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# Low-Temperature Addition of Organolithiums to Functionalized Vinylsilanes under Formation of Secondary α-Lithiated Alkylsilanes

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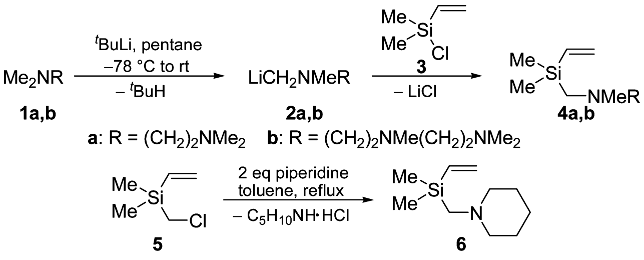
Silylated organolithium compounds are versatile reagents in organic or organometallic chemistry. They are of fundamental interest, for example, as intermediates in the Peterson olefination[1] or in the synthesis of functionalized alcohols[2] via successive Tamao-type cleavage of the Si−C bond.[3] Yet the selective synthesis of α-silylorganolithium reagents with longer alkyl chains next to the metalated carbon center is strongly limited or unknown: Selective α-halogenation or direct deprotonation of alkyl chains other than methyl groups next to silicon fails. Only the carbolithiation of vinylsilanes has been established as a tool to obtain the desired species − these reactions usually proceed in donor solvents at temperatures around 0 °C or higher.[4] Our recent investigations focused on a mild carbolithiation of vinylsilanes without donor solvents or additives at low temperatures to avoid side-reactions like deprotonations or polymerizations. Additional advantages should include readily available substrates and facile access to products containing variable chain lengths.

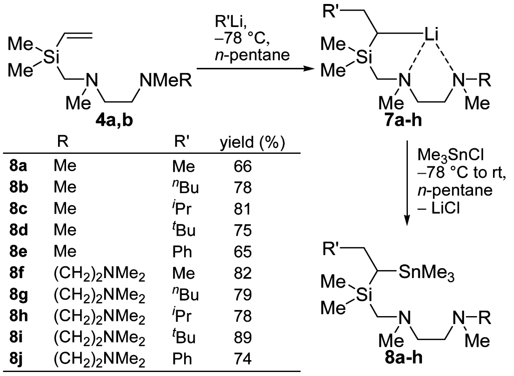
The relationship between the size of aggregates and reactivity of the involved species is clearly established;[5] diamine or triamine ligands are usually employed to break down the organolithium reagents into smaller, sufficiently reactive aggregates. Our approach was to incorporate commercially available di- or triamine auxiliaries into the desired vinylsilane systems. For model systems containing either two or three coordination sites, TMEDA[6] (**1a**) and PMDTA[7] (**1b**) were α-deprotonated with *t*-BuLi in *n*-pentane according to literature procedures, and subsequently reacted with commercially available chloro-(dimethyl)vinylsilane **3** (Scheme 1). After aqueous workup and distillation the vinylsilanes **4a**,**b** were isolated in yields of 55 and 78%, respectively. Vinylsilane **6** served as a model system with a single coordinating site in its side arm and was synthesized via amination of (chloromethyl)dimethylvinylsilane with piperidine in 90% yield.

***Scheme 1.*** Synthesis of the Investigated Vinylsilanes **4a,b** and **6**



Carbolithiations of vinylsilanes **4a** and **4b** and **6** at −78 °C were examined using commercial solutions of *t*-BuLi/*n*-pentane, *i*-PrLi/*n*-pentane, *n*-BuLi/hexane, PhLi/Bu$_2$O/*n*-pentane and MeLi/Et$_2$O/*n*-pentane and proceeded with variable results. No reaction of vinylsilane **6** with the latter three occurred over a period of several months while *t*-BuLi and *i*-PrLi afforded amorphous solids after two weeks which we attributed to an anionic polymerization. In contrast, carbolithiation of vinylsilanes **4a** and **4b** proceeded smoothly and rapidly. After 12 h at −78 °C, quenching with Me$_3$SnCl afforded the stannanes **8a**−**j** in good yields (Scheme 2).

