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A Monolithiated and Its Related 1,3-Dilithiated Allylsilane: Syntheses, Crystal Structures, and Reactivity

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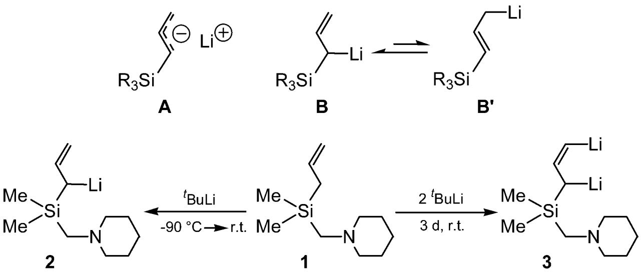
Silyl-substituted allyllithiums are ambidentate nucleophiles with reaction sites in the 1- and 3-position. The site selectivity is of considerable synthetic importance, and in combination with later Si−C bond cleavage, lithiated allylsilanes can be transformed into functionalized products.[1] Chan and co-workers showed that aminomethyl substituents on silicon are resulting in α-addition products of metalated allylsilanes upon reactions with organohalides in THF, while reactions with carbonyl compounds give preferentially γ-addition products in toluene.[2] These observations were discussed in the literature on the assumption of localized structures of type **B** and steric interactions.[1] Extensive NMR studies by Fraenkel et al.[3] in combination with crystal structure determinations[3a] indicate dynamic processes in polar solvents. The negative charge is delocalized, and the lithium cation is sited on the axis perpendicular with and close to the center of the allyl plane (**A** in Scheme 1). Localized structures of type **B**/**B′** are favored in systems with intramolecularly coordinated lithiums, and an additional silicon center stabilizes structure **B**.[3]

Scheme 1



Herein we report the crystal structure of the tetrameric monolithiated allylsilane $(\mathbf{2})_4$ and the first crystal structure of a 1,3-dilithiated allyl compound $(\mathbf{3})_6$. This analysis supplies vital structural information on the structure-determining principles of allyllithium compounds without external coordinating additives and represents the first examples of allyllithiums with only one donating ligand at lithium.[4] The reactivity profile of the lithiated systems **2** and **3** strongly depends on the solvents and electrophiles used in trapping reactions and can be rationalized on the basis of the observed molecular structures for **2** and **3** in combination with quantum chemical studies.

The allyl-substituted silane **1** is available in one step by amination of allyl(chloromethyl)dimethylsilane with piperidine as described by Chan et al.[2a] When treating **1** with 1 equiv of *t*-BuLi in pentane at −90 °C and warming to 20 °C, the monolithiated allylsilane **2** is formed after 6−24 h and can be isolated in the form of single crystals suitable for X-ray structural analysis (Scheme 1).[5] Figure 1 shows the molecular structure of **2** in the solid state, which crystallized as the S_4 symmetric tetramer $(\mathbf{2})_4$ in the tetragonal crystal system, space group $I\bar{4}$. The central structural motif of each tetramer is an eight-membered ring formed by four lithium centers and four allyl units. When treating **1** with 2 equiv of *t*-BuLi in pentane at −90 °C and warming to 20 °C for 48−72 h, the dilithiated allylsilane **3** is formed (Scheme 1) and crystallized as the S_6 symmetric hexamer $(\mathbf{3})_6$ in the hexagonal crystal system, space group $R\bar{3}$.[5] Deriving the molecular structure of hexameric $(\mathbf{3})_6$ from that of tetrameric $(\mathbf{2})_4$, the hydrogen atoms at C-3 in *cis* positions, which are pointing into the center of the ring, are replaced by lithium atoms. These lithium centers formally create a six-membered lithium ring in dilithiated hexameric $(\mathbf{3})_6$. Just as in monolithiated tetrameric $(\mathbf{2})_4$, the metalated allyl units are part of a larger "concentric" carbon−lithium ring that is 12-membered in $(\mathbf{3})_6$. Comparable arrangements were found by us in corresponding benzyllithiums.[6]

