

Reactions of [(2-*N,N*-Dimethylaminomethyl)phenyl]methylvinylchlorosilane with *t*-BuLi: Synthesis and Characterization of Five Isomeric 1,3-Disilacyclobutanes

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The reaction of [(2-*N,N*-dimethylaminomethyl)phenyl]methylvinylchlorosilane with *t*-BuLi in hexane solvent gave dimers, five isomeric 1,3-disilacyclobutanes which were separated and characterized. In trapping experiments with various trapping agents, no corresponding silene-trapping adduct was observed. We suggest that more important species for the formation of five isomeric dimers might be the zwitterionic species generated by virtue of intramolecular donor atom rather than the silene.

Keywords : Silene, Zwitterionic species, Dimer, Intramolecular donor atom.

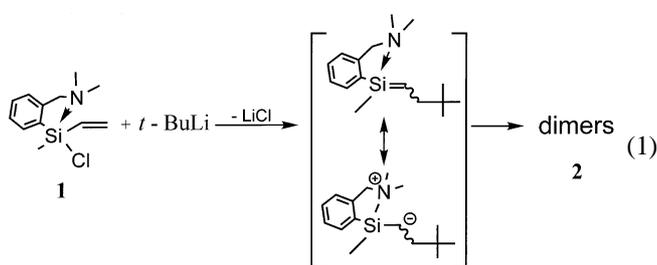
Introduction

Research on silenes has been the subject of considerable interest since 1967, when Gusel'nikov and Flowers presented the evidence for the first time that these species could exist.¹ They have frequently been postulated as reactive intermediates in the photolysis² and thermolysis of organosilicon compounds,³ usually on the basis of chemical trapping studies⁴ or matrix isolation spectroscopy,⁵ and several stable silenes have been synthesized.⁶ There have, however, been relatively few reports that describe the generation and reactivities of silene bearing intramolecular neutral donor atom. In 1992, Auner *et al.* reported that the reaction of amino-substituted chlorovinylsilane with *t*-BuLi generated pentacoordinated neopentylsilene which underwent the trimethylsilyl migration from N atom to the silenes carbon atom to give the diazasilacyclopentane containing Si-N bond without formation of dimer.⁷ Recently Oehme, *et al.* synthesized the intramolecularly donor-stabilized silene as a yellow crystalline from the reaction of dichloromethyltris(trimethylsilyl)silane with organolithium reagents.⁸

We report herein the generation and reactivities of 1-methyl-1-[(2-*N,N*-dimethylaminomethyl)phenyl]-2-neopentylsilene. Unexpected results regarding the reactivities of silene were encountered.

Results and Discussion

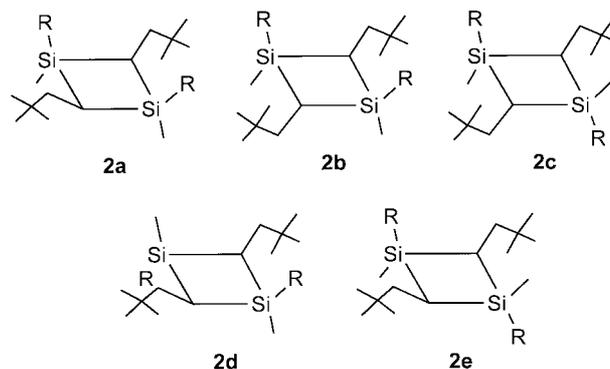
We prepared penta-coordinated organosilicon compound, [(2-*N,N*-dimethylaminomethyl)phenyl]methylvinylchlorosilane, **1** in 65% yield.⁹ Arylamino groups are well-known substituents for the syntheses of hypervalent silicon compounds and have also been introduced to stabilize the highly reactive silicon species such as silylenes, silanone and silathione through an intramolecular donor-acceptor interaction.¹⁰ The reaction of **1** with *t*-BuLi at -78 °C was carried out in hexane to generate the 1-methyl-1-[(2-*N,N*-dimethylamino-



methyl)phenyl]-2-neopentylsilene using β -elimination methods.¹¹

In the absence of trapping agents, the five isomeric 1,3-disilacyclobutanes, **2**, were obtained in 66% yield. The structures of these five isomers which were separated by prep. GC with TCD are illustrated in Chart 1.

