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Dianion Aggregates Derived from Lithiation of *N*-Silyl Allylamine

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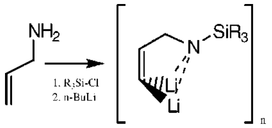
ABSTRACT

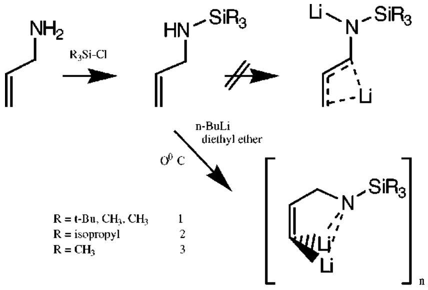


Three different *N*-silyl-protected allylamines, i.e., *N*-TMS, *N*-TBDMS, and *N*-TIPS allylamine, were lihtiated by reaction with excess *n*-butyllithium. Crystallization of the resulting dianions and X-ray structure determination yields three uniquely different aggregates.

Treatment of allyl alcohol and allylamine derivatives with strong base effects reactions in which synthetically useful allyl anions are formed. For example, deprotonation of allyl ethers leads to a Wittig rearrangement.[1] *O*-Indenyl carbamates react with *n*-butyllithium and electrophiles at either the carbon adjacent to the heteroatom or at the carbon γ to the heteroatom to yield enol ether or substituted allyl derivatives.[2] Recent attention has been directed toward developing the chemistry of chiral allyllithium complexes either with covalently attached chiral auxiliaries[3] or with the bis-chelating ligand sparteine.[4] A model for predicting the stereochemical course of the reactions of these chiral carbanion complexes was derived from X-ray diffraction analysis.[5]

An alternative to allylic deprotonation is observed with secondary allylamines. This reaction is observed exclusively upon reaction of *N*-monoalkyl and *N*-silyl allylamine with alkyllithium reagents as depicted in Scheme 1. Several examples of this vinylic anion forming reaction are documented.[6] The vinyllithium reagents generated in this reaction are necessarily formed as dianions with *Z* stereochemistry exclusively. These *Z*-vinyllithium reagents react with various

Scheme 1



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electrophiles to produce a wide variety of heterocyclic compounds, including borazoles, silylazoles, benzazepines, indoles, and pyrroles.[7]

Corriu et al. first noted the relatively mild conditions, i.e., 0 °C, diethyl ether, *n*-BuLi, required to form the dianion of *N*-trimethylsilyl (TMS) allylamine. Hence, we set out to generate the dianion of *N*-TMS allylamine and to crystallize it in an attempt to determine the aggregation state, the coordination number, and the geometry of the anionic centers in these species. In so doing we have discovered three novel and unique aggregates derived from the dianions of *N*-trimethylsilyl, *N*-triisopropylsilyl, and *N*-*tert*-butyldimethylsilyl allylamines (**1**−**3**).

The mono-*N*-silyl amines depicted in Scheme 1 were prepared in one step from allylamine and the trialkylsilyl chlorides. Reaction of these amines dissolved in diethyl ether under identical conditions with slightly more than 2 equiv of *n*-butyllithium yielded the dianions **1**−**3**. Formation of the dianions was established by quenching the reaction mixtures with D_2O followed by analysis of the product for deuterium incorporation. In all cases, GC-MS analysis revealed >90% deuterium incorporation at the terminal vinylic position. Solutions of the dianions were allowed to stand for an extended period ranging from overnight to several days at −20 °C, and crystalline material directly suitable for X-ray diffraction analysis was obtained reproducibly in varying yields from 20 to 50%. Quite surprisingly, each of the dianions **1**−**3** was obtained in a different and wholly unique aggregation state despite the fact that the only differences among the separate reactions are the alkyl groups attached to the silicon.

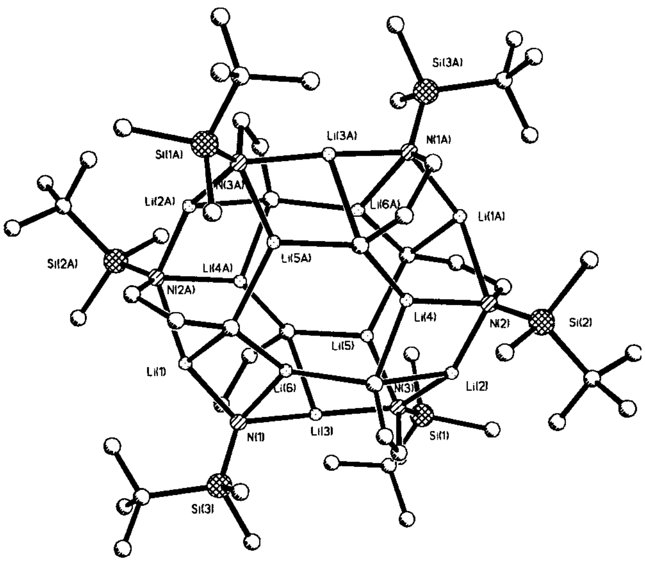

Figure 1. The hexameric aggregate of the lithium dianion **1** derived from *tert*-butyldimethylsilylallylamine showing only the aggregate core.

