ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 620 (2001) 127–132

Journal of Organo metallic Chemistry

Reactions of $[LiC(SiMe_2H)_3]\cdot 2THF$: Sterically hindered tris(dimethylsilyl)methane derivatives and their hydrosilylation

Eric J. Hawrelak, Daisuke Sata, Folami T. Ladipo *

Department of Chemistry, University of Kentucky, Chemistry-Physics Building, Lexington KY 40506-0055, USA

Received 6 June 2000; received in revised form 15 September 2000

Abstract

Treatment of $LiC(SiMe_2H)_3\cdot 2THF$ (**1**) with alkenylchlorosilanes produced sterically hindered alkenylsilanes (**4**–**10**) of structure $H_2C{=}CH{-}(CH_2)_nSiRR'C(SiMe_2H)_3$ ($R = Me$; $R' = Me$ or Cl; $n = 0$, 1, or 4). The Peterson reaction of **1** with carbonyl compounds gave sterically hindered olefins $R(R')C{=}C(SiMe_2H)_2$. Pt or Rh catalyzed intramolecular hydrosilylation of $H_2C{=}CHSiMe_2C(SiMe_2H)_3$ (**4**) occurred to produce a new 1,3-disilacyclobutane derivative **15**. Intermolecular hydrosilylation was favored for **5**, **8**, and **10**, producing oligomeric products. © 2001 Elsevier Science B.V. All rights reserved.

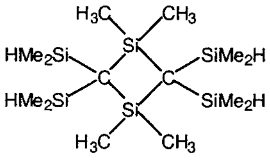
Keywords: Silicon; Tris(dimethylsilyl)methyl; Hydrosilylation; Bulky ligands

1. Introduction

Bulky silicon substituted alkyllithium species $[LiC(SiMe_2R)_3]$ ($R = Me$ [1], Ph [2], $CHMe_2$ [3], NMe_2 [4], C_6H_4Me-*o* [5], and OMe [6]) and $[LiC(SiMe_3)_2\text{-}SiMe_2R']$ ($R' = Ph$ [7], OMe [8], and SMe [9]) have allowed isolation of highly sterically hindered compounds of a range of elements, many of which possess unique structures and display novel reactivity [10,11]. In particular, compounds derived from $[LiC(SiMe_3)_3]$ have been widely studied [10]. Recently, we reported the synthesis of $[LiC(SiMe_2H)_3]\cdot 2THF$ (**1**), formed in excellent yield from reaction of $HC(SiMe_2H)_3$ with $(Me_2CH)_2NLi$ in THF [12]. We found that substitution of both chlorine atoms did not occur when $MeSiHCl_2$ was reacted with an excess of **1** in benzene-d_6 at room temperature (Eq. (1)) [12], indicative of a

$$3[\underset{\mathbf{1}}{LiC(SiMe_2H)_3}]\cdot 2THF \xrightarrow[RT,\ C_6D_6]{MeSiHCl_2} [\underset{\mathbf{2}}{ClHMeSiC(SiMe_2)_3}] \tag{1}$$

large steric hindrance by the $(HMe_2Si)_3C$ group to substitution at silicon. Remarkably, **1** reacted with $SiCl_4$, (two equivalents) to yield a product mixture from which the highly substituted 1,3-disilacyclobutane $[Me_2SiC(SiMe_2H)_2]_2$ (**3**) could be isolated in moderate yield [12].



3

In the present work, we have further explored the reactivity of **1**. In addition, we have explored hydrosilylation reactions of sterically encumbered alkenylsilanes of structure $H_2C{=}CH{-}(CH_2)_nSiRR'C(SiMe_2H)_3$ ($R = Me$; $R' = Me$ or Cl; $n = 0$, 1, or 4) derived from **1**.

2. Experimental

2.1. General details

All experiments were performed under a dry nitrogen atmosphere using standard Schlenk techniques or in a Braun Inc. glovebox. Solvents were dried and distilled by standard methods before use. $LiC(SiMe_2H)_3\cdot 2THF$ was prepared as previously described [12]. Benzalde-

---

* Corresponding author. Tel.: + 1-859-2577084; fax: + 1-859-3231069.

E-mail address: fladip0@pop.uky.edu (F.T. Ladipo).

0022-328X/01/$ - see front matter
PII: S0022-328X(00)00813-5

hyde, 4-trifluoromethylbenzaldehyde, 4-dimethylaminobenzaldehyde and benzophenone were purchased from Aldrich and distilled from $\mathrm{CaH_2}$. Allylchloride and 6-bromo-1-hexene were purchased from Aldrich and used without further purification. $\mathrm{H_2PtCl_6}$ was purchased from Alfa Aesar. $\mathrm{H_2C{=}CHSiMe_2Cl}$, $\mathrm{H_2C{=}CHSiMeCl_2}$, $\mathrm{H_2C{=}CHCH_2SiMe_2Cl}$, and $\mathrm{H_2C{=}CHCH_2SiMeCl_2}$ were purchased from Gelest and used without further purification. NMR spectra were recorded on a Varian Gemini 200 or a Varian VXR-400 spectrometer. ^{1}H and ^{13}C chemical shifts were measured relative to residual solvent signal, positive shifts representing deshielding; coupling constants are in Hertz. ^{29}Si chemical shifts were measured relative to an external tetramethylsilane (TMS) standard. Mass spectral data were obtained on a Hewlett–Packard 5890 series II gas chromatograph and a Hewlett–Packard 5972 series mass selective detector or from the University of Kentucky Mass Spectroscopy Center. Microanalyses were performed by E + R Microanalytical Laboratory, Inc., Corona, New York.

