

Thermal decomposition of $[\text{Me}_3\text{SiNCH}_2\text{CH}_2\text{NSiMe}_3] \cdot \text{Li}_2(\text{THF})_2$ to $[\text{LiN}(\text{SiMe}_3)_2 \cdot \text{THF}]_2$ via a 1,4-trimethylsilyl shift

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Received 29 January 1997

Abstract

The dilithium salt $[\text{Me}_3\text{SiNCH}_2\text{CH}_2\text{NSiMe}_3] \cdot \text{Li}_2(\text{THF})_2$ decomposes slowly upon heating forming a metastable structure of the crystalline $[\text{LiN}(\text{SiMe}_3)_2 \cdot \text{THF}]_2$. The crystal structure of the new form was established by single crystal X-ray diffraction showing a decrease in the *a* and *b* parameter values of the unit cell, and an expansion of the *c* value as compared with the structure obtained at room temperature. The major discrepancies among the known and the metastable crystalline framework are the Li–O bond length and the dihedral angle disposition of the trimethylsilyl groups as regarded to the middle Li–N–Li–N heterocyclobutane ring. Attempts to trap the expected additional lithium imine product were unsuccessful although quenching experiments produced polyethyleneimine. © 1997 Elsevier Science S.A.

Keywords: Lithium amide; X-ray crystal structure; Polyethyleneimine; TMS-shift

1. Introduction

Organonitrogen–lithium compounds, and particularly lithium amides (R_2NLi), are widely used in organic and organometallic syntheses. For the former, these strong bases are used as proton abstractors in the formation of ketone enolates, generating low steady-state concentration of some relatively unstable carbanions and for the preparation of heterocyclic thiazenes incorporating a RCN moiety using lithium amidinates [1–10]. For the later, these strong bases are used normally as halogen abstractors in the synthesis of transition metal amido-complexes [11]. The coordination chemistry of organolithium amido complexes and the mechanism of the organolithium-base reactions are uncommonly complex and poorly understood. This complexity stems from the high tendency to self assemble into higher aggregates which is considerably dependent on the solvent and precise preparation conditions [12]. We recently reported the use of $[\text{Me}_3\text{SiNCH}_2\text{CH}_2\text{NSiMe}_3] \cdot \text{Li}_2(\text{THF})_2$ as ancillary ligands for the preparation of group IV amido complexes such as $\text{Cp}_2\text{Zr}[\text{N}(\text{SiMe}_3)\text{CH}_2\text{CH}_2\text{N}(\text{SiMe}_3)]$, $\text{Zr}[\text{N}(\text{SiMe}_3)\text{CH}_2\text{CH}_2\text{N}(\text{SiMe}_3)]_2$,

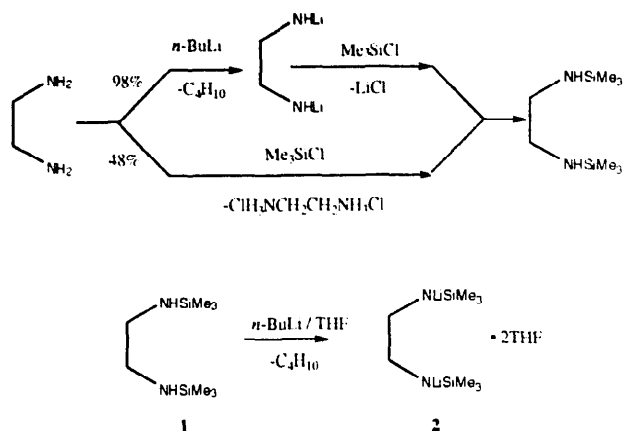
$\text{Cl}_2\text{Zr}[\text{N}(\text{SiMe}_3)\text{CH}_2\text{CH}_2\text{N}(\text{SiMe}_3)]$, and $\text{Cl}_2\text{Ti}[\text{N}(\text{SiMe}_3)\text{CH}_2\text{CH}_2\text{N}(\text{SiMe}_3)]$. These complexes were shown to be active catalysts for the polymerization of α -olefins. Interestingly, in all the catalysts synthetic preparations, the overall yields were among 45–60% regardless the use of either the solvated or the plain group IV chloride salts [13]. To increase the overall yield of the reactions, we decided to purify the lithium amide salt by slow sublimation in high vacuum as a facile technique for lithium containing trimethylsilyl groups purification [14]. Here, we report the thermal decomposition of $[\text{Me}_3\text{SiNCH}_2\text{CH}_2\text{NSiMe}_3] \cdot \text{Li}_2(\text{THF})_2$ to form a high temperature metastable¹ structure of the known crystalline complex $[\text{Li}(\text{NSiMe}_3)_2 \cdot \text{THF}]_2$ [15], together with a highly polydisperse polyethyleneimine.

