl-1-alkenyl]trimethylsilanes.[14] Examinations of this intermolecular introduction of an allyl or an alkynyl group gave interesting results. Thus, the cross-coupling reaction of **3a** with an equimolar amount of allyl bromide, carried out in a similar manner to the previous work,[14] provided (*Z*)-1,2-bis(trimethylsilyl)-1,4-pentadiene (**6**) in 99% yield based on **1** with a high isomeric purity (>99%) (estimated by GLC) (Scheme 4). Although isolation of **6** by column chromatography failed, essentially pure **6** was obtained by using preparative GLC.

In a similar reaction of **3a** with 1-bromo-1-hexyne (*Z*)-1,2-bis(trimethylsilyl)-1-octen-3-yne (**7**)[15] was produced in 74% yield with a high isomeric purity (>99%) (estimated by GLC). Isolation of **7** by column chromatography on basic aluminium oxide resulted in geometrical isomerization similarly to the case of **5** to give a mixture of **7** and its *E*-isomer, (*E*)-1,2-bis(trimethylsilyl)-1-octen-3-yne (**8**). However, interestingly UV irradiation on this mixture caused a complete isomerization of the residual **7** to provide pure **8** (Scheme 4).[16] This result led us to examine a similar isomerization of **6** to its *E*-isomer by the UV irradiation from a synthetic point of view. However, **6** did not isomerize to its *E*-isomer under the same conditions. The isomerization of **7** to **8** is of interest, though the reasons why **7** isomerizes to **8** and **6** does not are obscure at present.

We note that all of the products obtained in the present work are isomerically highly pure and thus the present study provides a new synthetic method for 1-substituted 1,2-bis(trimethylsilyl)ethenes, potential intermediates.

Experimental

Instruments. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL FX-200 (200 MHz) FT NMR spectrometer for $CDCl_3$ solutions. Chemical shifts are reported as δ-values relative to TMS, with chloroform ($\delta_H = 7.25$ and $\delta_C = 77.5$) or dichloromethane ($\delta_H = 5.28$ and $\delta_C = 54.0$) as internal standard for the ^{1}H and ^{13}C NMR spectra, respectively. IR spectra were recorded for liquid films inserted between NaCl plates in a Hitachi 285 spectrometer. Mass spectra were recorded with a Hitachi M-52 mass spectrometer. GLC analyses using the internal standard method were performed with a Shimadzu GC-8A gas chromatograph equipped with a glass column (10% PEG-20M on Diasolid M, 2 m or 5% FFAP on Diasolid M, 1 m), a flame ionization detector, and a Shimadzu C-R3A Chromatopac digital integrator-recorder.

Materials. Alkenes and solvents in the reactions were used after purification by methods generally employed in similar organoborane chemistry.[17)] Bis(trimethylsilyl)ethyne was dried over anhydrous sodium sulfate, purified by distillation, and stored under argon. A 1.0 mol dm^{-3} solution of $BH_2Br{\cdot}S(CH_3)_2$ in dichloromethane, a 1.0 mol dm^{-3} solution of DIBAH in hexanes, and a 1.4 mol dm^{-3} solution of methyllithium in diethyl ether were obtained from Aldrich Chemicals. A solution of BH_3 in THF,[18)] benzenesulfenyl chloride,[19)] and 1-bromo-1-hexyne[20)] were prepared by the literature methods.

Representative Procedure. Synthesis of (*E*)-1,2-Bis(trimethylsilyl)-1-cyclohexylethene (4a). A dry 100 cm^3 round-bottom flask, equipped with a gas inlet for argon, a sample inlet with a serum cap, and a magnetic stirring bar, was flushed with argon. In the flask, dicyclohexylborane (**2a**) (10 mmol) was prepared by the hydroboration of cyclohexene (1.64 g, 20 mmol) with BH_3 (10 mmol) in THF at 0°C for 2 h.

Bis(trimethylsilyl)ethyne (**1**) (1.70 g, 10 mmol) was added to **2a** at −15°C, and the reaction mixture was stirred for 2 h at 0°C to complete the hydroboration. To the reaction mixture was added 6 mol dm^{-3} aqueous sodium hydroxide (6 cm^3) at −15°C, followed by the dropwise addition of a solution of iodine (2.54 g, 10 mmol) in THF (10 cm^3). The mixture was warmed to 0°C, stirred for 0.5 h, and then oxidized by the successive addition of 3 mol dm^{-3} aqueous sodium hydroxide (2.5 cm^3) and 30% hydrogen peroxide (2.5 cm^3) at the same temperature. After stirring for 1 h at 0°C, the mixture was extracted three times with diethyl ether. The combined extracts were washed with brine, and dried over anhydrous sodium sulfate. The solvent was removed on a rotary evaporator under reduced pressure, and the residue was put on a basic aluminium oxide (Aluminiumoxid 90 aktiv basisch, Merck) column. 1.94 g (76% yield) of (*E*)-1,2-bis(trimethylsilyl)-1-cyclohexylethene (**4a**) was isolated by elution with pentane.

