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Configurational Stability of [Di(amino)silyl]lithiums Having Cyclic Structures

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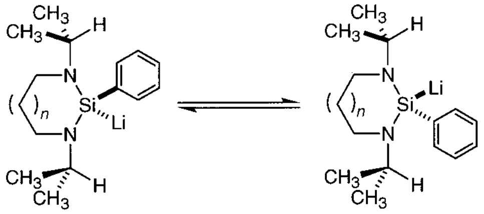
Summary: Cyclic diamino-substituted silyllithiums, [(N,N′-diisopropyldiamino)silyl]lithiums, were prepared by the reaction of lithium with the corresponding chlorosilanes. The methyls in the isopropyl groups are diastereotopic and anisochronous at room temperature in THF and in diglyme. Variable-temperature NMR experiments revealed that the configuration at the lithium-bearing silicon atom is stable up to 333 K in THF and 388 K in diglyme.

Introduction

Since the [(diethylamino)phenylsilyl]lithiums were reported as the first stable functionalized silyl anions in 1992,[1] their reactions,[1a,b] structures,[1c,d] and synthetic applications[1e,2] have continued to shed light on the nature of the amino-substituted silyl anions. Recently, Gehrhusand and Lappert's group[3] and West's group[4] reported the preparation of the amino-substituted disilanyl anion, disilanyl dianion, and silyl dianion, most of which are stable in solutions and could be analyzed by NMR spectroscopy and/or X-ray crystallography. Thus amino-substituted silyl anions now constitute a new family in the chemistry of stable silyl anions.

Among the characteristics of the [(amino)silyl]lithiums to be clarified, the configurational stability at the anionic silicon atom is essential since it should reflect the electronic state of the [(amino)silyl]lithiums. Lambert et al. revealed the configurational stability of [di(isopropyl)phenylsilyl]lithium using the diastereotopic methyls in the isopropyl groups as a probe for NMR experiments;[5] the silyllithium was configurationally stable at the lithium-bearing silicon atom even at 458 K in diglyme. From the observed chemical shift differences and the temperatures,[6] the lower limit to inversion about the trivalent silicon was estimated to be 24 kcal/mol. Several reports clarified that the optically active (triorganosilyl)lithiums were configurationally stable in keeping the optical purity at or below 0 °C.[7] There has been, however, no information on configurational stability of heteroatom-substituted silyl anions except for ab initio calculations reported by Hopkinson and Lien.[8] The calculations indicated that electronegative substituents on the silicon atom increased the inversion barrier of the silyl anions: the inversion barrier of an (amino)silyl anion, $(H_2N)H_2Si^-$, was estimated to be 42.8 kcal/mol. In contrast, a carbanion counterpart $(H_2N)H_2C^-$ has a much lower inversion barrier, which was calculated to be 11.0 kcal/mol.[9] Thus the α-amino-organolithium compounds have been known to be configurationally stable only at very low temperatures[10] (≤−78 °C) or in the presence of TMEDA.[11]

Scheme 1



1 ($n = 0$)
2 ($n = 1$)

To get experimental aspects of the configurational stability of amino-substituted silyllithiums, we have designed [di(amino)silyl]lithiums **1** and **2**, where an isopropyl group is bonded to each nitrogen atom and the two nitrogen atoms are linked to each other by an ethylene or propylene chain, based on Lambert's methodology, as shown in Scheme 1. Due to the planar geometry around the nitrogen atoms in an aminosilyllithium[1c] and the rigid cyclic system, the diastereotopic methyls in the isopropyl groups are expected to be a fine probe for the dynamic behavior at the silicon atom.