2. Results and discussion

The dilithium ligand $[\text{Me}_3\text{SiNCH}_2\text{CH}_2\text{NSiMe}_3] \cdot \text{Li}_2(\text{THF})_2$ (**2**) has been synthesized from the corre-

¹ The term metastable is used to indicate that dissolving and recrystallizing the high temperature obtained crystals, the same crystalline material as obtained by Engelhardt et al. is obtained [15].

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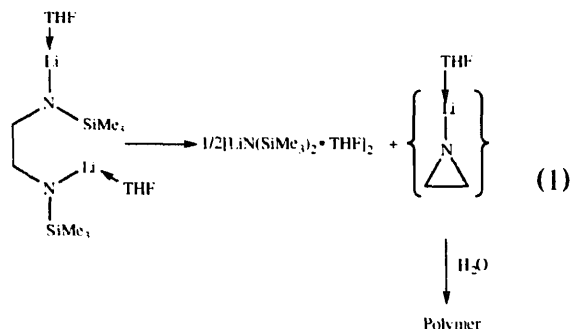


Scheme 1. Alternative synthetic pathways for the preparation of **1** and **2**.

sponding *N,N*-disilylethylene diamine, $(\text{Me}_3\text{Si})\text{NH}-\text{CH}_2\text{CH}_2\text{NH}(\text{SiMe}_3)$, (**1**) and BuLi in THF. Compound **1** can be easily prepared either as reported in the literature (48%) [16–18] or by a double lithiation pathway (80%) as shown in Scheme 1.

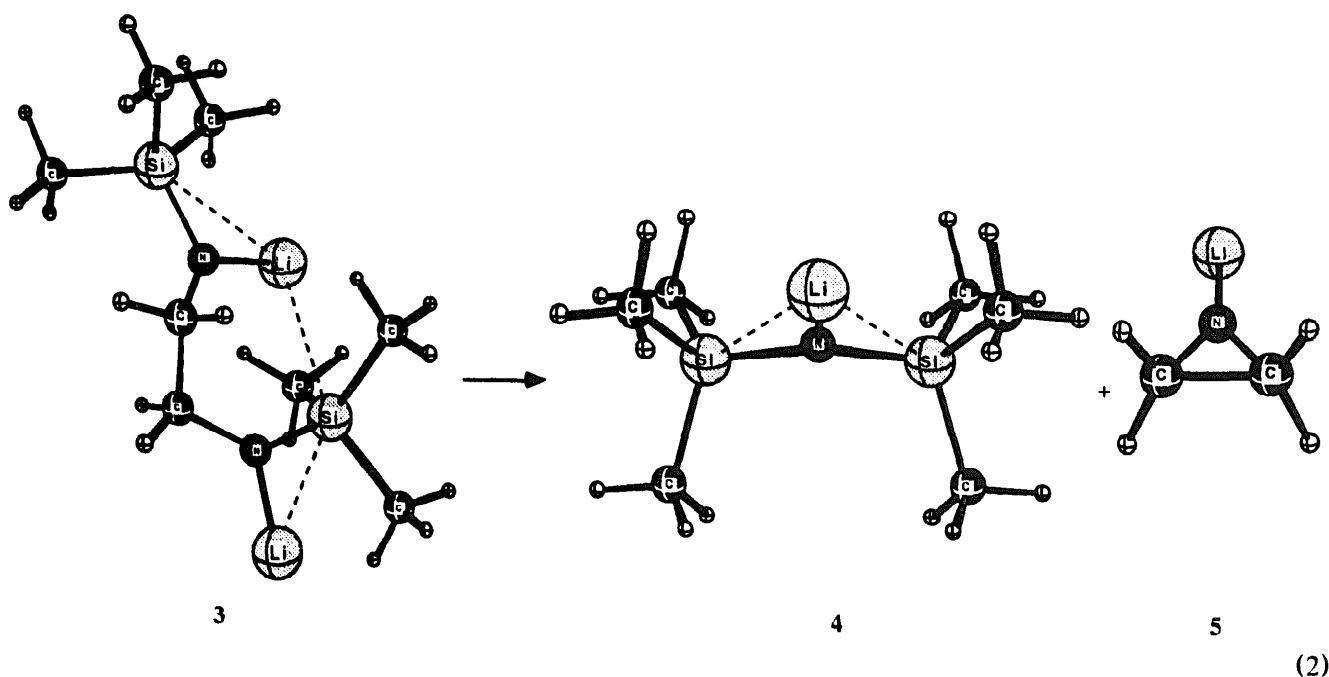
The dilithium salt **2** was found to decompose slowly upon heating to 150°C, producing as a sublimation product the lithium amide complex, $[\text{LiN}(\text{SiMe}_3)_2 \cdot \text{THF}]_2$, and presumably the corresponding lithium imine for which efforts to isolate were unsuccessful (Eq. 1). Quenching of the non-sublimable residue, with water, affords the exothermic formation of a mixture of polyethyleneimine polymers. Theoretically, the thermal decomposition of **2** involves the cleavage of a Si–N and C–N bonds, and formation of also a N–C and one N–Si bond. The enthalpy change for this reaction can be estimated to be close to $\Delta H \approx 0$ based on simple bond disruption energy values, without taking into account the destabilization strain energy necessary to obtain the