We were able to identify compounds **2b**, **2e** separated fully and certify compounds **2c**, **2d** separated partly by comparison with **2b**, **2e** spectra. Unfortunately, we were not able to separate compound **2a** which was identified as using GC/MS because of very low yield. The stereochemical characterization of five disilacyclobutane isomers was a non-trivial problem. The ¹H-NMR spectra of the isomers, Table 1, provided little help in the resolution of this problem. Based on the symmetry of the isomers, **2b** is the only isomer which should have chemically non-equivalent neopentyl groups



R = (*N,N*-dimethylaminomethyl)phenyl

Chart 1

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Table 1. $^1\text{H-NMR}$ (C_6D_6 , 250 MHz) data for the dimers

ppm	2b	2c	2d	2e
SiCH ₃	0.85	0.87	0.74	0.87-1.00
CH ₂ (<i>t</i> -Bu)	1.68-1.88	1.50-1.88	1.63-1.98	1.80-2.06
C(CH ₃) ₃	0.81, 1.01	0.99	0.99	0.92
N(CH ₃) ₂	2.29	2.11	2.34	2.28, 2.33
CH ₂ N	2.79	3.69	3.78	3.66, 3.83

Table 2. $^{13}\text{C-NMR}$ (C_6D_6 , 63 MHz) data for the dimers

ppm	2b	2c	2d	2e
SiCH ₃	0.62	1.50	-3.71	-3.96, 7.11
C(CH ₃) ₃	29.30, 29.63	29.59	29.81	29.66
C(CH ₃) ₃	32.00, 32.15	31.96	32.15	32.03
CH ₂ (<i>t</i> -Bu)	39.78, 41.00	40.55	40.86	40.65
SiCHSi	13.04, 15.03	13.43	12.89	15.58
N(CH ₃) ₂	45.46	45.62	45.50	45.54, 45.81
CH ₂ N	65.12	65.25	65.10	65.10, 65.66

and **2e** is the only isomer which should have chemically distinct (*N,N*-dimethylaminomethyl)phenyl groups and silicon-methyl groups. On this basis **2b** and **2e** were tentatively assigned.

The $^{13}\text{C-NMR}$ spectra, Table 2, for the isomers provided the key to solve the problem. Based on the symmetry of the isomers, consideration of bulk shielding permitted the identification of these isomers. In **2e**, one of the silicon-methyls has a *Z* relationship to both neopentyl groups and is therefore the most shielded -3.96 ppm. Also, in **2d**, the chemical shift for these methyl groups shielded -3.71 ppm, in accord with the shielding effects of the two neopentyl groups. In **2b** and **2c**, methyl groups shielded by only one neopentyl group have midway chemical shifts between those observed for shielding by two neopentyl groups and no neopentyl group. Similarly, in **2b** the chemical shifts for methylene carbon of neopentyl groups 39.8 ppm, 41.0 ppm are consistent with the shielding effects of the two aryl groups and two methyl groups, respectively. In **2c** and **2e**, the shielding effect of methylene groups is midway comparing with those of **2b**.

To prove the mechanism for the formation of 1,3-disilacyclobutanes, trapping experiments of the silene or the α -lithiosilane were carried out using anthracene, 2,3-dimethyl-1,3-butadiene, Me₃SiOMe, and Me₃SiCl as trapping agents, but the corresponding silene-trapping adducts were not observed. Only five isomeric dimers were obtained.

The distribution ratios of dimers obtained from trapping experiments were different, which might be attributed to the

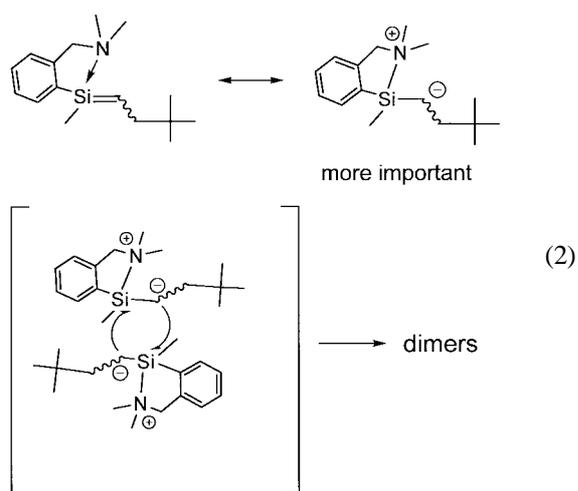
Table 3. The distribution ratio of dimers (GC area %)

Experiment	2a	2b	2c	2d+2e^a
Neat	1.00	4.49	8.41	11.85
2,3-dimethyl-1,3-butadiene	1.00	2.91	3.57	9.19
Anthracene in benzene	1.00	13.23	13.77	31.60
Me ₃ SiOMe	1.00	7.37	4.18	14.20
<i>n</i> -hexane-ether (8 : 3)	1.00	17.95	8.88	35.72

^aThe mixture of **2d** and **2e** is not separated by the GC column (HP-1, 15 m)

difference of trapping agents' polarity (Table 3).