2.2. Synthesis of tris(dimethylsilyl)methane derivatives ***4–14***

*2.2.1. $[(H_2C{=}CH)Me_2SiC(SMe_2H)_3]$ (**4**)*

$\mathrm{[LiC(SiMe_2H)_3]\cdot 2THF}$ (3.00 g, 8.80 mmol) was dissolved in THF (15 ml). The solution was cooled to − 78°C and a THF (5 ml) solution of chlorodimethylvinylsilane (1.06 g, 8.80 mmol) was added dropwise. The reaction mixture was stirred at − 78°C for 1 h and then allowed to warm to room temperature (r.t.). The solvent was removed in vacuo and the resulting yellow solid was extracted with pentane (25 ml). After filtration, the solvent was removed in vacuo, to give a yellow solid (2.11 g, 87.7%). Anal. Calc. for $\mathrm{C_{11}H_{30}Si_4}$: C, 48.13; H, 10.92; Found: C, 47.99; H, 10.91%. ^{1}H-NMR ($\mathrm{C_6D_6}$, 200 MHz): δ 0.27 (d, 18H, $\mathrm{Si}\mathit{Me}_2\mathrm{H}$), 0.28 (s, 6H, $\mathrm{Si}\mathit{Me}_2$), 4.33 (sept, 3H, $\mathrm{Si}\mathit{H}$), 5.64 (dd, 19.8, 3.6 Hz, 1H, vinyl), 5.87 (dd, 14.6, 3.6 Hz, 1H, vinyl), 6.39 (dd, 20.2, 14.8 Hz, 1H, vinyl). ^{13}C{^{1}H}-NMR ($\mathrm{C_6D_6}$, 50 MHz): δ 0.45 ($\mathrm{Si}\mathit{Me}_2\mathrm{H}$), 0.51 ($\mathrm{Si}\mathit{Me}_2$), 131.5 ($\mathrm{CH{=}\mathit{C}H_2}$), 141.0 ($\mathrm{\mathit{C}H{=}CH_2}$). ^{29}Si{^{1}H}-NMR ($\mathrm{C_6D_6}$, 79.4 MHz): δ − 7.1 (s, $\mathrm{SiMe_2}$), − 15.7 (s, $\mathrm{SiMe_2H}$). GC–MS (EI, 70 eV) *m*/*z*: 259 $[\mathrm{M - Me}]^+$. M.p.: 191–193°C.

*2.2.2. $[(CH_2{=}CHCH_2)SiMe_2C(SiMe_2H)_3]$ (**5**)*

Compound **5** was prepared from $\mathrm{[LiC(SiMe_2H)_3]\cdot 2THF}$ (3.00 g, 8.80 mmol) and chlorodimethylallylsilane (1.18 g, 8.80 mmol) by the method described for **4**. The product was obtained as dark red oil (2.25 g, 89.1%). Anal. Calc. for $\mathrm{C_{12}H_{32}Si_4}$: C, 49.96; H, 11.09; Found: C, 49.74; H, 10.90%. ^{1}H-NMR ($\mathrm{C_6H_6}$, 200 MHz): δ 0.23 (s, 6H, $\mathrm{Si}\mathit{Me}_2$), 0.25 (d, 18H, $\mathrm{Si}\mathit{Me}_2\mathrm{H}$), 1.80 (d, $\mathrm{Si{-}C\mathit{H}_2CH{=}CH_2}$), 4.29 (sept, Si–*H*), 4.89 (m, 1H, $\mathrm{CH_2CH{=}C\mathit{H}_2}$), 4.96 (m, 1H, $\mathrm{CH_2CH{=}C\mathit{H}_2}$), 5.74 (m, 1H, $\mathrm{CH_2C\mathit{H}{=}CH_2}$). ^{13}C{^{1}H}-NMR ($\mathrm{C_6D_6}$, 50 MHz): δ − 0.29 ($\mathrm{Si}\mathit{Me}_2\mathrm{H}$), − 0.36 ($\mathrm{Si}\mathit{Me}_2$), − 8.43 (quat. C), 25.6 ($\mathrm{\mathit{C}H_2CH{=}CH_2}$), 113.9 ($\mathrm{CH_2CH{=}\mathit{C}H2}$), 135.2 ($\mathrm{CH_2\mathit{C}H{=}CH_2}$). ^{29}Si{^{1}H}-NMR ($\mathrm{C_6D_6}$, 79.4 MHz): δ − 15.9 ($\mathrm{SiMe_2H}$), 0.15 ($\mathrm{SiMe_2}$). GC–MS (EI, 70 eV) *m*/*z*: 287 $[\mathrm{M - H}]^+$.

*2.2.3. $[(H_2C{=}CH)Me(Cl)SiC(SiMe_2H)_3]$ (**6**)*

Compound **6** was prepared from $\mathrm{[LiC(SiMe_2H)_3]\cdot 2THF}$ (3.00 g, 8.80 mmol) and dichloromethylvinylsilane (1.24 g, 8.80 mmol) by the method described for **4**. The product was obtained as a yellow solid (2.22 g, 85.8%). Anal. Calc. for $\mathrm{C_{10}H_{27}Si_4Cl}$: C, 40.70; H, 9.22; Found: C, 40.98; H, 9.28%. ^{1}H-NMR ($\mathrm{C_6D_6}$, 200 MHz): δ 0.31 (d, 18H, $\mathrm{Si}\mathit{Me}_2\mathrm{H}$), 0.56 (s, 3H, $\mathrm{Si}\mathit{Me}$), 4.32 (sept, 3H, $\mathrm{Si}\mathit{H}$), 5.85 (d, 1H, vinyl), 5.84 (d, 1H, vinyl), 6.29 (dd, 1H, vinyl). ^{13}C{^{1}H}-NMR ($\mathrm{C_6D_6}$, 50 MHz): δ 0.84 ($\mathrm{Si}\mathit{Me}_2\mathrm{H}$), 4.11 ($\mathrm{Si}\mathit{Me}\mathrm{Cl}$), 134.2 ($\mathrm{CH{=}\mathit{C}H_2}$), 137.7 ($\mathrm{\mathit{C}H{=}CH_2}$). ^{29}Si{^{1}H}-NMR ($\mathrm{C_6D_6}$, 79.4 MHz): δ − 15.7 ($\mathrm{SiMe_2H}$), 15.0 (SiMeCl). GC–MS (EI, 70 eV) *m*/*z*: 293 $[\mathrm{M - H}]^+$. M.p.: 212–215°C.