imine ring, or the stabilization energy obtained by the interactions of the Li atoms with the trimethylsilyl groups or the solvent THF [19–24].



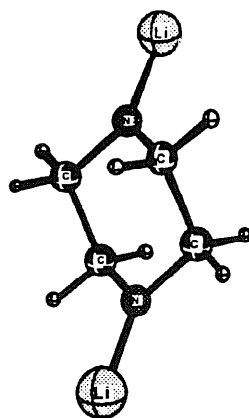
Thus, seems plausible to conclude that the driving force for this process is entropic. To support this hypothesis, semi-empirical and ab-initio calculations were performed for the solvated and non-solvated molecules, respectively, as described in Eqs. 1 and 2. The solvated molecules in Eq. 1 were optimized at the MNDO level of theory and energies for the reaction were calculated at the same level (instead of the dimer salt, the calculations were performed in the solvated monomeric structure). SPARTAN was used for all semi-empirical calculations [25]. The MNDO enthalpy of the reaction for the solvated system as described in Eq. 1 was found to be endothermic by 22.06 kcal/mol. Interestingly, calculating the similar solvated system, as described in Eq. 1, but eliminating the aziridine strain ring energy by calculating half of the energy of the solvated dilithiated piperazine, the enthalpy of the reaction was reduced to the endothermic value of 2.83 kcal/mol.

The ab-initio calculations were performed in the non-solvated systems as described in Eq. 2.



(2)

Molecules **3–5** were optimized at the B3LYP level of theory with 3–21 + G* basis set. The enthalpy of the reaction was calculated at B3LYP/3–21 + G* // B3LYP/3–21 + G* level of theory. Gaussian 94 series of program was used for ab-initio calculations [26]. The ab-initio enthalpy of the reaction as described in Eq. 2 was calculated to be endothermic by 28.01 kcal/mol. By reducing the strain ring energy by calculating, instead of the lithium imine (**5**), half of the energy for molecule **6**,



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the enthalpy of reaction for Eq. 2 was calculated to be exothermic by -1.12 kcal/mol. Hence, both semi-empirical and ab-initio calculations shows that entropic considerations are the major driving force for the decomposition of compound **2**.

