Unexpected Hydrolithiation of M=M′ Double Bond (M, M′ = Si, Ge) with ^{t}BuLi

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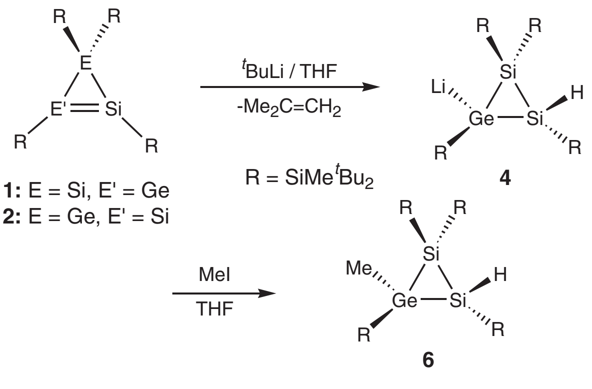
The reduction of 2- and 1-disilagermirenes **1** and **2** with ^{t}BuLi proceeded regio- and stereospecifically to produce germyllithium derivative **4**—the product of the formal addition of LiH across the M=M′ bond (M, M′ = Si, Ge) through single electron transfer steps. Reduction of 1,2-disila-3-germacyclopenta-2,4-diene derivative **3** with ^{t}BuLi also proceeded specifically, but with an opposite regioselectivity to form silyllithium derivative **7**.

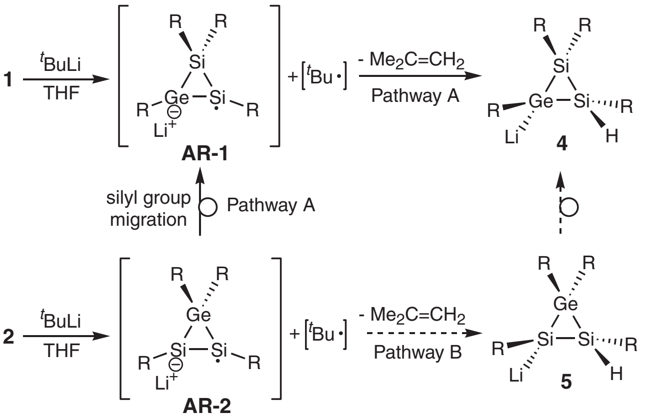
It is well established that metallenes and dimetallenes of the type M=M′ (M, M′—group 14 elements) are prone to easy reduction because of their low-lying, and thus easily accessible, LUMOs compared with those of the corresponding alkene analogues.[1] For example, the reaction of disilenes with metallic lithium resulted in the two-electron reduction of the Si=Si bond to form 1,2-dilithiodisilanes.[2] On the other hand, alkyllithium compounds can also act as selective reducing reagents towards M=M′ bonds, producing different lithio derivatives depending on the substrate.[3] Herein, we report on our study of the reaction of endocyclic M=M′ (M, M′ = Si, Ge) double bonds of 2- and 1-disilagermirenes **1** and **2**[4] as well as 1,2-disila-3-germacyclopenta-2,4-diene derivative **3**[5] with ^{t}BuLi resulting in the extremely clean regio- and stereospecific addition of LiH across the M=M′ double bond.

The reaction of 2-disilagermirene **1** with an equivalent amount of ^{t}BuLi in dry THF or THF-d_8 resulted in the immediate formation of a dark-red reaction mixture, whose NMR spectra showed the exclusive formation of a single product—*trans*-1,1,2,3-tetrakis[di-*tert*-butyl(methyl)silyl]-3-lithiodisilagermi-rane **4**—which was isolated after evaporation of the solvent and treatment of the residue with hexane in 52% isolated yield as a pale yellow solid (Scheme 1).[6] Because of its nonsymmetrical structure, compound **4** exhibited all non-equivalent Me- and ^{t}Bu-groups in the ^{13}C NMR spectrum, whereas the ^{29}Si NMR spectrum showed a total of six resonances, of which the four down-field signals at 12.9, 13.9, 18.0, and 19.8 ppm belong to ^{t}Bu$_2$MeSi substituents and the two up-field signals at −169.5 and −123.5 ppm are assigned to the skeletal (^{t}Bu$_2$MeSi)$_2$*Si* and (^{t}Bu$_2$MeSi)*Si*–H atoms, respectively.