*2.2.4. $[(H_2C{=}CHCH_2)Me(Cl)SiC(SiMe_2H)_3]$ (**7**)*

Compound **7** was prepared from $\mathrm{[LiC(SiMe_2H)_3]\cdot 2THF}$ (3.00 g, 8.80 mmol) and dichloromethylallylsilane (1.24 g, 8.80 mmol) by the method described for **4**. The product was obtained as a yellow oily solid (2.31 g, 87%). Anal. Calc. for $\mathrm{C_{11}H_{29}Si_4Cl}$: C, 42.74; H, 9.46; Found: C, 42.84; H, 9.68%. ^{1}H-NMR ($\mathrm{C_6D_6}$, 200 MHz): δ 0.28 (d, 18H, $\mathrm{Si}\mathit{Me}_2\mathrm{H}$), 0.52 (s, 3H, $\mathrm{Si}\mathit{Me}\mathrm{Cl}$), 2.02 (m, 2H, $\mathrm{Si{-}C\mathit{H}_2{-}CH{=}CH_2}$), 4.27 (sept, 3H, Si–*H*), 4.9–5.05 (m, 2H, $\mathrm{CH_2{-}CH{=}C\mathit{H}_2}$), 5.75–5.95 (m, 1H, $\mathrm{CH_2{-}C\mathit{H}{=}CH_2}$). ^{13}C{^{1}H}-NMR ($\mathrm{C_6D_6}$, 50 MHz): δ − 3.48, (quat C), 0.71 ($\mathrm{Si}\mathit{Me}_2\mathrm{H}$), 3.10 ($\mathrm{Si}\mathit{Me}\mathrm{Cl}$), 28.1 ($\mathrm{\mathit{C}H_2{-}CH{=}CH_2}$), 115.8 ($\mathrm{CH_2{-}CH{=}\mathit{C}H_2}$), 132.9 ($\mathrm{CH_2{-}\mathit{C}H{=}CH_2}$). ^{29}Si{^{1}H}-NMR ($\mathrm{C_6D_6}$, 79.4 MHz): δ − 15.8 ($\mathrm{SiMe_2H}$), 25.4 (SiMeCl). GC–MS (EI, 70 eV) *m*/*z*: 307 $[\mathrm{M - H}]^+$, 293 $[\mathrm{M - Me}]^+$.

*2.2.5. $[H_2C{=}CH(CH_2)_4SiMe_2C(SiMe_2H)_3]$ (**8**)*

Compound **8** was prepared from $\mathrm{[LiC(SiMe_2H)_3]\cdot 2THF}$ (5.00 g, 1.47 mmol) and chloro-hex-5-enyldimethylsilane [13] (2.59 g, 1.47 mmol) by the method described for **4**. The product was obtained as yellow oil (4.47 g, 92%). ^{1}H-NMR ($\mathrm{C_6D_6}$, 200 MHz): δ 0.23 (s, 6H, $\mathrm{Si}\mathit{Me}_2$), 0.28 (d, 18H, $\mathrm{Si}\mathit{Me}_2\mathrm{H}$), 0.80–2.05 (m, 8H, $\mathrm{(CH_2)_4}$), 4.38 (sept, 3H, Si–*H*), 4.9–5.1 (m, 2H, $\mathrm{{=}CH_2}$), 5.8 (m, 1H, =CH). ^{13}C{^{1}H}-NMR ($\mathrm{C_6D_6}$, 50 MHz): δ 8.24 (quat. C), − 0.19 ($\mathrm{SiMe_2H}$), 0.00 ($\mathrm{SiMe_2}$), 17.7, 23.9, 33.1, 33.7 {$\mathrm{(CH_2)_4}$}, 114.6 ($\mathrm{{=}CH_2}$), 1139.0 (=CH). ^{29}Si{^{1}H} ($\mathrm{C_6D_6}$, 79.4 MHz): δ − 15.9 ($\mathrm{SiMe_2H}$), 1.8 ($\mathrm{SiMe_2}$). GC–MS (EI, 70 eV) *m*/*z*: 315 $[\mathrm{M - Me}]^+$.

*2.2.6. $(H_2C{=}CHCH_2)C(SiMe_2H)_3]$ (**9**)*

Compound **9** was prepared from $\mathrm{[LiC(SiMe_2H)_3]\cdot 2THF}$ (3.00 g, 8.80 mmol) and allylchloride (0.67 g, 8.80 mmol) in THF at 0°C following the procedure described for **4**. The product was obtained as a clear gel (1.03 g, 51%). Anal. Calc. for $C_{10}H_{26}Si_3$: C, 52.09; H, 11.37; Found: C, 51.90; H, 11.37%. ^{1}H-NMR (C_6D_6, 200 MHz): δ 0.18 (d, 18H, Si*Me*$_2$H), 2.44 (m, 2H, C*H*$_2$CH=CH$_2$), 4.25 (sept, 3H, SiMe$_2$*H*), 4.90–5.05 (m, 2H, CH$_2$C*H*=CH$_2$), 6.02 (m, 1H, CH$_2$C*H*=CH$_2$). ^{13}C{^{1}H}-NMR (C_6D_6, 50 MHz): δ −3.05 (s, SiMe$_2$H), 1.57 (s, H$_2$C=CHCH$_2$*C*), 34.71 (s, H$_2$C=CH*C*H$_2$), 116.2 (s, H$_2$*C*=CHCH$_2$), 138.1 (s, H$_2$C=*C*HCH$_2$). ^{29}Si{^{1}H}-NMR (C_6D_6, 79.4 MHz): δ −11.5 (s, SiMe$_2$H). GC–MS (EI, 70 eV) *m*/*z*: 215 $[M-CH_3]^+$.

