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Intramolecular Hydrosilylation as a Route to 1-Aza-2,4-disilacyclobutanes

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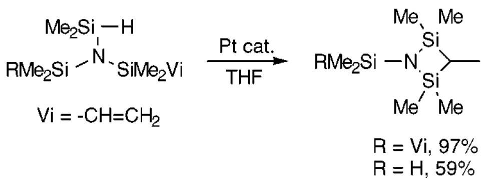
ABSTRACT



The addition of Pt catalyst to trisilyl-substituted amines results in the formation of intramolecular cyclization products. Unexpectedly, four-membered-ring products are formed predominantly, rather than the thermodynamically more stable five-membered rings resulting from endo cyclization. The products are quite thermally stable and resist reaction with *n*-BuLi and *n*-BuLi/TMEDA. The trisilyl-substituted amine starting materials are prepared from lithium bis(silyl)amides and chlorosilanes in high yields.

Cyclic silicon−nitrogen compounds are well-known. By far, most studies of these compounds have focused on the four-membered cyclodisilazane (1,3-diaza-2,4-disilacyclobutane) ring systems (**A**).[1−4] These compounds are excellent precursors to poly(silazanes).[5,6] 1-Aza-2,4-disilacyclobutanes (**B**) can also be polymerized to the corresponding poly(carbosilazanes) (Figure 1).[5] However, very little work has been done with these potentially useful compounds, perhaps due to the lack of convenient preparative procedures.[5,7,8] In this brief report we describe our inadvertent discovery of a convenient synthesis to substituted 1-aza-2,4-disilacyclobutanes.

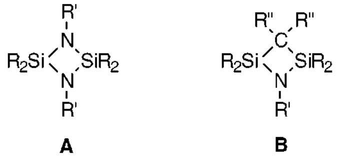
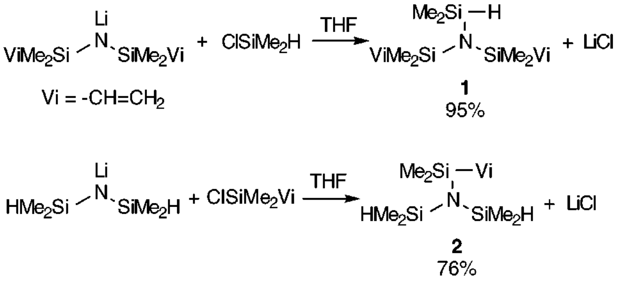


Figure 1. 1,3-Diaza-2,4-disilacyclobutanes **A** and 1-aza-2,4-disilacyclobutanes **B**.

On the basis of our interest in carbosilazane dendrimers,[9] we sought to prepare an analogous carbosilazane hyperbranched polymer. To achieve this, we prepared monomer **1** by the reaction of lithium bis(vinyldimethylsilyl)amide with chlorodimethylsilane (Scheme 1). Compound **1** was isolated in 95% yield after distillation as a clear, colorless, air- and moisture-stable liquid.[10] Compound **2** was obtained in 76% yield from a similar reaction of lithium bis(dimethylsilyl)amide with vinyldimethylchlorosilane (Scheme 1).

Scheme 1



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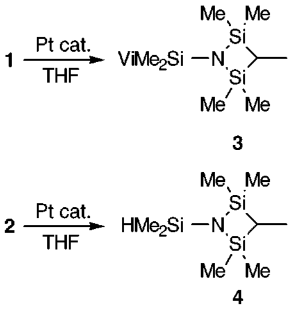
Compounds **1** and **2** are both AB_2 monomers and can conceivably lead to hyperbranched polymers via intermolecular hydrosilylation reactions.[11−14] Accordingly, compound **1** was refluxed in THF for 18 h in the presence of Karstedt's catalyst (platinum−divinyltetramethyldisiloxane complex). The reaction was deemed complete when the Si−H absorbance in the IR spectrum of the reaction mixture had completely disappeared. After removal of the THF by evaporation, we did not observe any traces of polymer but instead isolated the unexpected intramolecularly cyclized product **3** in 97% yield after distillation (Scheme 2).

