

Synthesis of Silenyllithiums $\text{Li}(\text{R}'_3\text{Si})\text{Si}=\text{C}(\text{SiR}_3)(1\text{-Ad})$ via Transient Silyne–Silylidene Intermediates

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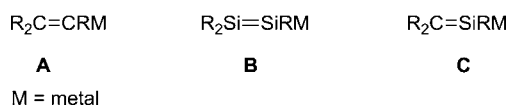
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S Supporting Information

ABSTRACT: The first two lithium silenides, $\text{Li}(\text{tBu}_2\text{MeSi})\text{Si}=\text{C}(\text{SiMe}_2\text{tBu}_2)(1\text{-Ad})$ (**1**) and $\text{Li}(\text{tBuMe}_2\text{Si})\text{Si}=\text{C}(\text{SiMe}_2\text{tBu}_2)(1\text{-Ad})$ (**2**) were prepared by THF addition to the corresponding lithium-silenolates, $[(\text{tBu}_2\text{MeSi})_2\text{Si}=\text{C}(\text{OLi})(1\text{-Ad})]\cdot(\text{R}_3\text{SiLi})$ (**3a**: $\text{R}_3\text{Si}=\text{tBu}_2\text{MeSi}$, **3b**: $\text{R}_3\text{Si}=\text{tBuMe}_2\text{Si}$). **1** and **2** were crystallized, and their structures were determined by X-ray crystallography. This process requires the presence of both coaggregated silyllithium (R_3SiLi) (**3a** and **3b**) and THF. Based on reaction products and DFT calculations, it is suggested that elimination of $\text{tBu}_2\text{MeSiOLi}$ from **3a** (or **3b**) produces first the corresponding silyne intermediate which rearranges to the corresponding silylidene which is then trapped by R_3SiLi giving **1** (or **2**).

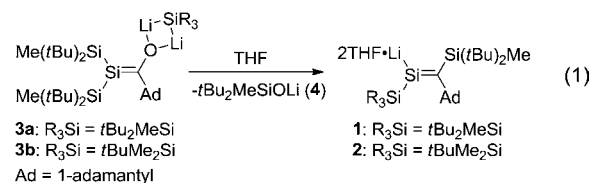
Since isolation of the first stable silene ($\text{R}_2\text{Si}=\text{CR}_2$)¹ and disilene ($\text{R}_2\text{Si}=\text{SiR}_2$)² in 1981, the field of multiply bonded silicon compounds developed rapidly leading to isolation of many doubly³ and recently triply bonded compounds.⁴ However, the chemistry of metal-substituted silenes and disilenes ($\text{MRSi}=\text{ER}_2$, M = metal, E=C, Si) is less explored. This situation contrasts the intensively studied chemistry of analogous metal-substituted olefins (A), which are widely used reagents in organic synthesis.⁵ Several metal-substituted disilenes (B) were recently isolated and characterized,^{6–9} exhibiting interesting reactions leading to novel types of compounds.¹⁰ Several π -bonded transition-metal silene complexes, where a transition metal is coordinated to a $\text{Si}=\text{C}$ double bond, were also reported.¹¹ The first metallosilene, a mercuriosilene, was reported by us.¹² However, alkali metal-substituted silenes (C), which are the missing link between alkenyllithiums (A)⁵ and disilenyllithiums (B)^{6–9} and have potential to be highly useful synthons, are not yet reported (Scheme 1).

Scheme 1



We report the synthesis, isolation, and X-ray molecular structure of the two first lithium substituted silenes (silenyllithiums or lithium silenides): $2\text{THF}\cdot\text{Li}(\text{tBu}_2\text{MeSi})\text{Si}=\text{C}(\text{SiMe}_2\text{tBu}_2)(1\text{-Ad})$ (**1**) and $2\text{THF}\cdot\text{Li}(\text{tBuMe}_2\text{Si})\text{Si}=\text{C}(\text{SiMe}_2\text{tBu}_2)(1\text{-Ad})$ (**2**).