2.2.7. *[H_2C=$CH(CH_2)_4C(SiMe_2H)_3$] (**10**)*

Compound **10** was prepared from [LiC(SiMe$_2$H)$_3$]·2THF (2.09 g, 6.13 mmol) and 6-bromo-1-hexene (1.00 g, 6.13 mmol) by the method described for **4**. The product was obtained as a creamy yellow oily liquid (1.27 g, 77%). ^{1}H-NMR (C_6D_6, 200 MHz): δ 0.19 (d, 18H, Si*Me*$_2$H), 1.18–2.02 (m, 8H, (CH$_2$)$_4$), 4.25 (sept, 3H, Si–*H*), 4.90–5.06 (m, 2H, =CH$_2$), 5.71 (m, 1H, –C*H*=CH$_2$). ^{13}C{^{1}H}-NMR (C_6D_6, 50 MHz): δ −3.03 (SiMe$_2$H), 1.73 (quat. C), 28.97, 30.16, 30.28, 33.64 {(CH$_2$)$_4$}, 114.72 (=CH$_2$), 138.85 (*C*H=CH$_2$). ^{29}Si{^{1}H} (C_6D_6, 79.4 MHz): δ −11.9 (SiMe$_2$H). GC–MS (EI, 70 eV) *m*/*z*: 257 $[M-Me]^+$.

2.2.8. *[(H_5C_6)CH=C($SiMe_2H)_2$] (**11**)*

[LiC(SiMe$_2$H)$_3$]·2THF (2.00 g, 5.88 mmol) and benzaldehyde (0.62 g, 5.88 mmol) were dissolved in toluene (50 ml). The reaction mixture was stirred at r.t. for 2 h. The solvent was removed in vacuo. The precipitate was dissolved in pentane and the solution was filtered through celite. After stripping the pentane, the clear liquid was dissolved in methylene chloride and then filtered through silica. The filtrate was dried over MgSO$_4$ followed by CaH$_2$. The solvent was evaporated in vacuo leaving a clear liquid gel (1.01 g, 77.5%). Anal. Calc. for $C_{12}H_{20}Si_2$: C, 65.38; H, 9.14; Found: C, 65.13; H, 9.08%. ^{1}H-NMR (CDCl$_3$, 200 MHz): δ 0.15 (d, 6H, Si*Me*$_2$H), 0.27 (d, 6H, Si*Me*$_2$H), 4.25 (sept, 1H, Si*Me*$_2$H), 4.30 (sept, 1H, SiMe$_2$*H*), 7.33–7.58 (m, 5H, Ph), 7.77 (s, 1H, C=C*H*). ^{13}C-NMR (CDCl$_3$, 50 MHz): δ −2.93 (s, SiMe$_2$H), −2.32 (s, SiMe$_2$H), 127.6, 127.8, 128.2, 141.1 (arom. C), 140.8 (s, Si$_2$C=), 156.1 (s, =CHPh). ^{29}Si{^{1}H}-NMR (CDCl$_3$, 79.4 MHz): δ −25.1 (s, SiMe$_2$H), −13.0 (s, SiMe$_2$H). GC–MS (EI, 70 eV) *m*/*z*: 220 $[M]^+$.

2.2.9. *[(p-$Me_2NC_6H_4$)CH=C($SiMe_2H)_2$] (**12**)*

Compound **12** was prepared from [LiC(SiMe$_2$H)$_3$]·2THF (0.50 g, 1.46 mmol) and 4-dimethylaminobenzaldehyde (0.21 g, 1.46 mmol) by the method described for **11**. The product was obtained as orange oil (0.30 g, 78%). Anal. Calc. for $C_{14}H_{25}NSi_2$: C, 63.81; H, 9.56. Found: C, 63.52; H, 9.84. ^{1}H-NMR (C_6D_6, 200 MHz): δ 0.03 (d, 6H, Si*Me*$_2$H), 0.04 (d, 6H, SiMe$_2$H), 2.78 (s, 6H, NMe$_2$), 4.12 (sept, 1H, SiMe$_2$*H*), 4.21 (sept, 1H, SiMe$_2$*H*), 6.47 (d, 2H, $J_{CH}=9$ Hz, Ph), 7.06 (d, 2H, $J_{CH}=9$ Hz, Ph), 7.45 (s, 1H, C=C*H*). ^{13}C{^{1}H}-NMR (CDCl$_3$, 50 MHz): δ −2.77 (s, SiMe$_2$H), −2.29 (s, SiMe$_2$H), 40.30 (s, NMe$_2$), 111.4, 128.9, 130.1, 150.1 (arom. C), 134.38 (s, Si$_2$C=), 156.24 (s, =CH). ^{29}Si{^{1}H}-NMR (CDCl$_3$, 79.4 MHz): δ −25.5 (s, SiMe$_2$H), −12.7 (s, SiMe$_2$H). GC–MS (EI, 70 eV) *m*/*z*: 263 $[M]^+$.