Results and Discussion

The preparation of the compounds are shown in Scheme 2. Phenyltrichlorosilane was allowed to react

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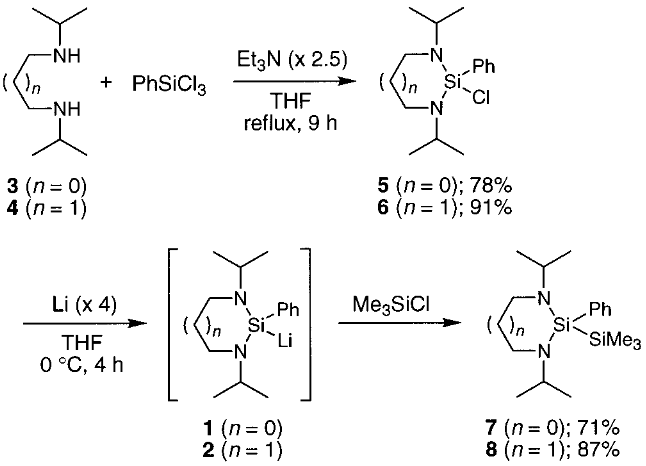
Scheme 2



with *N,N'*-diisopropyl-1,2-diaminoethane (**3**) and -propane (**4**) in THF in the presence of triethylamine, affording the di(amino)chlorosilanes **5** and **6**, respectively, in high yields. The methyl protons of the isopropyl groups are diastereotopic and appear as two sets of doublets: $\Delta\delta = 2.7$ Hz for **5** and 55.8 Hz for **6** in THF-d_8 at 293 K (270 MHz) (Figure 1).

The reaction of the chlorosilanes **5** and **6** with lithium (*granule*) gave the corresponding silyllithiums **1** and **2** in 71% and 87% yield, respectively (Scheme 2). The yields were determined by the isolation of **7** and **8** after trapping with trimethylchlorosilane. It was found that the di(amino)chlorosilanes **5** and **6** are more reactive than the acyclic analogue, bis(diethylamino)phenylchlorosilane, which requires a highly reactive lithium *dispersion* to give the corresponding silyllithium.[1a] The ^{29}Si resonances of **1** appeared at δ 17.6 and of **2** at δ 20.6, being resolved into quartet with $^{1}J[^{29}\text{Si}-^{7}\text{Li}] = 56.9$ Hz for **1** and 51.5 Hz for **2** in THF-d_8 at 173 K. Thus the silyllithiums **1** and **2** exist as monomers in THF solutions. The ^{29}Si resonances have downfield shifts compared to those of the corresponding chlorosilanes **5** at δ −18.6 and **6** at δ −27.0, which is a trend similar to the ^{29}Si resonance of the acyclic analogue, bis(diethylamino)phenylsilyllithium.[1c,d] As expected, the methyl protons of the isopropyl groups in **1** and **2** are diastereotopic and appear as two sets of doublets: $\Delta\delta = 27.5$ Hz in **1** and $\Delta\delta = 33.5$ Hz in **2** (Figure 1) in THF-d_8 at 293 K. The spectrum of **1** is much more noisy than that of **2** due to the lower yield of **1**.

To clarify the configurational stability of the [di(amiono)silyl]lithiums, we performed variable-temperature NMR experiments using **2**. The diastereotopic methyl protons in **2** were monitored by the ^{1}H NMR spectra in THF-d_8 up to 333 K, nearly the boiling point of the solvent, as shown in Figure 1. Although the shift difference, $\Delta\delta$, slightly decreased as the temperature was raised, the methyl groups still appeared as two sets of doublets ($\Delta\delta = 30.5$ Hz at 333 K). Thus the configuration at the lithium-bearing silicon atom in the [di(amino)silyl]lithium **2** is stable, and inversion is slow on the NMR time scale or may not occur in THF-d_8 up to 333 K.

Since the [di(amino)silyl]lithium **2** survived such high temperatures without significant decomposition, we next monitored the configurational stability of **2** at higher temperatures using diglyme as the solvent. After the silyllithium **2** was prepared in THF, the THF was removed in vacuo and diglyme was added to the residue, giving the solution of **2** in diglyme. The diastereotopic methyl protons displayed two distinct sets of signals in the ^{1}H NMR spectra up to 388 K, although the shift difference decreased as the temperature was raised ($\Delta\delta$ = 33.1 Hz at 293 K and 25.0 Hz at 388 K). The coalescence temperature could not be determined since the shape of signals became complicated above that temperature perhaps due to decomposition.