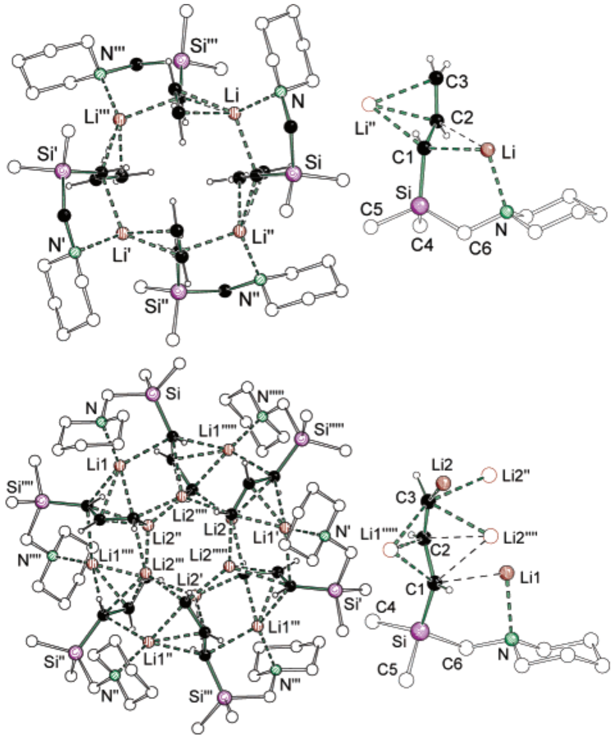


Figure 1. Molecular structures of $(\mathbf{2})_4$ (top) and $(\mathbf{3})_6$ (bottom) in the crystal; in addition, parts of both structures with Li−C contacts are shown (*Schakal* plots[7]). Selected bond lengths (Å) and angles (°) of $(\mathbf{2})_4$: Si−C(1) 1.819(3), Si−C(5) 1.868(3), Si−C(4) 1.880(3), Si−C(6) 1.905(3), Li−N 2.071(4), C(2)−Li″ 2.244(4), C(1)−Li″ 2.268(4), C(1)−Li 2.327(5), C(3)−Li″ 2.338(5), C(1)−C(2) 1.424(4), C(2)−C(3) 1.352(4); C(2)−C(1)−Si 124.90(18), C(3)−C(2)−C(1) 129.9(2). $(\mathbf{3})_6$: Si−C(1) 1.826(3), Si−C(4) 1.864(4), Si−C(5) 1.873(4), Si−C(6) 1.910(3), Li(1)−C(1) 2.493(5), Li(2)−C(3) 2.110(5), C(3)−Li(1)′′′′′ 2.163(5), C(2)−Li(1)′′′′′ 2.243(5), C(1)−Li(1)′′′′′ 2.372(5), C(3)−Li(2)″ 2.245(5), C(3)−Li(2)′′′′ 2.262(7), Li(1)−N 2.085(5), C(2)−C(3) 1.400(4), C(1)−C(2) 1.424(4); C(2)−C(1)−Si 126.3(2), C(3)−C(2)−C(1) 127.4(3).

For both lithiated silanes, the Si−C(1) bond lengths of 1.819(3) and 1.826(3) Å for $(\mathbf{2})_4$ and $(\mathbf{3})_6$, respectively, are shortened by the

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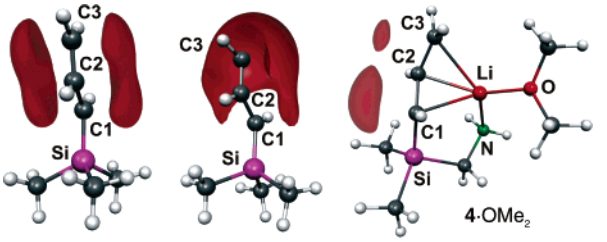


Figure 2. Visualization of the electrostatic potential of the mono- (left) and dianion (middle) of allyltrimethylsilane and of **4**·OMe$_2$ (optimized at the B3LYP/6-31+G(d) level; isosurfaces of −0.07) (*Molekel* plot[11]).

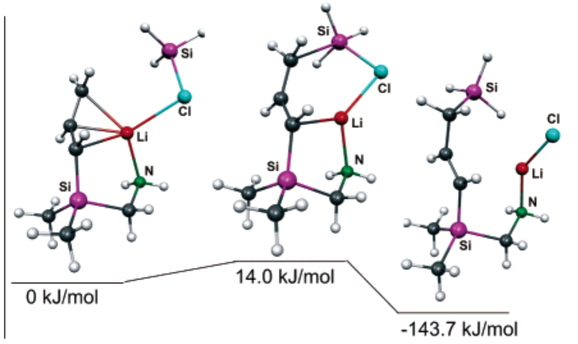


Figure 3. Relative energy profile of stationary points for the substitution reaction of **4** with H$_3$SiCl; B3LYP/6-31+G(d) (*Molekel* plot[11]).