2.2.10. *[(p-F_3C–C_6H_4)CH=C($SiMe_2H)_2$] (**13**)*

Compound **13** was prepared from [LiC(SiMe$_2$H)$_3$]·2THF (1.00 g, 2.93 mmol) and 4-trifluoromethylbenzaldehyde (0.51 g, 2.93 mmol) by the method described for **11**. The product was isolated as colorless oil (0.62 g, 73.5%). Anal. Calc. for $C_{13}H_{19}F_3Si_2$: C, 54.13; H, 6.63; Found: C, 52.13; H, 6.60%. ^{1}H-NMR (CDCl$_3$, 200 MHz): δ 0.14 (d, 6H, Si*Me*$_2$H), 0.27 (d, 6H, Si*Me*$_2$H), 4.27 (m, 2H, SiMe$_2$*H*), 7.35 (d, 2H, $J_{CH}=8$ Hz, Ph), 7.56 (d, 2H, $J_{CH}=8$ Hz, Ph), 7.77 (s, 1H, *H*C=C). ^{13}C-NMR (CDCl$_3$, 50 MHz): δ −3.12 (s, SiMe$_2$H), −2.47 (s, SiMe$_2$H), 124.3 (q, $^1J_{CF}=272$ Hz, CF$_3$), 124.9 (q, $^3J_{CF}=3.8$ Hz, Ph), 128.5 (s, Si$_2$C=), 129.6 (q, $^2J_{CF}=32.44$ Hz, Ph), 144.3 (q, $^4J_{CF}=1.5$ Hz, Ph), 144.8 (s, Ph), 154.1 (s, H*C*=C). ^{29}Si{^{1}H}-NMR (CDCl$_3$, 79.4 MHz): δ −25.1 (s, SiMe$_2$H), −12.65 (s, SiMe$_2$H). GC–MS (EI, 70 eV) *m*/*z*: 286 $[M-2H]^+$, 273 $[M-Me]^+$.

2.2.11. *[Ph_2C=C($SiMe_2H)_2$] (**14**)*

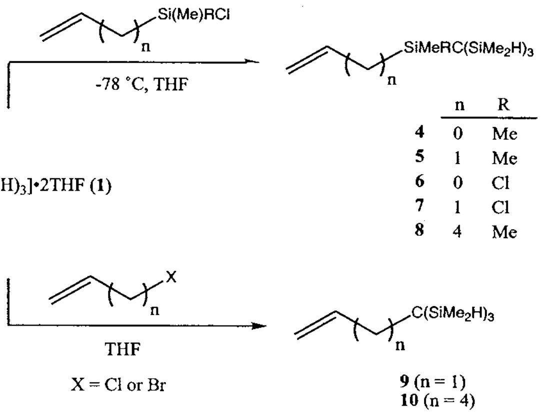
Compound **14** was prepared from [LiC(SiMe$_2$H)$_3$]·2THF (1.00 g, 2.93 mmol) and benzophenone (0.53 g, 2.93 mmol) in ether by the method described for **11**. The product was isolated as colorless oil (0.87 g, 65.1%). Anal. Calc. for $C_{18}H_{24}Si_2$: C, 72.9; H, 8.15; Found: C, 71.9; H, 8.13%. ^{1}H-NMR (CDCl$_3$, 200 MHz): δ 0.02 (d, 6H, Si*Me*$_2$H), 4.12 (sept, 2H, SiMe$_2$*H*), 7.37 (m, Ph). ^{13}C-NMR (CDCl$_3$, 50 MHz): δ −2.62 (s, SiMe$_2$H), 121.6 (s, C=*C*Si$_2$), 127.4, 127.7, 128.0, 142.09 (arom. C), 155.1 (s, C=*C*Ph$_2$). ^{29}Si{^{1}H}-NMR (CDCl$_3$, 79.4 MHz): δ −14.2 (s, SiMe$_2$H). GC–MS (EI, 70 eV) *m*/*z*: 296 $[M]^+$.

2.2.12. *Hydrosilylation of [(CH_2=CH)$SiMe_2C(SiMe_2H)_3$] (**4**): Formation of **15***

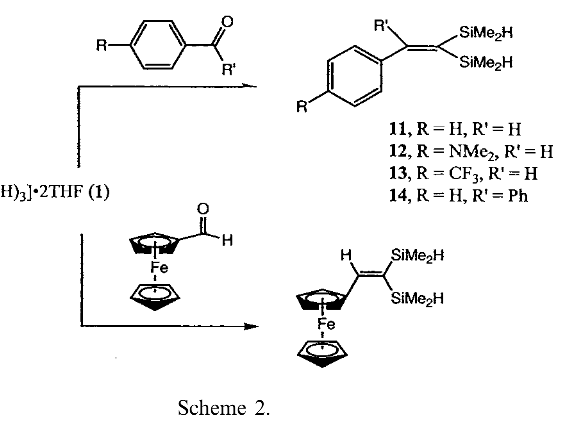
A 10 ml flask containing a heptane solution (3 ml) of [(H$_2$C=CH)SiMe$_2$C(SiMe$_2$H)$_3$] (1.02 g, 3.65 mmol) and H$_2$PtCl$_6$ (3.00 mg, 7.32×10^{-3} mmol) was heated at 60°C in an oil bath. The yellowish–brown solution was stirred for 4 h, after which time ^{1}H-NMR analysis of an aliquot showed complete disappearance of the vinyl peaks. The solution was extracted into pentane and filtered through silica to remove the catalyst. After filtration, the solvent was removed in vacuo to give an off-white solid. The solid was dissolved in a minimum of ether (~ 1.0 ml) and methyl alcohol (~ 4.0 ml) was added. White solids began to precipitate and the solution was placed in the freezer (− 15°C) to enhance the precipitation. The solvent was removed and the solids dried under vacuum to leave the product (**15**) as an air- and moisture-stable white solid (0.85 g, 86%). Anal. Calc. for $C_{11}H_{30}Si_4$: C, 48.10; H, 11.01; Found: C, 47.12; H, 10.63%. ^{1}H-NMR (C_6D_6, 200 MHz): δ 0.18 (d, 6H, Si*Me*$_2$H), 0.21 (d, 6H, Si*Me*$_2$H), 0.30 (s, 6H, $SiMe_2$), 0.33 (s, 6H, $SiMe_2$), 10.68 (q, 1H, C*H*Me), 1.06 (d, 3H, CH*Me*), 4.44 (m, 2H, Si–H). $^{13}C\{^1H\}$-NMR (C_6D_6, 50 MHz): δ − 1. 19 ($SiMe_2H$), 0.35 ($SiMe_2H$), 1.15 ($SiMe_2$), 1.68 (quat. C), 2.80 ($SiMe_2$), 8.25 (CH*Me*), 10.58 (*C*HMe). $^{29}Si\{^1H\}$-NMR (C_6D_6, 79.4 MHz): δ 1.7 (s, $SiMe_2$), − 22.7 (s, $SiMe_2H$), − 23.1 (s, $SiMe_2H$). GC–MS (EI, 70 eV) *m*/*z*: 259 [M − Me]$^+$.