X-ray analysis of a sublimed crystal shows that under the heating procedure, a metastable crystalline form of the lithium salt $[\text{LiN}(\text{SiMe}_3)_2 \cdot \text{THF}]_2$ (**3**) was produced.² Interestingly, the crystal structure obtained for complex **3** (Fig. 1) is almost identical with the previously solved structure [15]. The major differences among the two structures are given in Table 1. Thus, a larger Li–O distance [$1.960(2)$ Å] is obtained in the metastable compound which is comparable as in the dimeric ether solvated structure of $[\text{LiN}(\text{SiMe}_3)_2 \cdot \text{OEt}]_2$ [27,28]. This difference is formed because of the difference in the torsion angle of the Me_3Si groups, preventing the solvent to approach closer to the lithium atom and causing a shrinkage of the *a* and *b* cell parameter

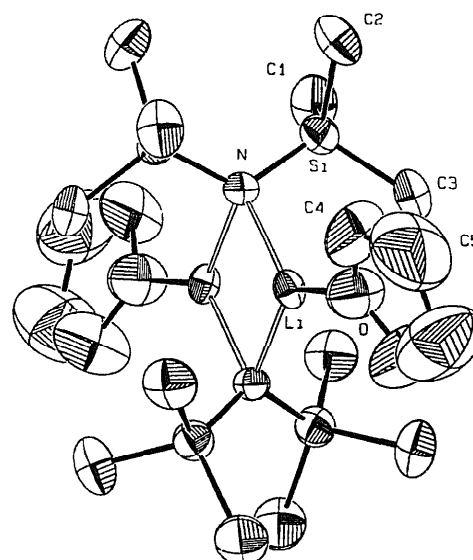
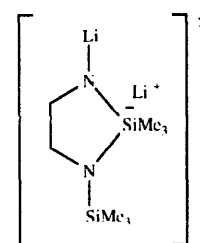


Fig. 1. ORTEP drawing of the molecular structure of $[\text{LiN}(\text{SiMe}_3)_2 \cdot \text{THF}]_2$. Thermal ellipsoids are shown at the 40% probability level.

values and increasing the *c* value by 0.372 Å. The most striking fact comparing both structures is the identical dihedral angle disposed by the THF molecules. Thus, the angle of 156.9° in both molecules resemble a minimum energy regarding the interactions of the planar N–Li–N–Li (0.0°) cyclobutane environment with the solvent.

Mechanistically, the Me_3Si group shift from a nitrogen atom to another nitrogen atom is a well known nucleophilic process involving, normally, a hypervalent silicon intermediate or transition state [29]. Based on similar systems, the hypervalent silicon complex **7** can be proposed as the transition state for Eq. 1 [30]. (Ab-initio calculations shows that a model complex of **7** does not exist as a minimum on the potential energy surface calculated with a MP2 level of theory).



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Our efforts to trap the expected lithium imine product were unsuccessful although quenching experiments with water resulted in the well known, base-induced polymerization of imines. The characterization of this polyethyleneimine by product was determined, as described in the literature, either by titration or spectrometrically [31].

² Crystal structure analysis of $[\text{LiN}(\text{SiMe}_3)_2 \cdot \text{THF}]_2$. Crystal data: $\text{C}_{20}\text{H}_{32}\text{Li}_2\text{N}_2\text{O}_2\text{Si}_4$, $M = 478.88$, tetragonal space group $P4n2$, $a = 9.3820(10)$, $c = 17.125(2)$ Å, $V = 1507.4(3)$ Å³, $Z = 2$, $D_c = 1.055$ mg/m³, $F(000) = 528$, 703 unique reflections ($R(\text{int}) = 0.0277$), refinement method = full-matrix least-squares on F^2 , GOF = 1.042, $R1 [I > 2\sigma(I)] = 0.0563$, $wR2$ (all data) = 0.1188. Absolute structure parameter 0.2(6), largest diff. peak and hole = 0.154 and -0.136 e Å⁻³.

Table 1
Comparison parameters for the two forms of $[\text{LiN}(\text{SiMe}_3)_2 \cdot \text{THF}]_2$

| Parameter | $[\text{LiN}(\text{SiMe}_3)_2 \cdot \text{THF}]_2$ | meta. $[\text{LiN}(\text{SiMe}_3)_2 \cdot \text{THF}]_2$ (3) |
|---|--|--|
| <i>a</i> (Å) | 9.970(1) | 9.382(1) |
| <i>c</i> (Å) | 16.753(1) | 17.125(1) |
| Space group | $P\bar{4}n2$ | $P\bar{4}n2$ |
| Volume (Å ³) | 1665 | 1507 |
| Density (calculated) (mg/m ³) | 0.954 | 1.055 |
| Temperature (K) | 295 | 223(2) |
| Li–O (Å) | 1.884(2) | 1.960(2) |
| Li–N–Si–C3 | 65.5 | 70.2 |