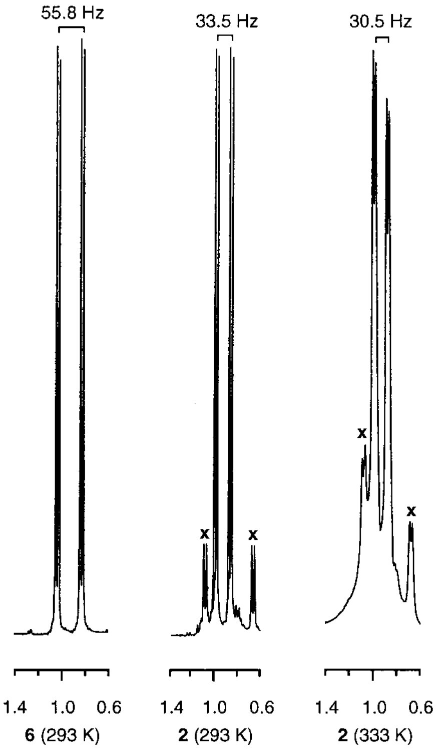


Figure 1. ^{1}H NMR spectra of the methyl protons of the isopropyl groups in **6** and **2** at different temperatures in THF-d_8; peaks marked with × are due to impurities.

Since the silyllithiums **1** and **2** exist as monomers in THF solutions[12] (and perhaps also in the more polar solvent, diglyme), we assumed a first-order process for the inversion[13,14] of the silyllithiums to estimate the inversion barrier at the silicon atom. The lower limit to the inversion of **2** was calculated to be 19.6 kcal/mol in diglyme.[15] Although the value seems to be underestimated in comparison with the calculated value (42.8 kcal/mol),[8] this is due to the limit of the thermal stability of **2** and the configurational stability may be comparable to that of the (triorganosilyl)lithiums.[5,7]

In conclusion, we prepared the cyclic diamino-substituted silyllithiums, [(*N,N'*-diisopropyldiamino)silyl]lithiums, where the methyls in the isopropyl groups

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[12] It has been reported that almost all of the silyllithium compounds exist as monomers in THF solutions, see: Tamao, K.; Kawachi, A. *Adv. Organomet. Chem.* **1995**, *38*, 1, and references therein.

[13] $\Delta G^{\ddagger}$(cal/mol) = $4.57T_c(10.32 + \log T_c - \log(\pi(\Delta\nu)/\sqrt{2}))$, where T_c = the coalesce temperature (K) and $\Delta\nu$ = the chemical shift difference (Hz). Günther, H. In *NMR Spectroscopy*, 2nd ed.; John Wiley & Sons: Chichester, 1995; Chapter 9.

[14] In contrast, aggregation states are considered to play an important role in the inversion process of organolithium compounds, see: Hæffner, F.; Brinck, T. *Organometallics* **2001**, *20*, 5134, and references therein.

[15] Since we could not observe the coalescence, we tentatively used the upper limit of the observed temperatures, 333 K in THF-d_8 and at 388 K in diglyme, according to the Lambert's procedure; see ref 5.

are diastereotopic and anisochronous at room temperature in THF and in diglyme. We could experimentally confirmed that the [di(amino)silyl]lithium is configurationally stable, as well as chemically stable, up to 333 K in THF-d_8 and 388 K in diglyme.

Experimental Section

General Remarks. The ^{1}H (270 MHz), ^{13}C (67.9 MHz), and ^{29}Si (53.7 MHz) NMR spectra were recorded on a JEOL EX-270 spectrometer, or ^{1}H (300 MHz) and ^{13}C (75.4 MHz) NMR spectra were recorded on a Varian Mercury 300 spectrometer. The dynamic ^{1}H NMR experiments were performed on a JEOL EX-270 spectrometer attached to a variable-temperature controller. The ^{1}H and ^{13}C chemical shifts were referenced to internal benzene-d_6 (^{1}H δ 7.200 ppm; ^{13}C δ 128.0 ppm) or THF-d_8 (^{1}H δ 1.70 ppm), and the ^{29}Si chemical shifts were referenced to external Me_4Si (^{29}Si δ 0.0 ppm). The mass spectra (EI) were measured at 70 eV on a JEOL JMS-DX300 mass spectrometer. The elemental analyses were performed at the Microanalysis Division of the Institute for Chemical Research, Kyoto University. Since the diaminosilane compounds except for **6** gave no satisfactory analysis data even after many trials due to their moisture sensitivity, they were analyzed by high-resolution mass spectroscopy (HRMS).

