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Syntheses and NMR study of [(2-dimethylaminomethyl)phenyl]vinylsilane derivatives and [(2-dimethylaminomethyl)phenyl]ethylsilane derivatives

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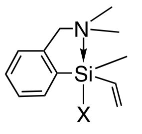
Abstract

Various vinylsilanes, $SiX(CH{=}CH_2)(CH_3)[2\text{-}(CH_3)_2NCH_2C_6H_4]$, and ethylsilanes, $SiX(CH_2CH_3)(CH_3)[2\text{-}(CH_3)_2NCH_2C_6H_4]$ [X = Cl (**1**); OMe (**2**); H (**3**); F (**4**); $OSiMe_3$ (**5**); NMe_2 (**6**); Me (**7**)], were synthesized in order to investigate the electronic effect of vinyl group on silicon atom having an intramolecular coordination arm. The magnitude of $\Delta\delta$ (ethyl → vinyl for ^{29}Si-NMR) of chlorosilane, **1**, was the biggest one among **1**–**7**. The differences of ^{29}Si chemical shifts between vinylsilanes and ethylsilanes increased in the following order: $X = Me, NMe_2 < H < OSiMe_3 < OMe < F < Cl$.

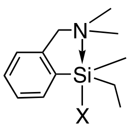
Keywords: Vinylsilane; Ethylsilane; ^{29}Si-NMR; Donor atom

1. Introduction

A ^{29}Si-NMR study on substituted pentacoordinate silicon complexes was carried out to investigate the electronic effect of various electronegative substituents (halogen, O, N) on silicon atoms [1]. However, to the best of our knowledge, a detailed study focussing on the electronic effect of substituents on vinylsilanes with intramolecular donor atom has not been reported. Recently, we found that the *meso* compound of diastereomeric 1,3-dihydroxy-1,3-bis[(2-dimethylaminomethyl)phenyl]-1,3-divinyldisiloxanes having both intramolecular coordination arms and vinyl groups showed a linear Si–O–Si skeleton, which was the first linear neutral disiloxandiol [2]. Interestingly, the Si–O–Si angle of the simple disiloxane with a vinyl group, $O[Si(vinyl)_3]_2$, was also 180° [3]. It thus appears that the electronic effect of vinyl group on Si should play an important role to form a linear structure. That has prompted us to carry out NMR studies on various [(2-dimethylaminomethyl)phenyl]vinylsilane derivatives and [(2-dimethylaminomethyl)phenyl]ethylsilane derivatives to investigate the electronic effect of a vinyl group on silicon atom in the presence of an intramolecular coordination arm.



1a-7a



1b-7b

1: X = Cl
2: X = OMe
3: X = H
4: X = F
5: X = $OSiMe_3$
6: X = NMe_2
7: X = Me

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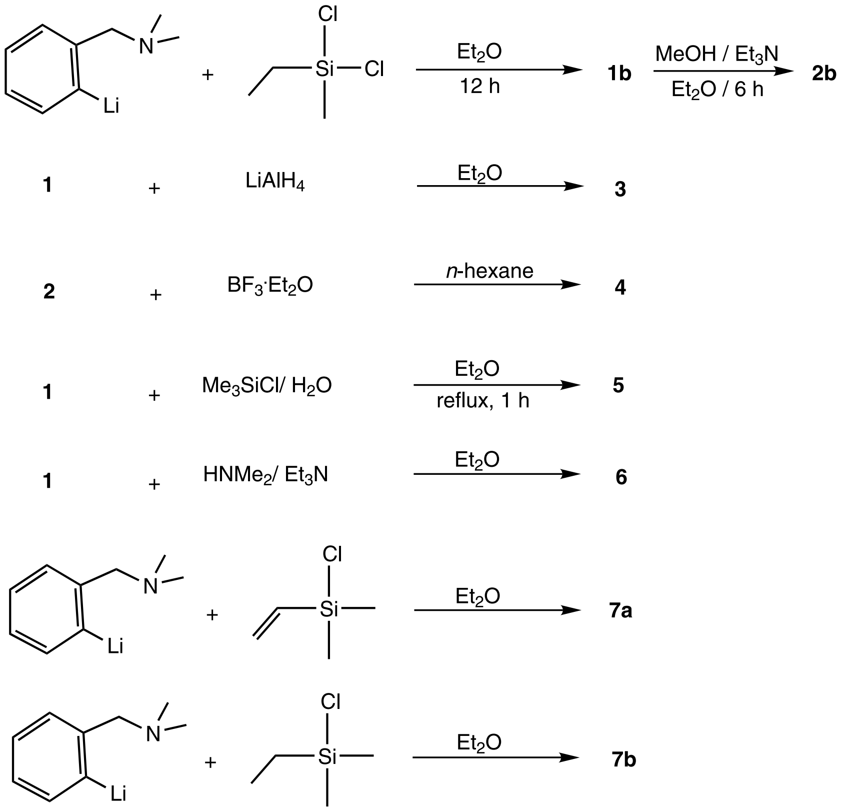

Scheme 1. Syntheses of **1**–**7**.