3. Results and discussion

Treatment of a THF solution of $[LiC(SiMe_2H)_3]\cdot 2THF$ (**1**) at − 78°C with one equivalent of $RSiMe_2Cl$ or $RSiMeCl_2$ ($R = H_2C{=}CH$ or $H_2C{=}CHCH_2$) led to exclusive formation of $(RMe_2Si)C(SiMe_2H)_3$ (**4** and **5**) or $(RMeClSi)C(SiMe_2H)_3$ (**6** and **7**), respectively (Scheme 1). Microanalysis and/or mass spectroscopy and NMR (^{1}H, ^{13}C, and ^{29}Si) data confirmed the formulation given for each compound. The ^{1}H-NMR spectrum of $H_2C{=}CHSiMe_2C(SiMe_2H)_3$ (**4**), for example, contains a doublet at δ 0.27 ppm ($SiMe_2H$), a singlet at 0.28 ppm ($SiMe_2$), a multiplet at 4.33 ppm (Si–H) and three sets of doublets at 5.64, 5.87, and 6.39 ppm (vinyl hydrogens) in the expected 18:6:3:1:1:1 ratio. The reaction between **1** and $CH_2{=}CH(CH_2)_4$-$SiMe_2Cl$ [13] at − 78°C in THF gave $CH_2{=}CH(CH_2)_4$-$SiMe_2C(SiMe_2H)_3$ (**8**) (Scheme 1). After work-up **8** was isolated in 92% yield as a mixture of two isomers, the major isomer (~ 90% of the mixture by ^{1}H-NMR and GC–MS [14]) contained a 5-hexenyl moiety. Attempts to separate the isomers via chromatography on a silica column or vacuum distillation were unsuccessful. Hence, hydrosilylation of the mixture of isomers of **8** was investigated (vide infra). $H_2C{=}CHCH_2C(SiMe_2H)_3$ (**9**) and $H_2C{=}CH(CH_2)_4C(SiMe_2H)_3$ (**10**) were produced from the reaction of **1** with $H_2C{=}CHCH_2Cl$ at 0°C or $H_2C{=}CH(CH_2)Br$ at − 78°C, respectively. Compound **10** was isolated in 77% yield as a yellow oily liquid containing a mixture of isomers; the major isomer (> 90% by ^{1}H-NMR) contained a 5-hexenyl moiety [15]. Interestingly, **4**–**10** are air and moisture-stable materials. The steric bulk of the compounds likely inhibits their hydrolysis. In this regard, the related compounds $H_2C{=}CHSiMe_2C(SiMe_3)_3$ and $H_2C{=}CHCH_2SiMe_2C(SiMe_3)_3$ are also air- and moisture-stable [11c].

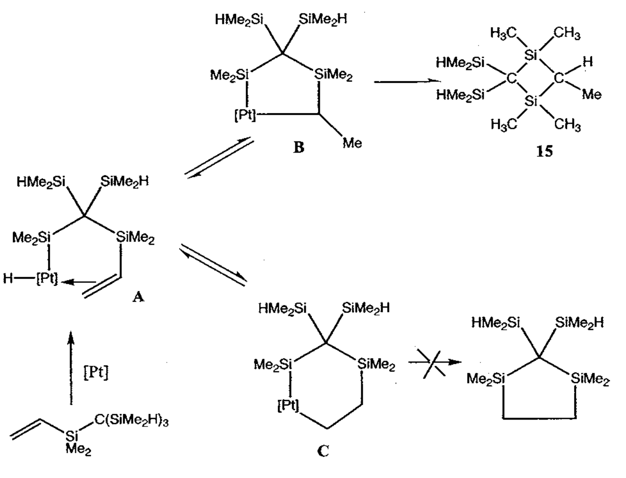


Scheme 1.



Scheme 2.

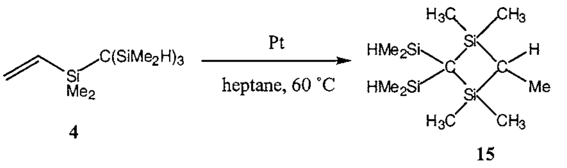
Results of the reactions of **1** with various carbonyl compounds are depicted in Scheme 2. The Peterson or Silyl–Wittig reaction [16] between **1** and benzaldehyde or its derivative (one equivalent) produced the corresponding olefin $RHC{=}C(SiMe_2H)_2$ (**11**–**13**) (R = Ph, *p*-$Me_2NC_6H_4$, or *p*-$F_3CC_6H_4$) in good yield. That **11**–**13** were obtained in pure form is confirmed by microanalysis and NMR data. The ^{1}H-NMR data of **11** is typical for the compounds: two doublets at δ 0.16 and 0.22 ppm (inequivalent $SiMe_2H$), two multiplets at 4.25 and 4.30 ppm (inequivalent Si–H), a multiplet at 7.33–7.58 ppm (phenyl), and a singlet at 7.77 ppm (C=CHPh) are observed in the spectrum. Unlike **11**–**13**, the product of the reaction of **1** with ferrocenecarboxaldehyde was not cleanly isolated [17]. The reaction of **1** with benzophenone in ether gave $Ph_2C{=}C(SiMe_2H)_2$ (**14**) in moderate isolated yield. The related compound $Ph_2C{=}C(SiMe_3)_2$ was prepared via analogous reaction starting from $LiC(SiMe_3)_3$ [18]. The reaction of ethyl acetate with **1** did not yield an olefinic product. Instead, **1** apparently abstracts a proton from ethyl acetate and $HC(SiMe_2H)_3$ was the only observable species in solution by ^{1}H-NMR [19]. These results are consistent with the observation that the Peterson reaction is limited by the facileness with which the nucleophile abstracts a