Since it is doubtful that dimers might already be formed at -78 °C, the reaction of **1** with *t*-BuLi was quenched with MeOH after stirring at -78 °C for 2 h. We only obtained the methoxyated compound of **1**, which strongly indicates that no *t*-BuLi addition to vinyl group was occurred. From the controlled experiments, we found that the addition reaction was occurred at *ca.* -30 °C.



It is reasonable to explain the results of trapping experiments for the silene that one of resonance structures of the silene, zwitterionic species, strongly participates in the formation of dimers. (eq 2) It is thought that intramolecular donor atom might assist the generation of charge separated zwitterionic species^{7,12} that would be dimerized more easily than the corresponding silene. It is very likely due to the fact that negatively charged carbon atom of zwitterionic species than that of silene might attack the silicon atom of another zwitterionic species rapidly. In comparison, when donor-free 1-methyl-1-phenyl-2-neopentylsilene was generated in the presence of trapping agents, the corresponding silene-adducts were obtained in moderate yield.¹³

In summary, the reaction of [(2-*N,N*-dimethylaminomethyl)phenyl]methylvinylchlorosilane, **1** with *t*-BuLi in hexane solvent gave dimers, five isomeric 1,3-disilacyclobutanes which were separated and characterized, respectively. In trapping experiments with various trapping agents, no corresponding silene-trapping adduct was observed. We suggest that the key species for the formation of five isomeric dimers might be the zwitterionic species generated by virtue of intramolecular donor atom rather than the silene.

Experimental Section

General Procedure. In all reactions where air-sensitive chemicals were used, the reagents and solvents were dried prior to use. Hexane and ether were distilled over Na/Ph₂CO. Other starting materials were purchased in reagent grade and used without further purification. Experiments were performed with oven-dried glassware under nitrogen or argon using standard Schlenk techniques. ^1H and ^{13}C NMR spectra were

recorded on a Bruker DPX 250 FT-NMR spectrometer and Bruker AMX 500 NMR spectrometer and referenced to residual protons of the solvent with chemical shifts being reported as δ ppm. Analyses of product mixtures were accomplished using a HP 5890 II with FID (HP-1, 15 m column) and with TCD (OV-1, 1/8 inch 6 ft column). Mass spectra were recorded on a low resolution Shimadzu GCMS QP-2000A mass spectrometer and a high resolution VG ANALYTICAL 70-VSEQ mass spectrometer.

Synthesis of [(2-*N,N*-dimethylaminomethyl)phenyl]methylvinylchlorosilane, 1. To dichloromethylvinylsilane (13 mL, 0.10 mol) at 0 °C was added slowly 2-(*N,N*-dimethylaminomethyl)phenyllithium (14.1 g, 0.10 mol) in 200 mL of ether. The reaction mixture was stirred for about 12 hr at room temperature. After filtration of precipitated LiCl, volatiles were distilled under vacuum. The residue was distilled to yield chlorosilane, **1**. 16.4 g (70% yield). b.p. 88–92 °C (0.15 torr). MS: *m/z* (relative intensity) 239 (M^+ , 9.1), 224 (14.7), 212 (2.7), 204 (15.6), 196 (100), 159 (18.7). ^1H NMR (CD_2Cl_2 , 500 MHz): 0.80 (s, 3H), 2.17 (s, 6H), 3.50–3.67 (m, 2H), 5.82–6.47 (m, 3H), 7.19–8.31 (m, 4H) ^{13}C NMR (CD_2Cl_2 , 125 MHz): 2.9 ($\text{C}(\text{H}_3)\text{Si}$), 45.4 ($\text{N}(\text{C}(\text{H}_3)_2)$), 64.2 ($\text{C}(\text{H}_2)\text{N}$), 126.96, 126.99, 127.3, 130.5, 134.2, 137.9, 138.9, 145.4 (aryl and vinyl) HRMS: $\text{C}_{12}\text{H}_{18}\text{NSiCl}$ 239.0897 (calcd), 239.0907 (found).