Scheme 2

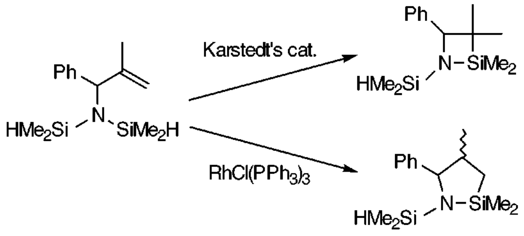


Likewise, under the same reaction conditions compound **2** yielded cyclic product **4** in 59% isolated yield (Scheme 2).

Splitting patterns and integral values in the ^1H NMR spectra of **3** and **4** clearly indicated that 4-exo rings resulting from α-addition were obtained in both cases. Five-membered rings (5-endo) resulting from *β*-addition were not observed in the reaction mixtures prior to distillation. GC-MS was used to verify the identity of the products and also to confirm that these compounds were not dimeric.

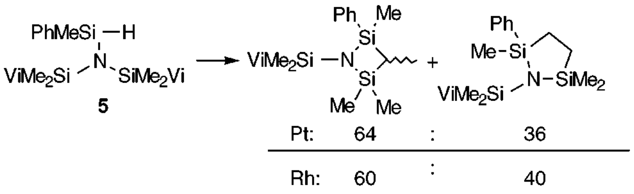
After an examination of the literature, we found that this chemistry parallels the work of Tamao and Ito, who examined the intramolecular hydrosilylation of *N*,*N*-bis(dimethylsilyl)allylamines in the presence of transition-metal catalysts.[15,16] Those researchers found that these compounds gave exclusively the four-membered-ring 1-aza-2-silacyclobutanes with platinum catalysis but gave the five-membered-ring products when the reaction was catalyzed with $RhCl(PPh_3)_3$ (Scheme 3).

Scheme 3



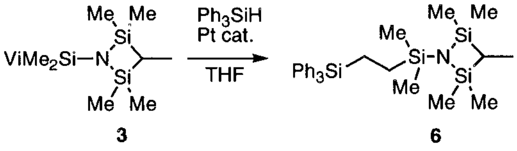
In contrast to these results, we found that refluxing compound **1** in the presence of $RhCl(PPh_3)_3$ still resulted in the predominant formation of **3** (83%) along with small amounts of the five-membered-ring product (17%). Similar results were also obtained with compound **2**. Furthermore, we found that monomer **5** yielded a mixture of four- and five-membered-ring products regardless of which catalyst was used (Scheme 4). The reasons for these differences are unclear and are currently under investigation.

Scheme 4



The 1-aza-2,4-disilacyclobutanes of this report are remarkably robust compounds. They may be distilled safely under vacuum and are stable to both air and moisture. These compounds also turned out to be quite stable toward highly reactive reagents. Thus, compound **3** was inert toward *n*-BuLi in refluxing hexane or THF, with or without added tetramethylethylenediamine (TMEDA). Both catalytic and stoichiometric amounts of *n*-BuLi were utilized in these experiments. The inertness of **3** was somewhat surprising, considering that these conditions are often employed for the ring opening of cyclodisilazanes[6,17] or the anionic polymerization of vinylsilanes.[18,19] The vinyl group in **3** did turn out to be somewhat reactive toward hydrosilylation. Refluxing a THF solution of compound **3** and triphenylsilane in the presence of Karstedt's catalyst resulted in the isolation of the expected *β*-addition product **6** in quantitative yield as a pale yellow waxy solid (Scheme 5). The reaction period was a rather lengthy 96 h. We were unable to obtain X-ray-quality crystals of **6** by recrystallization or sublimation.

Scheme 5



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In conclusion, we have shown that it is possible to obtain 1-aza-2,4-disilacyclobutanes in high yields via a straightforward intramolecular hydrosilylation process. These compounds are stable to strongly nucleophilic or basic reagents but can be modified further by hydrosilylation. The ready availability of these compounds can lead to further studies on their structures or use as polymer precursors.

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Supporting Information Available: Synthetic details and characterization data for compounds **1**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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