Synthesis of (*Z*)-1,2-Bis(trimethylsilyl)-1-cyclohexylethene (5a). The hydroboration of **1** (10 mmol) with **2a** (10 mmol) was carried out in the same manner as described in the synthesis of **4a**. To the hydroboration mixture was added a solution of methyllithium (7.14 cm^3, 10 mmol) in diethyl ether at 0°C, and the mixture was stirred for 0.5 h at the same temperature to form the corresponding ate-complex. Then, benzenesulfenyl chloride (1.45 g, 10 mmol) was added dropwise to the cooled solution (−78°C), and the reaction mixture was stirred for 0.5 h at the same temperature. The solution was brought to 0°C and stirred for an additional 0.5 h.

Synthesis of (*E*)-1,2-Bis(trimethylsilyl)-1-octene (4c). The experimental set-up was the same as described in the synthesis of **4a**. The flask was cooled to 0°C and charged with a solution of $BH_2Br{\cdot}S(CH_3)_2$ (10 cm^3, 10 mmol) in dichloromethane. To the stirred solution was added 1-hexene (1.68 g, 20 mmol) at 0°C, and the reaction mixture was stirred for 2 h at 25°C to complete the hydroboration. After removal of dichloromethane and dimethyl sulfide under reduced pressure with a water aspirator, dry diethyl ether (40 cm^3) and dry dimethyl sulfide (2 cm^3) were added to neat dihexylbromoborane at 0°C, and the solution was stirred for 0.5 h at the same temperature. Bis(trimethylsilyl)ethyne (**1**) (1.70 g, 10 mmol) was added to the cooled solution (−78°C), followed by the slow addition of a solution of DIBAH (10 cm^3, 10 mmol) in hexanes. The reaction mixture was brought to 0°C, stirred for 3 h at the same temperature and for an additional 2 h at room temperature to complete the hydroboration.

To the reaction mixture were added 6 mol dm^{-3} aqueous sodium hydroxide (12 cm^3) and THF (20 cm^3) at −15°C, followed by the dropwise addition of a solution of iodine (5.05 g, 20 mmol) in THF (20 cm^3). The reaction mixture was warmed to 0°C, stirred for 0.5 h, and then oxidized by the successive addition of 3 mol dm^{-3} aqueous sodium hydroxide (5 cm^3) and 30% hydrogen peroxide (5 cm^3) at the same temperature. After the same work-up as described in the synthesis of **4a**, 1.57 g (61% yield) of (*E*)-1,2-bis(trimethylsilyl)-1-octene (**4c**) was isolated by column chromatography on basic aluminium oxide (Aluminiumoxid 90 aktiv basisch, Merck) with pentane as eluent.

Synthesis of (*Z*)-1,2-Bis(trimethylsilyl)-1,4-pentadiene (6). The hydroboration of **1** (10 mmol) with **2a** (10 mmol) was carried out as described in the synthesis of **4a**. To the hydroboration mixture were added copper(I) iodide (0.19 g, 1 mmol) and allyl bromide (1.21 g, 10 mmol) at 0°C, followed by the dropwise addition of 3 mol dm^{-3} aqueous sodium hydroxide (10 cm^3). The reaction mixture was stirred for 1 h at 0°C, and oxidized with 30% hydrogen peroxide (2.5 cm^3) at the same temperature for 1 h to decompose the residual boron compound. After the same work-up as described in the synthesis of **4a**, (*Z*)-1,2-bis(trimethylsilyl)-1,4-pentadiene (**6**) was isolated by preparative GLC.

Synthesis of (*E*)-1,2-Bis(trimethylsilyl)-1-octen-3-yne (8). The cross-coupling reaction of **3a** (10 mmol) with 1-bromo-1-hexyne (1.61 g, 10 mmol) was carried out in the same manner as described in the synthesis of **6**. After the same work-up as described in the synthesis of **4a**, a mixture of **7** and **8** was obtained by column chromatography on basic aluminium oxide (Aluminiumoxid 90 aktiv basisch, Merck) with pentane as eluent. After removal of pentane, the mixture was irradiated in a silica glass tube with a high pressure mercury lamp (100 W) for 4 h at 20°C to give pure (*E*)-1,2-bis(trimethylsilyl)-1-octen-3-yne (**8**).