1 and **2** were obtained by THF addition to lithium silenolates $[(\text{tBu}_2\text{MeSi})_2\text{Si}=\text{C}(\text{OLi})(1\text{-Ad})]\cdot(\text{R}_3\text{SiLi})$ (**3a**: $\text{R}_3\text{Si}=\text{tBu}_2\text{MeSi}$, **3b**: $\text{R}_3\text{Si}=\text{tBuMe}_2\text{Si}$)¹³ (eq 1). Based on reaction



conditions and products and also on DFT calculations, we suggest that **1** and **2** are formed by elimination of $\text{tBu}_2\text{MeSiOLi}$ from **3a** (or **3b**) yielding the corresponding transient silyne–silylidene intermediates which are trapped by the aggregated R_3SiLi .

Addition of THF at rt to **3a**, a lithium silenolate aggregated with a R_3SiLi molecule,¹³ followed by solvent evaporation, and recrystallization from hexane yielded bright-orange crystals of silenyllithium **1** in 60% yield.¹⁴ $\text{tBu}_2\text{MeSiOLi}$ (**4**) is quantitatively formed in this reaction. The molecular structure of **1** was determined by X-ray crystallography¹⁵ and is shown in Figure 1.

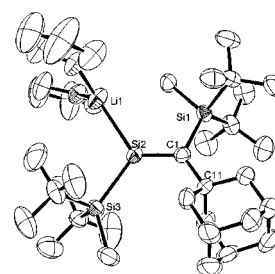


Figure 1. ORTEP drawing of the X-ray molecular structure of **1**. H-atoms were omitted for clarity. Thermal ellipsoids represent 60% probability. Selected bond distances (Å) and bond angles and dihedral angles (°): Si2–C1, 1.773(3); Si2–Si3, 2.434(5); Si2–Li1, 2.613(6); C1–Si1, 1.899(4); C1–C11, 1.555(4); Li1–Si2–C1, 124.6(2); C1–Si2–Si3, 122.82(12); Li1–Si2–Si3, 112.23(17); Si2–C1–Si1, 110.95(17); Si2–C1–C11, 125.6(3); Si1–C1–C11, 123.3(2); Si1–C1–Si2–Si3, 11.0(4); Li1–Si2–C1–C11, 14.0(4); Li1–Si2–C1–Si1, –18.3(5).

The C1=Si2 bond length in **1** of 1.773(3) Å is longer than in $(\text{tBuMe}_2\text{Si})(\text{Me}_3\text{Si})\text{Si}=\text{C}-\text{Ad}$ (**5**) ($r(\text{Si}=\text{C})$, 1.741 Å)^{16a} and

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is in the Si=C double-bond range. The doubly bonded Si2 and C1 atoms geometry in **1** is essentially planar (bond angles sum around Si2 and C1 is 359.7° and 359.9°, respectively), suggesting they both have sp² hybridization. The Si=C bond is slightly twisted, i.e., Li1–Si2–C1–C11 and Li1–Si2–C1–Si1 dihedral angles are 14.0° and –18.3°, respectively. The lithium atom is coordinated to two THF molecules. The Si2–Li1 bond distance of 2.613 Å resembles the Si–Li bond distance of 2.599 Å reported for Li(*t*Bu₂MeSi)Si=Si(SiMe₂–Bu₂)₂ (**6**),⁸ which carries the same silyl substituents as **1** and is also solvated by two molecules of THF. The ¹³C NMR chemical shift of the C=Si bond is at 175.0 ppm, 23.2 ppm upfield from the corresponding ¹³C chemical shift of silene **5** (198.2 ppm).^{16a} The ²⁹Si chemical shift of the doubly bonded Si2 atom appears at 243 ppm, strongly deshielded compared to **5** (51.7 ppm).¹⁶ A similar trend in ²⁹Si chemical shift is observed between disilene (*t*Bu₂MeSi)₂Si=Si(SiMe₂–Bu₂)₂ (**7**) (155.5 ppm)¹⁷ and the corresponding disilyllithium (**6**) (328 ppm).⁸ Overall, **1** exhibits the molecular structure expected for a silyllithium. The geometry of **1** was optimized at the DFT B3LYP/6-311G+(d) level of theory¹⁸ and was in good agreement with the experimental crystallographic structure.