Triethylamine was distilled under a nitrogen atmosphere over calcium hydride. THF was distilled under a nitrogen atmosphere over sodium benzophenone ketyl. THF-d_8 was distilled under a nitrogen atmosphere over Na/K alloy. *N,N′*-Diisopropyl-1,2-diaminoethane (**3**) and -propane (**4**) were purchased from Aldrich Chemical Co. and used as received. All reactions were carried out under an inert atmosphere.

2-Chloro-2-phenyl-1,3-diisopropyl-1,3-diaza-2-silacyclopentane (5). A solution of **3** (3.2 mL, 20 mmol) was slowly added to a suspension of $PhSiCl_3$ (3.6 mL, 20 mmol) and triethylamine (7.0 mL, 50 mmol) in THF (67 mL) at 0 °C over 0.5 h. The reaction mixture was allowed to warm to room temperature and refluxed for 9 h. The resulting $Et_3N{\cdot}HCl$ was removed by filtration. The filtrate was evaporated, and the residue was diluted with hexane (30 mL) and filtered. The filtrate was concentrated, and the residue was subjected to bulb-to-bulb distillation under reduced pressure (105−115 °C/0.5 mmHg (bath temeprature)) to give **5** (4.42 g, 78% yield) as a colorless oil. ^{1}H NMR (THF-d_8, 293 K): δ 1.03 (d, J = 6.2 Hz, 6H), 1.04 (d, J = 6.2 Hz, 6H), 3.08−3.21 (m, 6H), 7.35−7.38 (m, 3H), 7.77−7.81 (m, 2H). ^{13}C NMR (C_6D_6): δ 22.38, 44.53, 47.30, 128.09, 130.73, 135.48, 136.09. ^{29}Si NMR (THF-d_8, 293 K): δ 18.6. MS: *m*/*e* 282 (M^+), 269, 267, 141, 126. HRMS: calcd for $C_{14}H_{23}N_2SiCl$, *m*/*e* 282.1319; found, *m*/*e* 282.1333.

2-Chloro-2-phenyl-1,3-diisopropyl-1,3-diaza-2-silacyclohexane (6). This compound was prepared from $PhSiCl_3$ and **4** in the same manner as above in 91% yield as a colorless oil. Bp: 125−135 °C/0.5 mmHg (bath temperature). ^{1}H NMR (THF-d_8, 293 K): δ 0.84 (d, J = 6.8 Hz, 6 H), 1.04 (d, J = 6.8 Hz, 6H), 1.83−1.98 (m, 2H), 2.89−3.01 (m, 4H), 3.05 (septet, J = 6.5 Hz, 2H), 7.33−7.38 (m, 3H), 7.77−7.81 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 20.25, 20.59, 30.00, 39.81, 45.90, 127.44, 130.05, 134.13, 135.19. ^{29}Si NMR (THF-d_8, 293 K): δ −27.0. MS: *m*/*e* 296 (M^+), 281, 261, 224. Anal. Calcd for $C_{15}H_{25}N_2SiCl$: C, 60.68; H, 8.49; N, 9.43. Found: C, 60.60; H, 8.67; N, 9.59.

Preparation of 2-Lithio-2-phenyl-1,3-diisopropyl-1,3-diaza-2-silacyclopentane (1). A solution of **5** (141 mg, 0.5 mmol) in THF-d_8 (0.3 mL) was added dropwise to a suspension of granular lithium (17 mg, 2.5 mg-atom) in THF-d_8 (1.0 mL) at 0 °C. The resulting greenish mixture was stirred at 0 °C for 4 h to give a solution of **1** (ca. 0.3 M estimated from the yield of **7**, see below). For the NMR measurement, the solution was transferred to an NMR tube via a Teflon tube under an argon atmosphere. ^{1}H NMR (THF-d_8, 293 K): δ 0.91 (d, J = 6.2 Hz, 6H), 1.01 (d, J = 6.2 Hz, 6H), 2.99−3.19 (m, 6 H), 7.28−7.32 (m, 3H), 7.56−7.59 (m, 2H). ^{29}Si NMR (THF-d_8, 173 K): δ 17.6 (q, $^1J[^{29}Si-^7Li]$ = 56.9 Hz).