The products were identified by following data.

(*E*)-1,2-Bis(trimethylsilyl)-1-cyclohexylethene (4a): ^{1}H NMR $\delta=0.10$ (s, 9H), 0.11 (s, 9H), 1.10—1.80 (m, 10H), 2.35—2.55 (m, 1H), and 5.93 (s, 1H); ^{13}C NMR $\delta=0.85$ (CH_3–×3), 1.63 (CH_3–×3), 26.41 (–CH_2–), 26.97 (–CH_2–×2), 33.35 (–CH_2–×2), 50.13 (>CH–), 141.25 (–CH=), and 171.10 (>C=); IR 2925, 2850, 1440, 1245, 965, 890, 830, 750, and 680 cm^{-1}; MS m/z 254 (M^+); Found: C, 65.84; H, 12.09%. Calcd for $C_{14}H_{30}Si_2$: C, 66.06; H, 11.87%.

(*E*)-1,2-Bis(trimethylsilyl)-3,4-dimethyl-1-pentene (4b): ^{1}H NMR δ=0.10 (s, 9H), 0.11 (s, 9H), 0.77 (d, J=6.8

Hz, 3H), 0.91 (d, J=6.3 Hz, 3H), 1.01 (d, J=6.8 Hz, 3H), 1.45—1.75 (m, 1H), 2.05—2.30 (m, 1H), and 5.95 (s, 1H); ^{13}C NMR δ=1.19 (CH$_3$–×3), 1.82 (CH$_3$–×3), 20.33 (CH$_3$–), 21.57 (CH$_3$–), 23.01 (CH$_3$–), 32.30 (>CH–), 51.93 (>CH–), 141.57 (–CH=), and 171.49 (>C=); IR 2950, 1530, 1445, 1365, 1245, 1095, 980, 830, 750, and 680 cm^{-1}; MS m/z 242 (M$^+$); Found: C, 64.12; H, 12.65%. Calcd for $C_{13}H_{30}Si_2$: C, 64.38; H, 12.46%.

(*E*)-1,2-Bis(trimethylsilyl)-1-octene (4c): ^{1}H NMR δ=0.06 (s, 9H), 0.10 (s, 9H), 0.88 (t, J=6.8 Hz, 3H), 1.15—1.40 (m, 8H), 2.15—2.30 (m, 2H), and 5.95 (s, 1H); ^{13}C NMR δ=−0.45 (CH$_3$–×3), 0.85 (CH$_3$–×3), 14.40 (CH$_3$–), 23.01 (–CH$_2$–), 30.26 (–CH$_2$–), 31.35 (–CH$_2$–), 32.13 (–CH$_2$–), 37.24 (–CH$_2$–), 141.32 (–CH=), and 166.01 (>C=); IR 2930, 2850, 1450, 1245, 1120, 830, 750, and 680 cm^{-1}; MS m/z 256 (M$^+$).

(*E*)-1,2-Bis(trimethylsilyl)-4-methyl-1-heptene (4d): ^{1}H NMR δ=0.06 (s, 9H), 0.10 (s, 9H), 0.79 (d, J=6.8 Hz, 3H), 0.88 (t, J=6.8 Hz, 3H), 0.95—1.70 (m, 5H), 2.00—2.35 (m, 2H), and 6.01 (s, 1H); ^{13}C NMR δ=−0.16 (CH$_3$–×3), 1.04 (CH$_3$–×3), 14.69 (CH$_3$–), 19.75 (CH$_3$–), 20.77 (–CH$_2$–), 32.54 (>CH–), 40.08 (–CH$_2$–), 45.12 (–CH$_2$–), 142.69 (–CH=), and164.70 (>C=); IR 2950, 1540, 1450, 1370, 1245, 1010, 830, 750, and 680 cm^{-1}; MS m/z 256 (M$^+$); Found: C, 65.66; H, 12.40%. Calcd for $C_{14}H_{32}Si_2$: C, 65.54; H, 12.56%.