2. Results and discussion

*2.1. Syntheses of [(2-dimethylaminomethyl)phenyl]-vinylsilane derivatives (**1a**–**7a**) and [(2-dimethylaminomethyl)phenyl]ethylsilane derivatives (**1b**–**7b**) (Scheme 1)*

Compounds **1a** [4] and **2a** [5] were prepared according to literature methods. The reaction of *ortho*-lithiated (dimethylaminomethyl)phenyl with dichloroethylmethylsilane gave **1b** in 70% yield. Compound **2b** was obtained in 73% yield from the reaction of **1b** with MeOH in the presence of triethylamine, as an HCl acceptor. The reductions of **1a** and **1b** using $LiAlH_4$ gave **3a** [4] in 73% yield and **3b** in 67% yield, respectively. Compounds **4a** and **4b** were synthesized in 84 and 89% yields by the reactions of **2a** and **2b** with $BF_3 \cdot Et_2O$, respectively. Compounds **1a** and **1b** reacted with Me_3SiCl in the presence of water and triethylamine to give **5a** in 67% yield and **5b** in 68% yield, respectively. The reactions of **1a** and **1b** with dimethylamine in the presence of an excess of triethylamine gave **6a** in 62% yield and **6b** in 56% yield, respectively. The reactions of *ortho*-lithiated (dimethylaminomethyl)phenyl with chlorodimethylvinylsilane and chloroethyldimethylsilane afforded **7a** in 79% yield and **7b** in 81% yield, respectively. All compounds were purified and isolated by vacuum distillation.

Table 1
^{1}H-NMR spectral data (δ (ppm), 500 MHz, toluene-d_8, 293 K)

Compound	CH_2N (dd, 2H)	J (H, H_1 Hz)
1a	3.213, 3.303	13.31
1b	3.210, 3.079	13.06
2a	3.345, 3.255	12.81
2b	3.448, 3.321	12.70
3a	3.318, 3.238	12.74
3b	3.318, 3.283	12.50
4a	3.163, 3.058	13.20
4b	3.187, 3.097	13.00
5a	3.437, 3.340	12.81
5b	3.456, 3.405	13.20
6a	3.492, 3.435	13.20
6b	3.450 (s, 2H)	–
7a	3.364 (s, 2H)	–
7b	3.386 (s, 2H)	–

*2.2. NMR study of [(2-dimethylaminomethyl)phenyl]-vinylsilanes (**1a**–**7a**) and [(2-dimethylaminomethyl)-phenyl]ethylsilanes (**1b**–**7b**)*

The benzylic proton resonances of CH_2N are given in Table 1. The ^{1}H-NMR spectra of **1**–**5** and **6a** show the diastereotopism of benzylic protons [6]. The coupling constants of methylene protons of vinylsilanes increase in the order: $X = H < OSiMe_3 < OMe < NMe_2 < F < Cl$.

The ^{29}Si-NMR and $\Delta\delta$ (ethyl → vinyl) are given in Table 2. The increased shielding of silicon by the vinyl group, as expected, implies that π electrons of the vinyl substituent might be delocalized over the σ* orbital of Si–X bond through π–σ* conjugation [7]. This delocalization could partially affect the linear structures of two vinylsiloxanes mentioned in introduction, although the more complicated factors might be involved. The shielding of the Si atom in vinylsilane was enhanced by the presence of electronegative substituents (vinyl → Si → X). The magnitudes of $\Delta\delta$ increased in the order: $X = Me$, NMe_2, $H < OSiMe_3 < OMe < F < Cl$. The magnitude of $\Delta\delta$ of chlorosilane, **1**, was biggest, which shows no direct correlation with the electronegativities of substituents. In comparison with this result, ^{29}Si-NMR studies on the replacement of a methyl by a phenyl group in the absence of an intramolecular donor atom, done by Cragg and Lane [8], showed that the differential shifts of ^{29}Si-NMR for $Me_{2-n}Ph_nSiX_2$ by phenyl substitution increased in the order: $X = H < NMe_2 < OMe < Cl < F$. It was also reported that the differences of ^{29}Si chemical shifts between $SiMe_4$ and $SiMe_3X$ increased in the order: $X = NMe_2 < OMe < Cl < F$ [9].