The *tert*-butyl dimethyl silyl (TBDMS) substituted dianion **1** crystallizes as the hexamer depicted in Figure 1.[8] Note that the hydrogen atoms are not shown in this or any other crystal structure plots for clarity. The key infrastructure in this aggregate is a central hexagonal prismatic core made up of six lithiums and the terminal vinylic carbon atom of six allylamines. This hexagonal prismatic core in this aggregate was found in structures of cyclohexyllithium,[9] susbtututed cyclopropyllithium,[10] and lithium imines.[11] This aggregate is by far the most intricate of this type reported to date.

If the TBDMS group is replaced with triisopropyl (TIPS), the dianion **2** crystallizes as the tetrameric aggregate depicted

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(8) X-ray data were collected in 0.3° steps on a four-circle diffractometer in the ϕ-scan mode equipped with a Bruker SMART CCD 1K detector (Mo K_ radiation, $\lambda = 0.71073$ Å). All structures were solved by direct methods and refined with full matrix least squares on all reflections based on F2 using the SHELXTL programs commerically available from Bruker Analytical Instruments. Crystallographic data follows. (a) Hexameric aggregate derived from the TBDMS-allylamine anion **1**: crystallographic asymmetric unit $[C_9H_{19}Li_2NSi]_3$; $M_r = 549.67$; clear, colorless crystal of dimension 0.3 × 0.4 × 0.45 mm mounted on a quartz fiber under a stream of dry N_2 gas at −40 °C; monoclinic space group $P2_1/n$; $a = 14.20$ (0.10), $b = 12.65$ (0.9), and $c = 20.61$ (0.13) Å, $\beta = 100.32$ (3)°; $V = 3644$ (4) × 10^6 pm^3; $Z = 4$; $\rho_{\mathrm{calcd}} = 1.002$ g cm^{-3}; $\mu = 0.148$ mm^{-1} (no correction applied); 16011 reflections collected, 5155 independent ($R_{\mathrm{int}} = 0.0866$); θ range 1.61−23.37°, 97.3% completeness; 355 parameters; $R_1 = 0.0756$, w$R^2 = 0.169$ [$I > 2\sigma(I)$] for 5155 data; max/min. +0.339 and −0.279 e Å^{-3}; H atoms located in density maps and refined in fixed idealized positions. (b) Tetrameric aggregate derived from TIPS allylamine anion **2**·pentane solvate: crystallographic asymmetric unit $[C_{12}H_{25}Li_2NSi]_4 \cdot C_5H_{12}$; $M_r = 973.35$; clear, colorless crystal of dimension 0.2 × 0.2 × 0.15 mm mounted on a quartz fiber under a stream of dry N_2 gas at −40 °C; triclinic space group *P*-1; $a = 13.46$ (0.20), $b = 15.64$ (0.3), and $c = 17.89$ (0.2) Å, $\alpha = 111.95$ (10)°, $\beta = 100.32$ (3)°, $\gamma = 90.76$(10)°; $V = 3454.2$ (9) × 10^6 pm^3; $Z = 2$; $\rho_{\mathrm{calcd}} = 0.936$ g cm^{-3}; $\mu = 0.117$ mm^{-1} (no correction applied); 13380 reflections collected, 9316 independent ($R_{\mathrm{int}} = 0.0380$); θ range 1.24−23.30°, 93.6% completeness; 601 parameters; $R_1 = 0.0901$, w$R^2 = 0.2632$ [$I > 2\sigma(I)$] for 9316 data; max/min. +1.479 and −0.397 e Å^{-3}; H atoms located in density maps and refined in fixed idealized positions. (c) Mixed aggregate derived from TMS allylamine anion **3** was extremely unstable so that several differnt crystals were utilized: crystallographic asymmetric unit $[C_6H_{13}Li_2NSi]_3 \cdot C_6H_{14}LiNSi \cdot C_4H_{13}Li \cdot C_4H_{10}O$; $M_r = 726.70$; clear, colorless crystals of dimension 0.2 × 0.2 × 0.15 mm mounted on a quartz fibers under a stream of dry N_2 gas at −40 °C; triclinic space group *P*-1; $a = 13.46$ (3.0), $b = 13.73$ (2.0), and $c = 16.30$ (10.0) Å, $\alpha = 92.64$ (10)°, $\beta = 110.93$ (3)°, $\gamma = 105.86$ (10)°; $V = 2673.1$(9) × 10^6 pm^3; $Z = 2$; $\rho_{\mathrm{calcd}} = 0.903$ g cm^{-3}; $\mu = 0.136$ mm^{-1} (no correction applied); 11331 reflections collected, 7095 independent ($R_{\mathrm{int}} = 0.3703$); θ range 1.72−23.26°, 92.6% completeness; 469 parameters; $R_1 = 0.1383$, w$R^2 = 0.3417$ [$I > 2\sigma(I)$] for 7095 data; max/min. +1.389 and −0.619 e Å^{-3}; H atoms located in density maps and refined in fixed idealized positions.