Scheme 1.

The formation of **4** can be rationalized by assuming an initial single electron transfer process involving intermediate formation of the anion-radical of **1** (**AR-1**) and *tert*-butyl radical as a key radical pair, followed by the fast hydrogen abstraction by **AR-1** with the formation of germyllithium **4** (Scheme 2). Indeed, we have observed the simultaneous formation of the equivalent amount of isobutene as a sole side product by ^{1}H and ^{13}C NMR spectroscopy. In other words, **4** is a product of the formal 1,2-addition of lithium hydride across the Si=Ge double bond. It should be mentioned here that the reduction of doubly-bonded derivatives of heavier group 14 elements with alkyllithium compounds (MeLi, ^{t}BuLi) normally results in the 1,2-addition of RLi across the M=M′ double bond.[3,7]

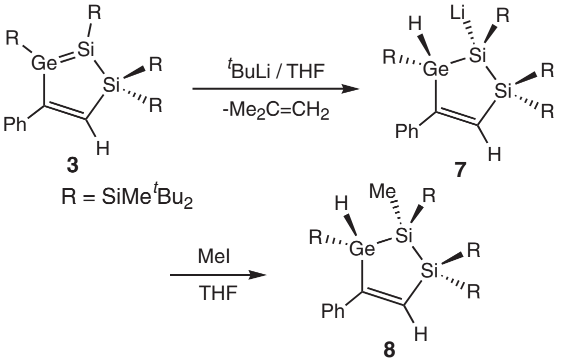


Scheme 2.

Surprisingly, we obtained the same product **4** by the reaction of an isomeric 1-disilagermirene **2** with ^{t}BuLi in THF or THF-d_8 (Schemes 1 and 2). The formation of the identical product **4** is the evidence for the same intermediate precursor, that is, **AR-1**. This implies the isomerization of the initially formed anion-radical **AR-2** to a more stable **AR-1** (Scheme 2, pathway A). The driving force for such an isomerization may be the higher electronegativity of the Ge atom, which favors an arrangement of the negative charge on it. At this moment, we cannot completely rule out the possibility of isomerization taking place after the hydrogen abstraction, that is, from silyllithium **5** to a germyllithium **4** (Scheme 2, pathway B). In the above reaction, we have also observed the formation of an equivalent amount of isobutene. Germyllithium derivative **4** represents the smallest cyclic germyllithium hitherto known,[8] and it can be smoothly methylated with an excess of MeI to form nearly quantitatively the corresponding methylated derivative **6**, *trans*-1,1,2,3-tetrakis[di-*tert*-butyl(methyl)silyl]-3-methyldisilagermirane, which was isolated as light-yellow crystals by recrystallization from hexane

(Scheme 1).[9] The ^{29}Si NMR spectrum of **6** showed six resonances, of which the most up-field shifted ones belong to the skeletal Si atoms: -152.0 $[(^t\text{Bu}_2\text{MeSi})_2\textit{Si}]$ and -140.1 $[(^t\text{Bu}_2\text{MeSi})\textit{Si}\text{–H}]$.

It is interesting that the same reaction course, that is, the addition of LiH to the Si=Ge double bond, was observed in the reaction of **3** with ^{t}BuLi in THF or THF-d_8. This reaction also proceeds extremely quickly and cleanly to yield specifically only one product, *trans*-1,1,2,3-tetrakis[di-*tert*-butyl(methyl)silyl]-2-lithio-4-phenyl-1,2-disila-3-germacyclopent-4-ene **7**, whose formation was demonstrated by NMR spectroscopy (Scheme 3).[10] The regioselectivity of LiH addition to the Si=Ge double bond of **3** is opposite to that observed in the above-mentioned reaction of 2-disilagermirene **1** with ^{t}BuLi, that is, the silyllithium instead of germyllithium derivative was exclusively formed. Such regioselectivity should be explained by the inverse polarity of the $\text{Si}(\delta^-)\text{=Ge}(\delta^+)$ double bond in **3** caused by the different environment around it: a carbon substituent attached to the germanium atom and a silicon substituent attached to the silicon atom.[4,11] The structure of silyllithium derivative **7** was confirmed by its methylated product **8**, *trans*-1,1,2,3-tetrakis[di-*tert*-butyl(methyl)silyl]-2-methyl-4-phenyl-1,2-disila-3-germacyclopent-4-ene, obtained by the reaction of **7** with an excess of MeI: the methyl group is attached to the silicon atom, whereas the germanium atom bears the hydrogen substituent (Scheme 3).[12]



Scheme 3.