Scheme 3.

proton, if one is available, rather than attack the carbonyl carbon [12,20].

Since the sterically encumbered compounds **4**–**10** possess both olefinic and multiple Si–H functional groups, the potential exists for intra and/or intermolecular reaction and their hydrosilylation reactions were therefore of interest [21]. H_2PtCl_6- or $Rh(PPh_3)_3Cl$-catalyzed hydrosilylation of $H_2C{=}CHSiMe_2C(SiMe_2H)_3$ (**4**) in heptane at 60°C resulted in exclusive formation of the 1,3-disilacyclobutane derivative **15** (depicted in Eq. (2)). After recrystallization from ether–methanol, the product was isolated as an air stable, white solid in 86% yield. Both mass spectroscopy and microanalysis data are consistent with formulation given. The NMR (^1H, ^{13}C, and ^{29}Si) spectra in benzene-d_6 showed the expected signals, including three signals in the ^{29}Si-NMR spectrum at δ 1.74 ppm for the bridging silicon atoms, and at δ −22.7 and −23.1 ppm for the terminal silicon atoms. The exclusive intramolecular hydrosilylation of **4** and the regiochemistry of **15** may be understood in terms of the mechanism illustrated in Scheme 3 [22].



(2)

Intramolecular hydrosilylation of **4** likely reflects both a kinetic preference for coordination of vinyl group as in **A**, and steric inhibition of competitive coordination of the vinyl group of free **4**. The preference for α-addition to form **15** presumably reflects the greater stability of the resulting five-membered ring intermediate **B** versus a six-membered ring intermediate **C** which would result from β-addition. Similar explanations have been proposed for the observed regioselectivities of the hydrosilylation products of related compounds $HMe_2Si(CH_2)_nSiMe_2R$ (where $n = 2$–4 and $R = CH{=}CH_2$ [13,23] or $C{\equiv}CR'$ [24]).

Contrary to the situation with **4**, H_2PtCl_6-catalyzed hydrosilylation of $H_2C{=}CHCH_2SiMe_2C(SiMe_2H)_3$ (**5**), $H_2C{=}CH(CH_2)_4SiMe_2C(SiMe_2H)_3$ (**8**) or $H_2C{=}CH(CH_2)_4C(SiMe_2H)_3$ (**10**) in heptane at 80°C produced complex mixtures of products. Both GC–MS and gel permeation chromatography (GPC) analysis of the product mixtures established formation of oligomeric species. For example, GPC analysis of the product mixture obtained from the hydrosilylation of **10** revealed a polydisperse molecular weight distribution with average molecular weight of 1700 (versus polystyrene). As might be expected, both steric inhibition of intermolecular hydrosilylation and preference for intramolecular hydrosilylation decrease as the double bond gets further away from the bulky $C(SiMe_2H)_3$ group. Indeed, analysis of the ^1H-NMR data of the product mixtures suggests that double bond isomerization is competitive with hydrosilylation for **8** and **10** [25].

4. Summary

Hydrosilylation reactions of the sterically encumbered alkenylsilanes **4**, **5**, **8** and **10** were examined. The steric properties of $(H_2C{=}CH)Me_2SiC(SiMe_2H)$ (**4**) disfavored intermolecular reaction and led to exclusive formation of a new 1,3-disilacyclobutane derivative **15**. Increasing the separation between bulky $C(SiMe_2H)_3$ and the double bond favored intermolecular hydrosilylation, and may represent a useful route for preparing hyperbranched oligomers and polymers from monomers bearing the $C(SiMe_2H)_3$ group.

Acknowledgements

Thanks are expressed to the Kentucky National Science Foundation EPSCoR Program (grant number EPS-9452895) and the Chemistry Department of the University of Kentucky for financial support.

References

[1] (a) M.A. Cook, C. Eabom, D.R.M. Walton, J. Organomet. Chem. 24 (1970) 293. (b) M.A. Cook, C. Eabom, A.E. Jukes, D.R.M. Walton, J. Organomet. Chem. 24 (1970) 529. (c) A.H. Cowley, N.C. Norman, M. Pakulski, G. Becker, M. Layh, E. Kirchner, M. Schmidt, Inorg. Synth. 27 (1990) 235.

[2] (a) C. Eaborn, P.B. Hitchcock, J.D. Smith, A.C. Sullivan, J. Chem. Soc., Chem. Commun. (1983) 1390. (b) C. Eabom, P.B. Hitchcock, P.D. Lickiss, J. Organomet. Chem. 221 (1981) 13.

[3] A.I. Almansour, C. Eabom, J. Organomet. Chem. 489 (1995) 181.

[4] F. Adam, C. Eaborn, P.B. Hitchcock, J.D. Smith, Chem. Commun. (1996) 741.

[5] A.I. Almansour, C. Eabom, S.A. Hawkes, P.B. Hitchcock, J.D. Smith, Organometallics 16 (1997) 6035.