In conclusion, the shift of Me_3Si groups in a 1,4-dinitrogen system is an easy thermal decomposition pathway. $[\text{Me}_3\text{SiNCH}_2\text{CH}_2\text{NSiMe}_3] \cdot \text{Li}_2(\text{THF})_2$ gave $[\text{LiN}(\text{SiMe}_3)_2 \cdot \text{THF}]_2$ as the decomposition product. The expected lithium imine by-product remains evasive, but a polymerization-quenched polymer was trapped. The high temperature decomposition of complex **2** allowed the formation of a metastable structure with no monomeric or non-solvated co-products.

3. Experimental

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual manifold Schlenk line, or interfaced to a high vacuum (10^{-5} Torr) line, or in a nitrogen-filled 'Vacuum Atmospheres' glove box with a medium capacity recirculator (1–2 ppm O_2). Argon, and nitrogen gases were purified by passage through a MnO oxygen-removal column and a Davison 4 Å molecular sieve column. Ether solvents (THF-*d*8) were distilled under argon from sodium benzophenone ketyl. Hydrocarbon solvents (benzene-*d*6) were distilled under nitrogen from Na/K alloy. All solvents for vacuum line manipulations were stored in vacuo over Na/K alloy in resealable bulbs. NMR spectra were recorded on Bruker AM 200 spectrometer. Chemical shifts for ¹H NMR and ¹³C NMR are referenced to internal solvent resonances and are reported relative to tetramethylsilane. The NMR experiments were conducted in teflon valve-sealed tubes (J-Young) after vacuum transfer of the liquids in a high-vacuum line. *n*-BuLi (solution in hexane) was purchased from Aldrich. $[(\text{Me}_3\text{Si})\text{NHCH}_2\text{CH}_2\text{NH}(\text{SiMe}_3)]$, $[\text{Me}_3\text{SiNCH}_2\text{CH}_2\text{NSiMe}_3] \cdot \text{Li}_2(\text{THF})_2$ were prepared according to published procedures [14]. The polyethyleneimine analysis of the obtained polymer was characterized according to published procedures [31].

3.1. Thermal decomposition

Into a glove box, a sublimator equipped with a J-Young interface valve was charged with 3.2 g (8.46 mmol) of the ligand **2** and connected to the high vacuum line. The line was pumped and back-filled with argon three times before the interface valve was opened. The system was pumped off to 1×10^{-5} mm Hg and slowly heated in an oil bath maintained at 150°C for 48 h. A mixture of a crystalline and powder material start to be deposited at the cold finger slowly yielding 0.5 g (25%) of the decomposition product.

3.2. X-ray analysis

Owing to the extreme sensitivity of the expected dilithium starting complex toward moisture and oxygen, a suitable sublimed crystal for X-ray analysis was covered with Kel-F oil (Voltalef) inside a glove box and then mounted on the diffractometer where it was held in a cold stream of nitrogen at 223 K. Reflections were collected on an Enraf-Nonius CAD4 diffractometer with graphite monochromatized Mo- K_{α} radiation ($\lambda = 0.71073$ Å). Cell data were based upon setting angles of 25 reflections with $6 < \theta < 17^\circ$.

Structure solution was accomplished with the SHELXS 86 [32] program with direct method. Structure refinement was completed with the SHELXL 93 [33] program. Hydrogen atoms were fixed at idealized positions. An empirical absorption correction (DIFABS [34]) was applied. For the graphic representation the program ZORTEP [35] was used. Additional material deposited at the Cambridge Crystallographic Data Center includes final atomic coordinates, thermal parameters, list of bond angles and bond lengths, hydrogen coordinates and F_{obs} and F_{calc} .

Acknowledgements

This research was supported by the Technion V.P.R. Fund Promotion of Sponsored Research. H.M. thanks the Max-Planck-Gesellschaft for a MINERVA post-doctoral fellowship. The authors thank the Minerva Center for Computational Quantum Chemistry, Technion, Haifa, for computational time and Professor Y. Apeloig.

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