In conclusion, the reaction of 2- and 1-disilagermirenes **1** and **2** as well as 1,2-disila-3-germacyclopenta-2,4-diene derivative **3** with ^{t}BuLi represents a new pathway for the reduction of disilenes (and germasilenes) with alkyllithium reagents: the formal addition of LiH across the M=M′ double bond instead of direct alkyllithiation.

References and Notes

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6 Compound **4**: Tetrakis[di-*tert*-butyl(methyl)silyl]-1-disilagermirene **2** (200 mg, 0.26 mmol) and *tert*-butyllithium (18 mg, 0.28 mmol) were placed in a glass tube, and dry THF (1.2 mL) was vacuum-transferred. Reaction took place immediately, even at low temperature, to give a dark-red reaction mixture, which according to NMR spectra contained only one product, **4**. After evaporation of the solvent in vacuum, the residue was treated with hexane to give **4** as a yellow solid (104 mg, 52%). ^{1}H NMR (THF-d_8, δ) 0.11 (s, 3 H), 0.12 (s, 3 H), 0.14 (s, 3 H), 0.22 (s, 3 H), 1.11 (s, 18 H), 1.12 (s, 18 H), 1.13 (s, 18 H), 1.15 (s, 9 H), 1.22 (s, 9 H), 2.75 (s, 1 H, Si-H); ^{13}C NMR (THF-d_8, δ) -3.3, -1.8, -1.6, 0.0, 22.6, 22.85, 22.88, 23.0, 23.1, 23.3, 23.8, 24.0, 30.9, 31.3, 31.6, 31.9, 32.2, 32.3, 32.8, 33.0; ^{29}Si NMR (THF-d_8, δ) -169.5 (ring Si), -123.5 (ring Si-H), 12.9, 13.9, 18.0 19.8; ^{7}Li NMR (THF-d_8, δ) -0.6. The *trans*-arrangement of Li and H in **4** was deduced on the basis of the structure of its methylated product **6**, which has a *trans*-arrangement of Me- and H-substituents.

7 Only for the polar Ge=C double bond LiH addition upon the reaction with ^{t}BuLi has been reported, although the corresponding lithium derivative was not isolated, being proved only by quenching reactions with MeOH and MeI. M. Lazraq, C. Couret, J. Escudié, J. Satgé, and M. Soufiaoui, *Polyhedron*, **10**, 1153 (1991).

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9 Compound **6**: light-yellow crystals, mp 212–214 °C; ^{1}H NMR (THF-d_8, δ) 0.21 (s, 3 H), 0.25 (s, 3 H), 0.32 (s, 3 H), 0.36 (s, 3 H), 0.80 (s, 3 H), 1.15 (s, 27 H), 1.17 (s, 9 H), 1.18 (s, 9 H), 1.20 (s, 27 H), 2.77 (s, 1 H, Si–H); ^{13}C NMR (THF-d_8, δ) -4.2, -3.1, -0.4, 0.9, 3.2, 22.4, 22.5, 22.8, 23.08, 23.11, 23.5, 24.1, 24.6, 30.2, 30.3, 30.4, 30.6, 31.4 (2C), 31.7, 32.2; ^{29}Si NMR (THF-d_8, δ) -152.0 (ring Si), -140.1 (ring Si–H), 20.7, 21.0, 22.5, 26.2. Although the crystal structure of **6** with a *trans*-arrangement of Me- and H-substituents was determined by X-ray analysis, we do not discuss it because of the positional disorder between the skeletal Si and Ge atoms.