In summary, the various vinylsilanes, $SiX(CH{=}CH_2)(CH_3)[2\text{-}(CH_3)_2NCH_2C_6H_4]$, and ethylsilanes, $SiX(CH_2CH_3)(CH_3)[2\text{-}(CH_3)_2NCH_2C_6H_4]$, having an intramolecular donor atom were synthesized. The magnitude of $\Delta\delta$ (ethyl → vinyl for ^{29}Si-NMR) of chlorosilane, **1**, was 28.59 ppm, which indicates the significant electronic effect of the vinyl group. The differences of ^{29}Si chemical shifts between vinylsilanes and ethylsilanes also increased in the following order: $X = Me$, NMe_2, $H < OSiMe_3 < OMe < F < Cl$.

3. Experimental

3.1. General comments

In all reactions where air-sensitive chemicals were used, the reagents and solvents were dried prior to use. Diethyl ether and *n*-hexane were distilled from Na/Ph_2CO. Other starting materials were purchased in reagent grade and used without further purification. Glassware was flame-dried under nitrogen or argon flushing prior to use. Experiments were performed under a nitrogen or argon atmosphere. ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra were recorded on a Bruker AMX 500 NMR spectrometer and referenced to residual protons of the solvent, carbons of solvent, and silicons of $SiMe_4$, respectively. Analyses of product mixtures were accomplished using a HP 5890 II with FID (HP-1, 15 m column). Mass spectra were recorded on a low-resolution HP 5971A mass spectrometer and a high-resolution VG ANALITICLA 70-VSEQ mass spectrometer.

Table 2
^{29}Si-NMR spectral data (δ (ppm, TMS), 99 MHz, toluene-d_8, 293 K)

Compound (X)	Vinylsilane (a)	Ethylsilane (b)	$\Delta\delta$
1 (Cl)	−15.53	13.06	28.59
4 (F)	−13.21	8.97	22.18
2 (OMe)	−7.85	8.30	16.15
5 ($OSIMe_3$)	−16.02	−1.10	14.92
3 (H)	−26.71	−15.19	11.52
6 (NMe_2)	−8.21	2.31	10.52
7 (Me)	−7.21	3.01	10.22

3.2. Synthesis of *1b*

To dichloroethylmethylsilane (6.7 ml, 0.050 mol) at 0 °C was added slowly 2-(*N*,*N*-dimethylaminomethyl)phenyllithium (7.1 g, 0.050 mol) in 200 ml of diethyl ether. The reaction mixture was stirred for about 12 h at room temperature (r.t.). After filtration of precipitated LiCl, volatiles were distilled under vacuum. The residue was distilled to yield **1b** (8.4 g) in 70% yield. b.p.: 80–85 °C (0.15 Torr). MS: *m/z* (relative intensity) 241 (M^+, 4.8), 226 (17.5), 169 (7.5), 107 (5.0), 91 (15.5), 58 (100), 42 (7.8). ^{1}H-NMR (toluene-d_8, 500 MHz): δ 0.58 (s, 3H), 0.96–1.11 (m, 5H), 1.78 (s, 6H), 3.07–3.22 (dd, 2H), 6.92–8.33 (m, 4H). ^{13}C-NMR (toluene-d_8, 125 MHz): δ 2.23 ($SiCH_3$), 7.70, 11.24 (ethyl), 44.63 ($N(CH_3)_2$), 64.64 (NCH_2), 127.1, 130.0, 134.1, 137.4, 138.4, 145.4 (C_6H_4). HRMS—$C_{12}H_{20}ClNSi$: 241.1054 (Calc.); 241.1047 (Found).