***Scheme 2.*** Carbolithiation of **4a** and **4b** and Trapping of the Resulting Lithiated Species **7a**−**j** with Me$_3$SnCl



| | R | R' | yield (%) |
|---|---|---|---|
| **8a** | Me | Me | 66 |
| **8b** | Me | $^n$Bu | 78 |
| **8c** | Me | $^i$Pr | 81 |
| **8d** | Me | $^t$Bu | 75 |
| **8e** | Me | Ph | 65 |
| **8f** | (CH$_2$)$_2$NMe$_2$ | Me | 82 |
| **8g** | (CH$_2$)$_2$NMe$_2$ | $^n$Bu | 79 |
| **8h** | (CH$_2$)$_2$NMe$_2$ | $^i$Pr | 78 |
| **8i** | (CH$_2$)$_2$NMe$_2$ | $^t$Bu | 89 |
| **8j** | (CH$_2$)$_2$NMe$_2$ | Ph | 74 |

The addition of *n*-BuLi, *i*-PrLi and *t*-BuLi to **4a** and **4b** is favorable even in the absence of coordinating solvents.

Compounds **7a** and **7f**, the products of the addition of MeLi to **4a** and **4b**, respectively, can be crystallized from *n*-pentane/Et$_2$O at −78 °C (Figure 1).

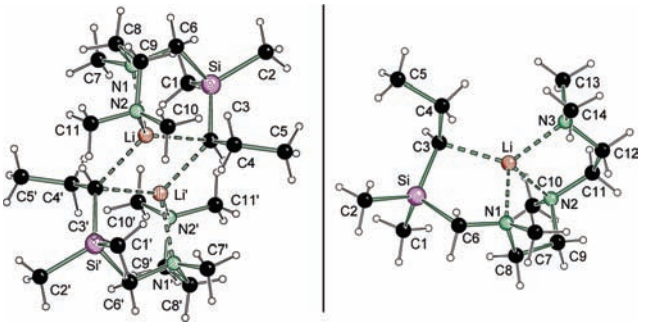


***Figure 1.*** Molecular structures (Schakal representation)[8] and drawing of (**7a**)$_2$ (left) and **7f** (right). Selected bond lengths (Å) and angles (deg): (**7a**)$_2$ - two slightly different dimers are found in the asymmetric unit, represented by two sets of bond lengths and angles: Li−Li′ 2.548(6)/2.578(6), C3−Li 2.285(5)/2.277(6), C3−Li′ 2.258(6)/2.249(6), C3−Si 1.806(3)/1.813(3). **7f**: C3−Li 2.180(6), C3−Si 1.799(3).

Both **7a** and **7f** crystallize in the triclinic crystal system, space group $P\bar{1}$.[9] The asymmetric unit of **7a** contains two molecules which form two slightly different inversion symmetric dimers in the crystal. The central structural motif is a planar four-membered ring formed by the two lithium atoms and two metalated carbon atoms of each moiety. The bond between silicon and metalated carbon C(3) is shortened to 1.806(3) and 1.813(3) Å due to the α-carbanionic stabilizing effect of silicon.[10]

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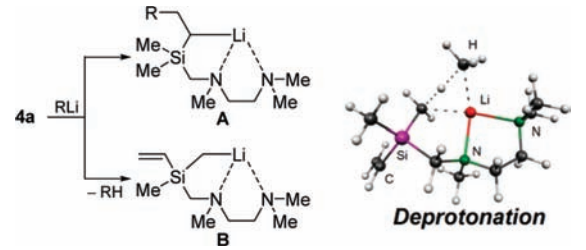
In contrast, the additional coordination site provided by the PMDTA-derived side arm of **4b** accounts for the monomeric carbolithiation product **7f**. With a Si−C(3) bond length of 1.799(3) Å the shortening is more significant than in the dimer.