10 Compound **7**: ^{1}H NMR (THF-d_8, δ) -0.08 (s, 3 H), 0.09 (s, 3 H), 0.21 (s, 3 H), 0.26 (s, 3 H), 0.83 (s, 9 H), 0.87 (s, 9 H), 0.93 (s, 9 H), 1.00 (s, 9 H), 1.11 (s, 9 H), 1.14 (s, 9 H), 1.15 (s, 9 H), 1.30 (s, 9 H), 5.12 (s, 1 H, Ge–H), 6.85 (t, $J = 7$ Hz, 1 H), 7.01 (t, $J = 7$ Hz, 2 H), 7.14 (s, C=C*H*), 7.29 (d, $J = 7$ Hz, 2 H); ^{13}C NMR (THF-d_8, δ) -3.3, -2.0, -1.4, -0.7, 22.1, 22.7 (2 C), 22.9, 23.4, 23.6, 24.1, 24.2, 30.7, 31.0, 31.5, 31.7, 32.0, 32.1 (2 C), 32.3, 124.4, 127.5, 127.9, 154.9 (C_{ipso}), 155.4 (C=*C*H), 163.6 (*C*=CH); ^{29}Si NMR (THF-d_8, δ) -146.4 (ring *Si*–Li), -44.7 (ring Si), 0.6, 10.2, 11.9, 20.6; ^{7}Li NMR (THF-d_8, δ) -0.5. The *trans*-arrangement of Li and H in **7** was deduced on the basis of the structure of its methylated product **8**, which has a *trans*-arrangement of Me- and H-substituents (see Ref. 12).

11 Normally, in a symmetrical environment, the Si=Ge double bond is polarized: $\text{Si}(\delta^+)\text{=Ge}(\delta^-)$ according to the difference in electronegativity of the Si and Ge atoms: a) C. E. Dixon, M. R. Netherton, and K. M. Baines, *J. Am. Chem. Soc.*, **120**, 10365 (1998). b) K. M. Baines, C. E. Dixon, J. M. Langridge, H. W. Liu, and F. Zhang, *Organometallics*, **18**, 2206 (1999). c) V. Ya. Lee, M. Ichinohe, and A. Sekiguchi, *J. Organomet. Chem.*, **636**, 41 (2001). d) see Ref. 5.

12 Compound **8**: pale-yellow crystals, mp 203–205 °C; ^{1}H NMR (THF-d_8, δ) 0.27 (s, 3 H), 0.34 (s, 3 H), 0.40 (s, 3 H), 0.54 (s, 3 H), 0.57 (s, 9 H), 0.87 (d, $J^2 = 1.3$ Hz, 3 H), 0.89 (s, 9 H), 1.05 (s, 9 H), 1.15 (s, 9 H), 1.177 (s, 9 H), 1.183 (s, 9 H), 1.19 (s, 9 H), 1.21 (s, 9 H), 4.80 (br. q, $J^2 = 1.3$ Hz, 1 H, Ge-H), 7.08 (t, $J = 7.2$ Hz, 1 H), 7.19 (s, C=C*H*), 7.19 (t, $J = 7.2$ Hz, 2 H), 7.27 (d, $J = 7.2$ Hz, 2 H); ^{13}C NMR (THF-d_8, δ) -2.31, -2.25, -1.4, 0.5, 4.1, 21.7, 21.8, 22.2, 22.3, 23.2, 23.9, 24.1, 24.2, 29.7 (2 C), 30.9, 31.3, 31.5, 31.6, 31.9, 32.0, 127.0, 127.9, 128.7, 151.0 (C_{ipso}), 152.1 (C=*C*H), 161.1 (*C*=CH); ^{29}Si NMR (THF-d_8, δ) -50.9, -36.7, 15.0 (2 Si), 18.1, 20.8. Crystal data for **8** at 120 K: $C_{45}H_{94}GeSi_6$, fw = 876.33, triclinic, $a = 12.9740(10)$, $b = 14.3940(11)$, $c = 16.0930(6)$ Å, $\alpha = 103.726(4)$, $\beta = 90.632(4)$, $\gamma = 113.867(3)°$, $V = 2650.4(3)$ Å^3, space group = $P1$, $Z = 2$, $D_{\text{calcd}} = 1.098\ \text{g·cm}^{-3}$. The final R factor was 0.0488 ($R_w = 0.1377$ for all data) for 8787 reflections with $I > 2\sigma(I)$. GOF = 0.989.

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