(*E*)-1,2-Bis(trimethylsilyl)-4-phenyl-1-pentene (4e): ^{1}H NMR δ=0.10 (s, 9H), 0.12 (s, 9H), 1.17 (d, J=6.8 Hz, 3H), 2.50—2.60 (m, 2H), 2.80—3.05 (m, 1H), 6.09 (s, 1H), and 7.05—7.40 (m, 5H); ^{13}C NMR δ=0.19 (CH$_3$–×3), 1.28 (CH$_3$–×3), 20.82 (CH$_3$–), 39.77 (>CH–), 46.28 (–CH$_2$–), 126.53 (–CH=), 127.38 (–CH=×2), 128.97 (–CH=×2), 144.19 (–CH=), 148.52 (>C=), and 163.95 (>C=); IR 2950, 1490, 1445, 1245, 1010, 830, 750, and 690 cm^{-1}; MS m/z 290 (M$^+$); Found: C, 70.05; H, 10.51%. Calcd for $C_{17}H_{30}Si_2$: C, 70.27; H, 10.40%.

(*E*)-1,2-Bis(trimethylsilyl)-1-cyclopentylethene (4f): ^{1}H NMR δ=0.10 (s, 9H), 0.11 (s, 9H), 1.40—1.80 (m, 8H), 2.70—2.90 (m, 1H), and 5.98 (s, 1H); ^{13}C NMR δ=0.97 (CH$_3$–×3), 1.41 (CH$_3$–×3), 25.90 (–CH$_2$–×2), 33.30 (–CH$_2$–×2), 50.74 (>CH–), 142.03 (–CH=), and 168.64 (>C=); IR 2945, 2860, 1530, 1440, 1400, 1245, 1070, 830, 750, and 680 cm^{-1}; MS m/z 240 (M$^+$); Found: C, 64.83; H, 11.89%. Calcd for $C_{13}H_{28}Si_2$: C, 64.92; H, 11.72%.

(*E*)-1,2-Bis(trimethylsilyl)-1-(*exo*-bicyclo[2.2.1]hept-2-yl)ethene (4g): ^{1}H NMR δ=0.11 (s, 9H), 0.13 (s, 9H), 1.10—1.70 (m, 8H), 2.05—2.30 (m, 2H), 2.55—2.65 (m, 1H), and 5.96 (s, 1H); ^{13}C NMR δ=1.09 (CH$_3$–×3), 1.92 (CH$_3$–×3), 28.99 (–CH$_2$–), 31.69 (–CH$_2$–), 36.92 (>CH–), 37.70 (–CH$_2$–), 39.21 (–CH$_2$–), 42.61 (>CH–), 52.66 (>CH–), 142.83 (–CH=), and 168.71 (>C=); IR 2940, 2860, 1520, 1445, 1395, 1245, 1100, 1010, 940, 830, 750, 675, and 640 cm^{-1}; MS m/z 266 (M$^+$); Found: C, 67.70; H, 11.25%. Calcd for $C_{15}H_{30}Si_2$: C, 67.59; H, 11.33%.

(*Z*)-1,2-Bis(trimethylsilyl)-1,4-pentadiene (6): ^{1}H NMR δ=0.13 (s, 9H), 0.15 (s, 9H), 2.94 (dd, J=6.8 and 1.5 Hz, 2H), 4.90—5.10 (m, 2H), 5.65—5.90 (m, 1H), and 6.30 (s, 1H); ^{13}C NMR δ=1.00 (CH$_3$–×3), 1.34 (CH$_3$–×3), 47.60 (–CH$_2$–), 115.98 (CH$_2$=), 138.21 (–CH=), 145.36 (–CH=), and 160.10 (>C=); IR 2945, 2880, 1630, 1395, 1245, 990, 905, 830, 745, and 675 cm^{-1}; MS m/z 212 (M$^+$); Found: C, 61.98; H, 11.52%. Calcd for $C_{11}H_{24}Si_2$: C, 62.19; H, 11.38%.

(*E*)-1,2-Bis(trimethylsilyl)-1-octen-3-yne (8): ^{1}H NMR δ=0.10 (s, 9H), 0.15 (s, 9H), 0.91 (t, J=6.8 Hz, 3H), 1.30—1.60 (m, 4H), 2.37 (t, J=6.8 Hz, 2H), and 6.39 (s, 1H); ^{13}C NMR δ=−1.74 (CH$_3$–×3), −0.58 (CH$_3$–×3), 13.86 (CH$_3$–), 19.85 (–CH$_2$–), 22.33 (–CH$_2$–), 31.28 (–CH$_2$–), 82.63 (–C≡), 100.26 (–C≡), 146.24 (>C=), and 151.95 (–CH=); IR 2925, 1245, 1040, 830, 750, and 685 cm^{-1}; MS m/z 252 (M$^+$); Found: C, 66.68; H, 11.09%. Calcd for $C_{14}H_{28}Si_2$: C, 66.59; H, 11.17%.

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