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in Figure 2. This aggregate consists of two cubes which share a common face. This motif is also known for a few alkali metal amido complexes.[12]

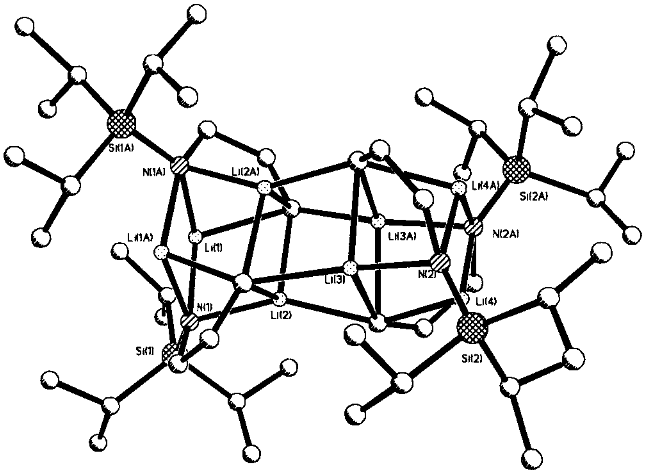

Figure 2. Tetrameric aggregate of the lithium dianion **2** derived from tris-triisopropylsilylallylamine.

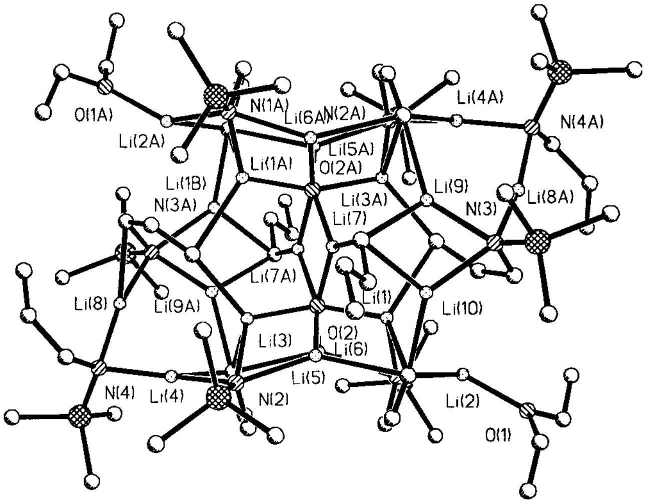

Figure 3. Anion aggregate derived from lithiation of trimethylsilylallylamine with *n*-butyllithium. Aggregate is composed of six TMS-allylamine dianions, two TMS-allylamine monoanions, two molecules of *n*-butyllithium, two solvating diethyl ethers, and two Li_2O molecules.

Finally, the dianion derived from *N*-trimethylsilyl (TMS) allylamine crystallizes in the wholly different and unique aggregate depicted in Figure 3. This aggregate is not directly comparable to those depicted in Figures 1 or 2 because this unique structure consists of six dianions derived from *N*-TMS allylamine, two monoanionic allylamine residues, two butyllithium residues,[13] two solvating molecules of ether, and two nearly octahedrally coordinated O^{2-} anions. The origin of the Li_2O in this structure is not known although the O^{2-} anion is also found in structures such as $Mg_4Br_6{\cdot}O{\cdot}$diethyl ether.[14]

In the aggregates depicted in Figures 1−3, all lithium−carbon contacts less than 2.45 Å are shown. The dianion aggregates in Figures 1−3 are built from units of the monomeric dianions **1**−**3** shown in Scheme 1. Indeed, this monomeric dianion motif is present in these aggregates although several additional carbon−lithium interactions are present. The distinguishing feature in all of the aggregates is the coordination of the terminal vinylic carbon to more than two lithiums. It is entirely unclear to us why the change in the silyl substitutents leads to such diverse aggregates in the crystal structures. We are attempting to correlate these solid-state structures with the solution aggregation states and to assess their relative stabilities

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Supporting Information Available: Details on the crystallographic asymmetric unit and relevant parameters, coordinates, and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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