Silenolate **3a** has the same silyl group (i.e., *t*Bu₂MeSi) as a substituent on doubly bonded silicon and in coaggregated silyllithium (R₃SiLi). It is impossible to determine if the silyl substituent attached to doubly bonded C1 in **1** originates from silenolate or from aggregated silyllithium. To determine the source of the silyl substituent attached to C1 in **1**, THF was added to silenolate **3b** which has *t*Bu₂MeSi substituents on the doubly bonded silicon atom of silenolate (as in **3a**) but with an aggregated *t*BuMe₂SiLi molecule instead of *t*Bu₂MeSiLi in **3a**. THF addition to **3b** produced a different silyllithium 2THF·Li(*t*BuMe₂Si)Si=C(SiMe₂–Bu₂)(1-Ad) (**2**) (eq 1) in 40% yield. **2** cocrystallizes with an aggregate of four *t*Bu₂MeSiOLi (**4**) molecules, and its molecular structure was determined by X-ray crystallography (Figure 2).¹⁹ Silyllithium **2** has a *t*Bu₂MeSi

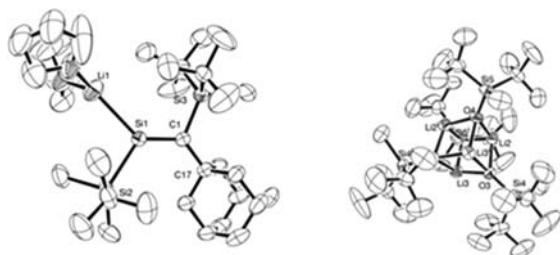


Figure 2. ORTEP drawing of the X-ray molecular structure of **2** cocrystallized with four *t*Bu₂MeSiOLi molecules. H- atoms were omitted. Thermal ellipsoids represent 50% probability. Selected bond distances (Å) and bond angles and dihedral angles (°): Si1–C1, 1.778(3); Si1–Si2, 2.408(11); Si1–Li1, 2.618(5); C1–Si3, 1.897(2); C1–C17, 1.542(3); Li1–Si1–C1, 134.3(7); C1–Si1–Si2, 123.7(9); Li1–Si1–Si2, 101.6(7); Si1–C1–Si3, 111.0(6); Si3–C1–C17, 120.5(4); Si1–C1–C17, 128.4(3); Si2–Si1–C1–Si3, 166.9(8); Li1–Si1–C1–C17, 173.3(0); Li1–Si1–C1–Si3, 7.0(3); Si2–Si1–C1–C17, 12.6(8).

group on the doubly bonded C1 atom (originating from silenolate) and a *t*BuMe₂Si group on the doubly bonded Si1 atom (originating from aggregated *t*BuMe₂SiLi in **3b**).

Molecular structure of silyllithium **2** closely resembles the structure of **1**, with C1=Si1 and Si1–Li1 bond lengths of 1.778 and 2.618 Å, respectively (Li atom is solvated by two

THF molecules, as in **1**). Si1 and C1 are essentially planar (bond angles sum is 359.8° and 359.9°, respectively). Twist angles around the Si=C bonds, Li–Si1–C1–C17 and Si2–Si1–C1–Si3, are 13.1° and 6.7°, respectively. Thus, **2**, similar to **1**, has the expected structure of a silyllithium.

Calculated HOMO and HOMO-1 orbitals of *t*Bu(Me₂Si)C=Si(SiMe₃)Li (**8**) (Figure 3), close model of **1** and **2**, are

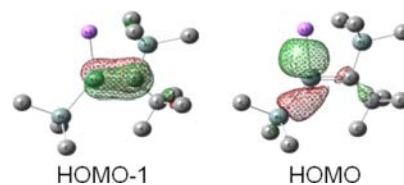


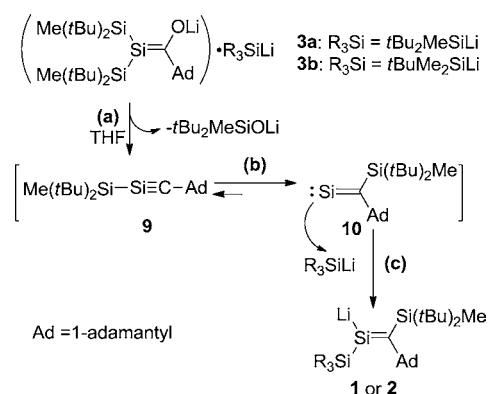
Figure 3. Schematic drawing of *t*Bu(Me₂Si)C=Si(SiMe₃)Li(**8**) HOMO-1 and HOMO.

consistent with the silyllithium description, showing HOMO-1 is the π(C=Si) orbital and HOMO is the σ(Si–Li) orbital strongly coupled (antibonding interaction) with the geminal σ(Si–Si) orbital.