[6] F.I. Aigbirhio, N.H. Buttrus, C. Eaborn, S.H. Gupta, P.B. Hitchcock, J.D. Smith, A.C. Sullivan, J. Chem. Soc., Dalton Trans. (1992) 1015.

[7] S.S. Al-Juaid, C. Eabom, A. Habtemariam, P.B. Hitchcock, J.D. Smith, J. Organomet. Chem. 437 (1992) 41.

[8] (a) C. Eaborn, P.B. Hitchcock, A. Kowalewska, Z.-R. Lu, J.D. Smith, W.A. Stanczyk, J. Organomet. Chem. 521 (1996) 113. (b) C. Eaborn, P.B. Hitchcock, J.D. Smith, S.E. Sozerli, Organometallics 16 (1997) 5653.

[9] (a) N. Wiberg, G. Preiner, O. Schieda, Chem. Ber. 114 (1981) 2087. (b) D.A. Antonov, C. Eaborn, J.D. Smith, P.B. Hitchcock, E. Molla, V.I. Rosenberg, W.A. Stanczyk, A. Kowalewska, J. Organomet. Chem. 521 (1996) 109.

[10] (a) C. Eabom, A. Farook, P.B. Hitchcock, J.D. Smith, Organometallics 17 (1998) 3135. (b) C. Eaborn, P.B. Hitchcock, J.D. Smith, S.E. Sozerli, Organometallics 17 (1998) 4322. (c) C. Eabom, K. Izod, J.D. Smith, J. Organomet. Chem. 500 (1995) 89. (d) C. Eabom, J.D. Smith, Coord. Chem. Rev. 154 (1996) 125. (e) C. Eabom, S.A. Hawkes, P.B. Hitchcock, J.D. Smith, Chem. Commun. (1997) 1961. (f) Y. Nakadaira, K. Oharu, K.H. Sakurai, J. Organomet. Chem. 309 (1986) 247. (g) D.G. Anderson, D.W. Rankin, H.E. Robertson, A.H. Cowley, M. Pakulski, J. Mol. Struct. 196 (1989) 21.

[11] See for example: (a) C. Eaborn, D.A.R. Happer, K.D. Safa, D.R.M. Walton, J. Organomet. Chem. 157 (1978) C50. (b) C. Eabom, D.A.R. Happer, S.P. Hopper, K.D. Safa, J. Organomet. Chem. 170 (1979) C9. (c) R.I. Damja, C. Eaborn, W.-C. Sham, J. Organomet. Chem. 291 (1985) 25.

[12] E.J. Hawrelak, F.T. Ladipo, D. Sata, J. Braddock-Wilking, Organometallics 18 (1999) 1804.

[13] J.V. Swisher, H.-H. Chen, J. Organomet. Chem. 69 (1974) 83.

[14] This is presumably a result of H_2=CH(CH_2)$_4$SiMe_2Cl comprising a mixture of isomers: chloro-hex-5-enyldimethylsilane (84%), chloro-hex-4-enyldimethylsilane (8.6%) and 7.4% of an unidentified isomer (by ^{1}H-NMR and GC–MS).

[15] The olefinic starting material comprised 95% of 6-bromo-1-hexene isomer.

[16] See for example: (a) G. Wittig, U. Sch6llkopf, Chem. Ber. 87 (1954) 1318. (b) G. Wittig, G. Geissler, Liebigs Ann. Chem. 580 (1953) 44. (c) L. Homer, H. Hoffman, H.G. Wippel, Chem. Ber. 91 (1958) 61. (d) D.J. Peterson, J. Org. Chem. 32 (1967) 1717. (e) D.J. Peterson, J. Org. Chem. 33 (1968) 780.

[17] The compound was characterized in CA solution by ^{1}H-NMR as follows: 0.27 (d, 6H, SiMe_2H), 0.32 (d, 6H, SiMe_2H), 3.98 (s, 5H, C_5H_5), 4.04 (t, 2H, C_5H_4), 4.40 (t, 2H, C_5H_4), 4.60 (sept, 1H, Si–H), 4.77 (sept, 1H, Si–H), 7.61 (s, 1H, $C_5H_4C\mathit{H}$=CSi_2)

[18] See for example: (a) B.-T. Grobel, D. Seebach, Chem. Ber. 110 (1977) 852. (b) D. Seebach, R. Burstinghaus, B.-T. Grobel, M. Kolb, Liebigs Ann. Chem. (1977) 830.

[19] The presumed by-product $CH_3C(O)O(Li)CHCH_3$ was not characterized.

[20] I. Fleming, C.D. Floyd, J. Chem. Soc., Perkins Trans. I (1981) 969.

[21] Since **4**–**10** contain an olefinic and multiple Si–H functional groups, intermolecular hydrosilylation could possibly lead to hyperbranched polycarbosilanes. See for example: (a) L.J. Mathias, W.C. Carother, Adv. Dendritic Macromolecules 2 (1995) 101. (b) S. Rubinsztajn, J. Stein, J. Inorg. Organometal. Polym. 5 (1995) 43.

[22] For a discussion of the mechanism of alkene hydrosilylation, see for example: (a) J.L. Speier, J.L. Adv. Organomet. Chem. 17 (1979) 407. (b) D.A. Armitage, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 2, Pergamon Press, New York, 1982, pp. 115–120.

[23] H. Sakuri, T. Hirose, A. Hosomi, J. Organomet. Chem. 86 (1975) 197.

[24] M.G. Steinmetz, B.S. Udayakumar, J. Organomet. Chem. 378 (1989) 1.

[25] For a discussion of double bond isomerization promoted by transition metals, see: F.R. Hartley, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry, Vol. 4, Pergamon, London, 1982, p. 677.