3.3. Synthesis of *2b*

A mixture of MeOH (3.0 ml, 0.074 mol) and Et_3N (10.3 ml, 0.074 mol) was slowly added to 2.9 g (0.012 mol) of **1b** in 100 ml of diethyl ether at 0 °C. After the addition was completed, the mixture was refluxed for 6 h. The reaction mixture was cooled, the precipitated $Et_3N^+HCl^-$ was removed by filtration, and volatiles were distilled from the filtrate under vacuum. The residue was distilled off to afford **2b** in 73% yield (2.1 g). b.p.: 62–65 °C (0.15 Torr). MS: *m/z* (relative intensity) 237 (M^+, 10.0), 222 (32.5), 208 (12.5), 194 (100), 165 (20.0), 135 (22.5), 119 (12.3), 58 (55.0). ^{1}H-NMR (toluene-d_8, 500 MHz): δ 0.36 (s, 3H), 0.88–1.05 (m, 5H), 2.02 (s, 6H), 3.35 (s, 3H), 3.31–3.45 (dd, 2H), 7.14–7.71 (m, 4H). ^{13}C-NMR (toluene-d_8, 125 MHz): δ −3.46 ($SiCH_3$), 7.42, 8.04 (ethyl), 45.14 ($N(CH_3)_2$), 50.28 (OMe), 64.94 (NCH_2), 126.7, 128.2, 136.0, 136.2, 137.5, 144.3 (C_6H_4). HRMS—$C_{13}H_{23}NOSi$: 237.1549 (Calc.); 237.1547 (Found).

3.4. Synthesis of **3b**

To **1b** (2.6 g, 0.011 mol) in 100 ml of diethyl ether was added $LiAlH_4$ (0.104 g, 0.0027 mol) at 0 °C. After the mixture was refluxed for 3 h, it was stirred for 12 h at r.t. The precipitate was removed by filtration and volatiles were distilled from the filtrate under vacuum. The residue was distilled off to afford **3b** in 67% yield (1.5 g). b.p.: 55–60 °C (0.15 Torr). MS: *m/z* (relative intensity) 207 (M^+, 3.6), 192 (14.1), 178 (91.7), 162 (19.3), 135 (64.1), 133 (100), 107 (14.4), 91 (13.3), 58 (53.0), 43 (13.4). ^1H-NMR (toluene-d_8, 500 MHz): δ 0.31 (s, 3H), 0.80–1.07 (m, 5H), 1.99 (s, 6H), 3.27–3.33 (dd, 2H), 4.44–4.51 (m, 1H), 7.09–7.55 (m, 4H). ^{13}C-NMR (toluene-d_8, 125 MHz): δ −4.42 ($SiCH_3$), 6.66, 8.80 (ethyl), 44.42 ($N(CH_3)_2$), 64.98 (NCH_2), 126.7, 128.1, 136.0, 137.0, 137.4, 146.1 (C_6H_4). HRMS—$C_{12}H_{21}NSi$: 207.1443 (Calc.); 207.1445 (Found).

3.5. Syntheses of **4a** and **4b**

To **2a** (3.5 g, 0.015 mol) in 100 ml of *n*-hexane was added slowly $BF_3 \cdot Et_2O$ (1.3 ml, 0.0065 mol) at r.t. The reaction mixture was stirred for 1 h at r.t. The gel was removed by filtration and volatiles were distilled from the filtrate under vacuum. The residue was distilled off to give **4a** in 84% yield (2.8 g). In a similar manner using **2b**, **4b** was obtained in 89% yield (1.8 g). **4a**—b.p.: 55–60 °C (0.10 Torr). MS: *m/z* (relative intensity) 223 (M^+, 15.0), 208 (35.0), 180 (100), 132 (18.8), 115 (12.5), 91 (21.8), 63 (17.3), 58 (95.0), 47 (15.0). ^1H-NMR (toluene-d_8, 500 MHz): δ 0.37, 0.40 (d, 3H), 1.78 (s, 6H), 3.05–3.18 (dd, 2H), 5.91–6.15 (m, 3H), 7.12–8.05 (m, C_6H_4). ^{13}C-NMR (toluene-d_8, 125 MHz): δ −1.68, −1.85 ($SiCH_3$), 44.78 ($N(CH_3)_2$), 64.37 (CH_2N), 128.70, 132.48 (vinyl), 127.24, 130.04, 136.85, 137.42, 137.48, 145.5 (C_6H_4). HRMS—$C_{12}H_{18}FNSi$: 223.1193 (Calc.); 223.1189 (Found). **4b**—b.p.: 100–105 °C (1.0 Torr). MS: *m/z* (relative intensity) 225 (M^+, 10.0), 210 (31.3), 196 (7.8), 153 (17.5), 125 (7.5), 91 (27.0), 63 (7.3), 58 (100). ^1H-NMR (toluene-d_8, 500 MHz): δ 0.33, 0.34 (d, 3H), 0.78–1.10 (m, 5H), 1.81 (s, 6H), 3.08–3.20 (dd, 2H), 6.94–7.98 (m, C_6H_4). HRMS—$C_{12}H_{20}FNSi$: 225.1349 (Calc.); 225.1342 (Found).