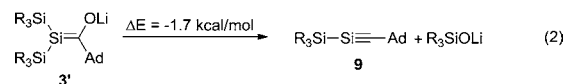
How are **1** and **2** formed from **3a** and **3b**, respectively? Importantly, in the absence of coaggregated R₃SiLi, silenolate **3'** (i.e., **3a** or **3b** without coaggregated R₃SiLi) is stable upon THF addition at rt and does not transform to **1**.²⁰ Thus, coaggregation by R₃SiLi and THF addition is required for transformation of **3a** and **3b** to silyllithiums **1** and **2**, respectively.

Quantitative formation of *t*Bu₂MeSiOLi (**4**) in eq 1 suggests that the first step is the elimination of **4** from silenolates **3a** or **3b** to form silyne **9** (Scheme 2a). Analogous elimination reactions

Scheme 2

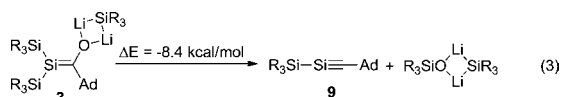


were reported, i.e., elimination of R₃SiOLi from (R₃Si)₃SiC(OLi)(2-Ad) to give (R₃Si)₂Si=(2-Ad)¹⁶ and from enolate (R₃Si)RC=CR'(OLi) to form acetylenes.²¹ DFT quantum mechanical calculations at the B3LYP/6-311G+(d) level of theory¹⁸ show that elimination of **4** from silenolate **3'** to give silyne **9** (eq 2)



is slightly exothermic ($\Delta E = -1.7$ kcal/mol). However, elimination of (*t*Bu₂MeSiOLi)·(*t*Bu₂MeSiLi) from aggregated silenolate **3a** (eq 3) is much more exothermic (–8.4 kcal/mol). These computational results support the feasibility of the elimination step (Scheme 2a) and are consistent with experimental observation

that elimination occurs only from a silenolate– R_3SiLi coaggregate, i.e., **3a** or **3b**. Furthermore, solvation of the two lithium atoms



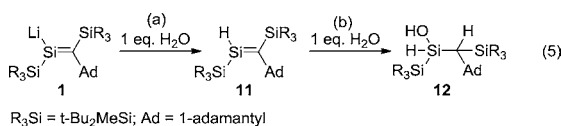
of **3a** by one THF molecule enhances significantly the elimination reaction, making it exothermic by -23.1 kcal/mol (eq 4).



This computational result is consistent with the experimental observation that **3a** and **3b** are stable in hexane solution but undergo elimination upon THF addition. A similar THF enhancing effect on R_3SiOLi elimination from sila-alcoholates to give silenes was reported.¹⁶

What is the fate of intermediate silyne **9**? Previous calculations show that isomerization of silynes **9** substituted with small alkyl and silyl substituents to isomeric silylidenes **10** is very exothermic.²² This is also true with the larger 1-adamantyl and $t\text{Bu}_2\text{MeSi}$ substituents, where rearrangement of **9** to **10** (Scheme 2b) is exothermic by 12.8 kcal/mol, and the energy barrier for the rearrangement is 0.06 kcal/mol (B3LYP/6-311G+ (d)). So, **9** to **10** rearrangement (Scheme 2b) and elimination of R_3SiOLi (step a) are probably concerted. Insertion of silylidene **10** into the Si–Li bond of R_3SiLi (Scheme 2c) yields **1** or **2**.²³ Interestingly, only the E-isomer is obtained in eq 1, probably due to larger steric repulsion in the transition state leading to preferable formation of the E-isomer relative to the Z-isomer.