Preparation of 2-Lithio-2-phenyl-1,3-diisopropyl-1,3-diaza-2-silacyclohexane (2). A solution of **6** (148 mg, 0.5 mmol) in THF-d_8 (0.2 mL) was added dropwise to a suspension of granular lithium (17 mg, 2.5 mg-atom) in THF-d_8 (1.0 mL) at 0 °C. The resulting greenish mixture was stirred at 0 °C for 4 h to give a solution of **2** (ca. 0.3 M estimated from the yield of **8**, see below). For the NMR measurements, the solution was transferred to an NMR tube via a Teflon tube under an argon atmosphere. ^{1}H NMR (THF-d_8, 293 K): δ 0.86 (d, J = 6.8 Hz, 6H), 0.99 (d, J = 6.8 Hz, 6H), 1.87−1.91 (m, 2H), 2.85−3.02 (m, 6H), 7.28−7.31 (m, 3H), 7.56−7.60 (m, 2H). ^{1}H NMR (diglyme, 293 K): δ 0.80 (d, J = 6.8 Hz, 6H), 0.92 (d, J = 6.8 Hz, 6H), 1.80−1.85 (m, 2H), 2.80−2.93 (m, 6H), 7.22−7.28 (m, 3H), 7.47−7.53 (m, 2H). ^{29}Si NMR (THF-d_8, 173 K): δ 20.6 (q, $^1J[^{29}Si-^7Li]$ = 51.5 Hz).

2-Trimethylsilyl-2-phenyl-1,3-diisopropyl-1,3-diaza-2-silacyclopentane (7). A solution of **5** (566 mg, 2.0 mmol) in THF (3.0 mL) was added dropwise to a suspension of granular lithium (69 mg, 10 mg-atom) in THF (3.0 mL) at 0 °C. After the resulting greenish mixture was stirred at 0 °C for 4 h, the solution was transferred to a precooled reaction flask via a Teflon tube under an argon atmosphere. Trimethylchlorosilane (0.30 mL, 2.4 mmol) was added to the reaction mixture at 0 °C, and the mixture was stirred overnight at ambient temperature. The reaction mixture was then filtered, and the filtrate was evaporated. The residue was diluted with hexane (5 mL) and filtered. The filtrate was concentrated and the residue was subjected to bulb-to-bulb distillation under reduced pressure (122−140 °C/0.4 mmHg (bath temperature)) to give **7** (452 mg, 71% yield) as a colorless oil. ^{1}H NMR (C_6D_6): δ 0.43 (s, 9H), 1.00 (d, J = 6.5 Hz, 6H), 1.10 (d, J = 6.5 Hz, 6H), 2.95−3.26 (m, 6H), 7.28−7.30 (m, 3H), 7.80−7.83 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 0.15, 22.68, 23.22, 44.80, 46.83, 128.00, 129.80, 134.76, 142.18. MS: *m*/*e* 320 (M^+), 305, 247. HRMS: calcd for $C_{17}H_{32}N_2Si_2$, *m*/*e* 320.2104; found, *m*/*e* 320.2110.

2-Trimethylsilyl-2-phenyl-1,3-diisopropyl-1,3-diaza-2-silacyclohexane (8). This compound was prepared in the same manner as above from **6** (594 mg, 2.0 mmol) as a colorless oil (579 mg, 87% yield). Bp: 125−135 °C/0.5 mmHg (bath temperature). ^{1}H NMR (C_6D_6): δ 0.45 (s, 9H), 0.84 (d, J = 6.3 Hz, 6H), 1.08 (d, J = 6.3 Hz, 6H), 1.65−1.83 (m, 2H), 2.92 (t, J = 6.0 Hz, 4H), 3.06 (septet, J = 6.3 Hz, 2H), 7.28−7.32 (m, 3H), 7.81−7.84 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 0.40, 20.36, 21.48, 30.91, 40.06, 46.18, 127.14, 128.88, 134.50, 141.97. MS: *m*/*e* 334 (M^+), 261. HRMS: calcd for $C_{18}H_{34}N_2Si_2$, *m*/*e* 334.2261; found, *m*/*e* 334.2274.

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