3.6. Syntheses of **5a** and **5b**

Water (10.0 ml, 0.56 mol) was slowly added to a mixture of Me_3SiCl (34.0 ml, 0.27 mol), Et_3N (74.1 ml, 0.53 mol), and **1a** (9.0 g, 0.038 mol) in 100 ml of diethyl ether at 0 °C. After the addition was completed, the reaction mixture was refluxed for 1 h. The reaction mixture was cooled, the precipitated $Et_3N^+HCl^-$ was removed by filtration, and volatiles were distilled from the filtrate under vacuum. The residue was distilled off to give **5a** in 67% yield (7.5 g). In a similar manner using **1b**, **5b** was prepared in 68% yield (7.6 g). **5a**—b.p.: 60–65 °C (0.15 Torr). MS: *m/z* (relative intensity) 278 ($M^+ - 15$, 20.0), 251 (23.5), 250 (100), 207 (8.1), 193 (10.0), 159 (7.5), 133 (13.3), 117 (7.8), 73 (8.5), 58 (27.5). ^1H-NMR (toluene-d_8, 500 MHz): δ 0.18 (s, 9H), 0.46 (s, 3H), 2.00 (s, 6H), 3.33–3.45 (dd, 2H), 5.76–6.35 (m, 3H), 7.16–7.83 (m, 4H). ^{13}C-NMR (toluene-d_8, 125 MHz): δ 0.34 ($SiCH_3$), 2.25 ($OSiMe_3$), 44.91 ($N(CH_3)_2$), 64.73 (CH_2N), 128.9, 131.5 (vinyl), 126.6, 129.5, 135.8, 137.2, 139.9, 145.5 (C_6H_4). ^{29}Si-NMR (toluene-d_8, 99 MHz): δ 7.88, −16.02. HRMS—$C_{15}H_{27}NOSi_2$: 293.1631 (Calc.); 293.1631 (Found). **5b**—b.p.: 90–95 °C (1.2 Torr). MS: *m/z* (relative intensity) 295 (M^+, 7.2), 280 (33.6), 226 (18.3), 207 (23.6), 190 (38.0), 179 (27.0), 161 (28.1), 133 (22.0), 58 (100). ^1H-NMR (toluene-d_8, 500 MHz): δ 0.18 (s, 9H), 0.40 (s, 3H), 0.85–1.05 (m, 5H), 2.05 (6H), 3.39–3.47 (m, 2H), 6.97–7.77 (m, C_6H_4). ^{29}Si-NMR (toluene-d_8, 99 MHz): δ 7.16, −1.10. HRMS—$C_{15}H_{29}NOSi_2$: 295.1788 (Calc.); 295.1786 (Found).

3.7. Syntheses of **6a** and **6b**

A mixture of dimethylamine (130 ml, 0.26 mol) diluted to 2.0 M in THF and Et_3N (45.0 ml, 0.32 mol) was slowly added to a solution of **1a** (3.9 g, 0.016 mol) in 100 ml of diethyl ether at 0 °C. After the addition was completed, the reaction mixture was stirred at r.t. for 12 h. The precipitated $Et_3N^+HCl^-$ was removed by filtration and volatiles were distilled from the filtrate under vacuum. The residue was distilled off to give **6a** in 62% yield (2.5 g). In a similar manner using **1b**, **6b** was prepared in 56% yield (1.9 g). **6a**—b.p.: 80–85 °C (0.10 Torr). MS: *m/z* (relative intensity) 248 (M^+, 8.3), 233 (14.4), 196 (100), 159 (33.0), 132 (13.8), 105 (11.1), 91 (20.4), 58 (70.7). ^1H-NMR (toluene-d_8, 500 MHz): δ 0.44 (s, 3H), 2.09 (s, 6H), 2.49 (s, 6H), 3.42–3.51 (dd, 2H), 5.69–6.38 (m, 3H), 7.13–7.60 (m, C_6H_4). HRMS—$C_{14}H_{24}N_2Si$: 248.1709 (Calc.); 248.1712 (Found). **6b**—b.p.: 87–90 °C (0.55 Torr). MS: *m/z* (relative intensity) 250 (M^+, 5.2), 235 (19.7), 207 (45.2), 161 (23.0), 58 (100). ^1H-NMR (toluene-d_8, 500 MHz): δ 0.35 (s, 3H), 0.89–1.01 (m, 5H), 2.11 (s, 6H), 2.44 (s, 6H), 3.45 (s, 2H), 7.12–7.55 (m, C_6H_4). HRMS—$C_{14}H_{26}N_2Si$: 250.1865 (Calc.); 250.1870 (Found).