Addition of 1 equiv of water to **1** at rt yields hydrosilene **11** (eq 5a).²⁴ Adding a second equivalent of water to **11** results in addition of a water molecule to the Si=C bond, as in other silenes,^{3h} yielding silanol **12**²⁴ (eq 5).



In conclusion, we have synthesized, isolated, and characterized by X-ray crystallography the two first silenyllithiums **1** and **2**. We have demonstrated experimentally and by DFT calculations that to obtain **1** and **2** from silenolate **3a** or **3b**, both coaggregated silyllithium and THF addition are required. We suggest that these reactions proceed by $t\text{Bu}_2\text{MeSiOLi}$ elimination from **3a** or **3b** to yield a transient silyne which rapidly (or concertedly) rearranges to a more stable isomeric silylidene, which is trapped by coaggregated silyllithium. We continue to study the properties, reactions, and synthetic potential of **1** and **2** as well as exploring the possibility to use this reaction to synthesize a stable silyne, one of the “Holy Grail” of silicon chemistry.

ASSOCIATED CONTENT

Supporting Information

Experimental details, characterization data, and all ref 18 authors. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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- Experimental details are given in SI. NMR of **1** (in benzene with DMSO- d_6 capillary as external standard, δ in ppm): ^{29}Si 243.87 (LiSi=C); -2.83 ($t\text{Bu}_2\text{MeSi}$); -10.27 ($t\text{Bu}_2\text{MeSiSi}$); ^{13}C 174.9 (C=Si); -3.0 ($t\text{Bu}_2\text{MeSi}$); 22.4, 29.0 ($t\text{Bu}_2\text{MeSi}$); 1.1 ($t\text{Bu}_2\text{MeSiSi}$); 30.6, 26.9 ($t\text{Bu}_2\text{MeSiSi}$); 48.6, 30.6, 37.7, 22.4 (1-Ad); ^1H 0.55, s, 3H ($t\text{Bu}_2\text{MeSi}$); 1.61, s, 18 H ($t\text{Bu}_2\text{MeSi}$); 0.85, s, 3H ($t\text{Bu}_2\text{MeSiSi}$); 1.59, s, 18H ($t\text{Bu}_2\text{MeSiSi}$); 1.95–2.46, broad m, 15H (1-Ad).

(15) **1** crystal data (240 K): $C_{37}H_{73}LiO_2Si_3$; $F_w = 641.16$, monoclinic; space group $P2_1/c$; $a = 16.155(3)$, $b = 14.310(3)$, $c = 17.608(4)$ Å; $\beta = 94.99(2)^\circ$; $V = 4055.2(15)$ Å³; $Z = 4$; $D_{calc} = 1.050$ mg/m³; $R = 0.0615$ [$I > 2\sigma(I)$]; $wR2 = 0.1347$ (all data); $GOF = 0.985$.

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(18) Gaussian 03 series program used. All molecules were fully optimized at the B3LYP 6-311G+(d) level of theory, and all structures were confirmed as local minima by calculating second-order derivatives. Full details are in SI.

(19) **2** crystal data for (240 K); $C_{52}H_{109}Li_3O_4Si_5$; $F_w = 959.66$, monoclinic; space group $C2/c$; $a = 21.474(4)$, $b = 11.565(2)$, $c = 50.33(1)$ Å; $\beta = 92.25(1)^\circ$; $V = 12490(4)$ Å³; $Z = 8$; $D_{calc} = 1.021$ mg/m³; $R = 0.0527$ [$I > 2\sigma(I)$]; $wR2 = 0.0908$ (all data); $GOF = 0.919$.

(20) **3'** is stable in THF solution at rt, and after hydrolysis gives corresponding acylsilane $H(tBu_2MeSi)_2SiC(=O)(1-Ad)$. Details in SI.

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(23) We exclude possibility that **1** or **2** are obtained by R_3SiLi addition to silicon–carbon triple bond of silyne (**9**), as this is expected to give two isomeric products: $(tBuMe_2Si)(tBu_2MeSi)Si=C(1-Ad)Li$ (**14**) and $Li(tBu_2MeSi)Si=C(tBuMe_2Si)(1-Ad)$ (**15**); neither was observed.

(24) Experimental details and spectroscopic data for **11** and **12** are in SI.