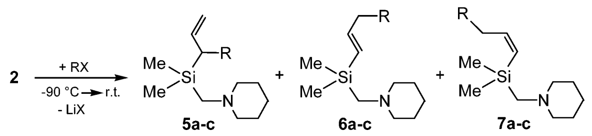
α-carbanionic stabilizing polarization effect of silicon. The C(1)−C(2) bond length of 1.424(4) Å for both systems is elongated by metalation, while the C(2)−C(3) bond is elongated from 1.352(4) Å for $(\mathbf{2})_4$ to 1.400(4) Å for $(\mathbf{3})_6$ by dimetalation, resulting in a nonequivalent allylic C−C bond length in $(\mathbf{2})_4$[3a] compared to the almost identical allylic bond lengths in $(\mathbf{3})_6$.[8] The metalated C−C bonds are elongated due to the negative charge, which can be rationalized for model system $(\mathbf{4})_4$ by DFT calculations.[9,10]

The visualization of the negative electrostatic potential of the mono- and dianion of allyltrimethylsilane (optimized at the B3LYP/6-31+G(d) level[10]) shows the delocalization of the negative charge and explains the *side on* arrangement of anions and cations to a cyclic structure. For the 1,3-dianion, an additional large part of the negative potential is observed around C-3, resulting in Li contacts to C-3 as much as possible. Model system **4**·OMe$_2$, which represents the lithiated allylsilane **2** with an additional coordinating ether ligand, shows a large part of the isosurface of the calculated negative electrostatic potential around C-1, and one would expect therefore predominantly α-addition products from reaction of **2** with non-coordinating electrophiles (Figure 2).

In nonpolar solvents, such as toluene, coordinating electrophiles should precoordinate on lithium, and based on this proximity effect, γ-addition through a cyclic transition state is reasonable. DFT calculations on $(\mathbf{4})_4$ and the corresponding monomer **4** with precoordinated H$_3$SiCl provide the energies involved in this process (only the exo isomer considered).[10] The energy of 47.8 kJ/mol for the process 0.25 $(\mathbf{4})_4$ + H$_3$SiCl to **4**·H$_3$SiCl indicates precoordination as the rate-determining step and the energy difference of 14.0 kJ/mol as the low barrier for the following substitution (Figure 3).

For studying the reactivity of **2** and **3**, we choose MeI (noncoordinating), Me$_3$SiCl (coordinating), and Me$_3$SnCl (coordinating) as trapping reagents. In trapping reactions of $(\mathbf{2})_4$ with Me$_3$SiCl or Me$_3$SnCl in toluene, we observed mainly the γ-products **6b/c** with *E*-configuration and smaller amounts of the γ-product **7b** with *Z*-configuration, which could both be formed via the precoordination (Table 1).

Table 1. Product Selectivity with Different Electrophiles and Solvents



	MeI			Me$_3$SiCl			Me$_3$SnCl		
solvent/RX	**5a**	**6a**	**7a**	**5b**	**6b**	**7b**	**5c**	**6c**	**7c**
toluene	69%	22%	9%	0%	98%	2%	1%	99%	0%
THF	85%	13%	2%	0%	98%	2%	21%	79%	0%

Changing the solvent from toluene to THF led to a lower α/γ-selectivity (**5c**/**6c**) for trapping with Me$_3$SnCl. In reactions of $(\mathbf{2})_4$ with MeI, we observed the α-addition product **5a** as the predominant isomer in THF and toluene (85 and 69%). The coordinating solvent THF seems to favor α-addition due to the suppressed or missing proximity effect of precoordination. Therefore, the same reaction in toluene displays lower α-selectivity.

Side arm donation allows mono- and dilithiation of a allyl(aminomethyl)silane by deprotonation in nonpolar solvents. Trapping reactions showed that product selectivity is influenced by the ability of both the solvent and the electrophile to coordinate the lithium center. Similar studies with the difunctional title compound $(\mathbf{3})_6$ are currently underway, but additional reaction pathways and lower solubility result in a more complex product pattern which needs further investigation.

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Supporting Information Available: Crystallographic (CIF), experimental, computational data, and complete ref 10. This material is available free of charge via the Internet at http://pubs.acs.org.

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