To support the high reactivity and selectivity of **4a** and **4b** observed in the experiment, theoretical studies were performed and the barriers for the carbolithiation of **4a** as the model compound were computed.[11] Additionally, the barrier for the deprotonation of the methyl groups next to silicon was calculated since similar deprotonation reactions at low temperatures are known in literature (cf. Scheme 3).[2c,12]

***Scheme 3.*** (Left) Computed Reaction Routes of **7a** with Alkyllithiums: Carbolithiation (**A**) and α-Deprotonation (**B**); (Right) Transition State of the Deprotonation Route (Molekel Plot[13])



The computational studies reveal a barrier of 18 kJ/mol for the addition of MeLi to **4a** starting from the monomeric adduct [**4a**·MeLi] (Figure 2).[14] Whereas the assumption of a monomeric reaction path in case of the addition of MeLi may be questionable due to the lack of known comparable complexes the analogous addition of *t*-BuLi to **4a**, was determined at 12 kJ/mol. In case of *t*-BuLi a monomeric complex [**4a**·*t*-BuLi] and reaction route can be justified because structures are known in which bidentate nitrogen ligands break *t*-BuLi down to monomers.[15]

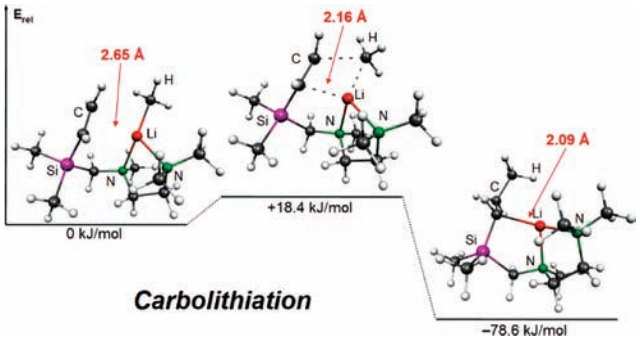


***Figure 2.*** Relative energy of the stationary points found for the carbolithiation of **4a** with MeLi; B3LYP/6-31+G(d) (Molekel plot[13]). Noted in red are the distances between lithium and the carbon center undergoing lithiation.

Competitive carbolithiation experiments at −78 °C with 1 eq of vinylsilane and 1 eq of MeLi and *t*-BuLi each reveal that the addition of the latter is favored and its respective addition products are exclusively formed. It was further found that external coordinating additives like TMEDA were insufficient in inducing a carbolithiation of **6** at −78 °C.[16]

Under no reaction conditions unreacted adducts between vinylsilane and organolithiums could be isolated due to the high reactivity toward carbolithiation of both **4a** and **4b**.

In contrast to the activation energy for the addition, the barrier for the deprotonation of the methyl groups next to silicon is considerably higher at 74 kJ/mol for MeLi (71 kJ/mol for *t*-BuLi), thus explaining why **4a** and **4b** undergo carbolithiation rather than deprotonation under kinetic conditions if reacted with alkyllithiums. Furthermore, a comparison of the geometries of the participating optimized structures reveals a very small distance (2.16 Å) between the lithium center and the carbon undergoing metalation which is very close to the C−Li bond length in the product (2.09 Å). This tightly packed, product-like transition state brings the coordinating moiety which surrounds the lithium center proximate to the double bond. This crowding should account for an efficient differentiation between the energies of diastereomeric transition states in suitable chiral substrates similar to the stereoselective carbolithiations of 6-lithio-1-pentenes,[17] cinnamyl alcohols[18] and β-methylstyrenes[19] already reported.

In summary, two readily synthesized vinylsilanes undergo rapid carbolithiation by organolithiums at low temperatures. Two or three internally coordinating amino moieties are required for rapid and selective reaction at low temperatures. The exceptional reactivity of these functionalized vinylsilanes prompts us to expand our investigations to include stereoselective addition steps via chiral functionalized substrates.

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**Supporting Information Available:** Crystallographic (CIF), experimental and computational data. This material is available free of charge via the Internet at http://pubs.acs.org.

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