Reaction of chlorosilane 1 with *t*-BuLi. To a stirred solution of 2.5 g (10 mmol) chlorosilane **1** in 100 mL of *n*-hexane cooled to -78 °C was added dropwise 6.5 mL (11 mmol) of *t*-BuLi diluted to 1.7 M in pentane. The reaction mixture was allowed to warm slowly to room temperature and then stirred for 24 h at room temperature. After quenching with saturated sodium chloride solution, the organic layer was separated, combined with ethyl ether extraction of the aqueous layer and dried over anhydrous sodium sulfate. After evaporation of the solvents using rotary evaporator, viscous yellow oil was obtained (66% yield).

1,3-bis[(2-*N,N*-dimethylaminomethyl)phenyl]-1,3-dimethyl-2,4-dineopentyl-1,3-disilacyclo-butane, **2**; MS: *m/z* (relative intensity) 135 (31.4), 204 (49.6), 246 (55.2), 260 (47.1), 420 (21.9), 462 (22.4), 465 (100), 507 (20.2), 522 (41.3). HRMS: $\text{C}_{32}\text{H}_{54}\text{N}_2\text{Si}_2$ 522.3826 (calcd), 522.3827 (found).

Reaction of *t*-BuLi with 1 in cosolvents. This experiment was run in the same manner as described above except using *n*-hexane-ether (8:3) cosolvents. The distribution ratio of dimers was similar in trapping experiment with methoxytrimethylsilane (Table 3).

Trapping experiment with methoxytrimethylsilane. To a stirred solution of 4.59 g (19.2 mmol) of the compound **1** and 10.4 g (100 mmol) of methoxytrimethylsilane in 150 mL of *n*-hexane cooled to -78 °C was added dropwise 11.5 mL (19.6 mmol) of *t*-BuLi diluted to 1.7 M in pentane. The reaction mixture was allowed to warm slowly to room temperature and then stirred for 24 hr at room temperature. Dimers which have different distribution ratios in neat experiment were obtained as a viscous yellow oil (Table 3).

Trapping experiment with 2,3-dimethyl-1,3-butadiene.

To a stirred solution of 4.80 g (20.1 mmol) of the compound **1** and 8.2 g (100 mmol) of 2,3-dimethyl-1,3-butadiene in 100 mL of *n*-hexane cooled to -78 °C was added dropwise 12.0 mL (20.4 mmol) of *t*-BuLi diluted to 1.7 M in pentane. The reaction mixture was allowed to warm slowly to room temperature and then stirred for 24 hr at room temperature. No corresponding silene-trapping adduct was obtained. Dimers and unreacted starting materials were obtained.

Trapping experiment with anthracene. To a stirred solution of 2.27 g (9.5 mmol) of the compound **1** and 5.1 g (28.6 mmol) of anthracene in 180 mL of benzene was added dropwise 6.0 mL (10.2 mmol) of *t*-BuLi diluted to 1.7 M in pentane. The reaction mixture was stirred for 24 hr at room temperature. No corresponding silene-trapping product was observed. Dimers and unreacted starting materials were obtained.

Trapping experiment with chlorotrimethylsilane. To a stirred solution of 12.0 mL (20.4 mmol) of *t*-BuLi diluted to 1.7 M in pentane cooled to -78 °C was added dropwise 4.50 g (18.8 mmol) of the compound **1** and 2.1 g (19.3 mmol) of chlorotrimethylsilane in 100 mL of *n*-hexane. No corresponding silene-trapping product was observed. Dimers and unreacted starting materials were obtained.

Trapping experiments with various trapping agents such as *t*-butyldiphenylimine, MeOH, NaOMe/MeOH and AcOH/MeOH. A solution of 2.1 g (8.8 mmol) of the compound **1** in 100 mL of hexane was treated dropwise at -78 °C with 6 mL (10.2 mmol) of *t*-BuLi (1.7 M in *n*-hexane). After the reaction mixture was allowed to warm slowly to 30 °C, 2.1 g (8.9 mmol) of *t*-butyldiphenylimine in 10 mL of hexane was dropped into reaction mixture. Only dimers and unreacted *t*-butylimine were obtained. The trapping experiments with various trapping agents such as MeOH, NaOMe/MeOH and AcOH/MeOH were carried out in the same manner as the trapping experiment with *t*-butyldiphenylimine. Each experiment gave only dimers and unreacted starting materials.

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