3.8. Syntheses of **7a** and **7b**

To dimethylvinylchlorosilane (2.8 ml, 0.020 mol) at 0 °C was added slowly 2-(*N*,*N*-dimethylaminomethyl)phenyllithium (2.8 g, 0.020 mol) in 120 ml of diethyl ether. The reaction mixture was stirred for 12 h at r.t. After filtration of precipitated LiCl, volatiles were distilled under vacuum. The residue was distilled to yield **7a** (3.5 g) in 79% yield. In a similar manner using ethyldimethylchlorosilane, **7b** was prepared in 81% yield

(3.6 g). **7a**—b.p.: 75–80 °C (0.15 Torr). MS: *m*/*z* (relative intensity) 219 (M^+, 4.0), 204 (10.0), 176 (100), 159 (5.5), 145 (7.5), 105 (7.5), 91 (6.3), 84 (5.5), 58 (32.0). ^{1}H-NMR (toluene-d_8, 500 MHz): δ 0.39 (s, 6H), 2.01 (s, 6H), 3.36 (s, 2H), 5.69–6.41 (m, 3H), 7.11–7.57 (m, C_6H_4). HRMS—$C_{13}H_{21}NSi$: 219.1443 (Calc.); 219.1443 (Found). **7b**—b.p.: 70–75 °C (0.10 Torr). MS: *m*/*z* (relative intensity) 221 (M^+, 12.5), 206 (30.0), 192 (40.0), 176 (15.5), 149 (39.0), 121 (17.5), 105 (11.3), 87 (15.8), 58 (100). ^{1}H-NMR (toluene-d_8, 500 MHz): δ 0.33 (s, 3H), 0.84–1.01 (m, 5H), 2.05 (s, 6H), 3.39 (s, 2H), 7.13–7.54 (m, C_6H_4). HRMS—$C_{13}H_{23}NSi$: 221.1600 (Calc.); 221.1607 (Found).

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References

[1] (a) D. Kost, I. Kalikhman, in: Z. Rappoport, Y. Apeloig (Eds.), The Chemistry of Organic Silicon Compounds, vol. 2, Wiley, Chichester, UK, 1998, p. 1339;
(b) R.J.P. Corriu, J.C. Young, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of Organic Silicon Compounds, Wiley, Chichester, UK, 1989, p. 1241;
(c) B.J. Helmer, R. West, R.J.P. Corriu, M. Poirier, G. Royo, A. de Saxcé, J. Organomet. Chem. 251 (1983) 295.

[2] M.E. Lee, H.M. Cho, D.J. Kang, J.-S. Lee, J.H. Kim, Organometallics 21 (2002) 4297.

[3] W.S. Sheldrick, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of Organic Silicon Compounds, Wiley, Chichester, UK, 1989, p. 227.

[4] M. Weinmann, A. Gehrig, B. Schiemenz, G. Huttner, B. Nuber, G. Rheinwald, H. Lang, J. Organomet. Chem. 563 (1998) 61.

[5] (a) M. Weinmann, O. Walter, G. Huttner, H. Lang, J. Organomet. Chem. 561 (1998) 131;
(b) M.E. Lee, H.M. Cho, C.H. Kim, Bull. Korean Chem. Soc. 21 (2000) 793.

[6] (a) C. Chuit, R.J.P. Corriu, C. Reye, J.C. Young, Chem. Rev. 93 (1993) 1371;
(b) R.J.P. Corriu, A. Kpoton, M. Poirier, G. Royo, A. de Saxcé, J.C. Young, J. Organomet. Chem. 395 (1990) 1.

[7] (a) A.R. Bassindale, P.G. Taylor, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of Organic Silicon Compounds, Wiley, Chichester, UK, 1989, p. 893;
(b) J. Schraml, V. Chvalovský, M. Mägi, E. Lippmaa, Collect. Czech. Chem. Commun. 42 (1977) 306.

[8] R.H. Cragg, R.D. Lane, J. Organomet. Chem. 277 (1984) 199.

[9] E.A. Williams, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of Organic Silicon Compounds, Wiley, Chichester, UK, 1989, p. 511.