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Isolation and Reactivity of a Digerma Analogue of Vinyllithiums: a Lithium Digermenide

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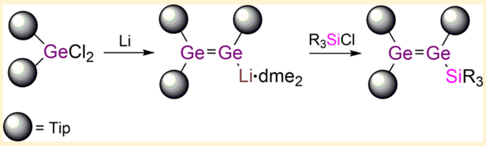
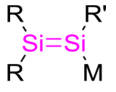
Ⓢ *Supporting Information*

ABSTRACT: The versatile reactivity of disilenides, heavier analogues of vinyl anions, opened the door to novel heavier group 14 structure motifs with residual functionalities in the periphery around the Si═Si moiety. The corresponding germanium analogue, digermenide $Tip_2Ge{=}Ge(Tip)Li \cdot dme_2$ (Tip = 2,4,6-triisopropylphenyl, dme = 1,2-dimethoxyethane), has now been obtained from the reduction of Tip_2GeCl_2 with 3.3 equiv of Li powder and a catalytic amount of naphthalene in dme at −70 °C. The lithium digermenide was characterized by NMR spectroscopy, UV/vis spectroscopy, X-ray diffraction, and DFT calculations. As proof of principle for its suitability for the nucleophilic transfer of the Ge═Ge motif, the reaction with chlorosilanes leads to the unsymmetrically substituted digermenes $Tip_2Ge{=}Ge(Tip)SiR_3$.



The incorporation of functional groups in the periphery of unsaturated low-valent motifs of group 14 is a rapidly evolving field.[1] Highly functionalized unsaturated heavier group 14 molecules are anticipated to play a central role in the synthesis of more extended, possibly conjugated systems. In this context, disilenides, heavier analogues of vinyllithium, serve as versatile building blocks in heavier group 14 chemistry.[2] Lithium disilenides **1**[3a] and **2**[3b] were the first fully characterized examples. The persilylated disilenides **3** are available as lithium, sodium, and potassium salts[3c] and benefit from a similarly straightforward synthetic access as perarylated **1** (Scheme 1).

Scheme 1. Examples of Disilenides 1−3 (1, R = R′ = Tip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$, M = Li, K; 2, R = SiMe^{t}Bu$_2$, R′ = Mes = 2,4,6-Me$_3$C$_6$H$_2$, M = Li; 3. R = R′ = SiMe^{t}Bu$_2$, M = Li, Na, K)[3]

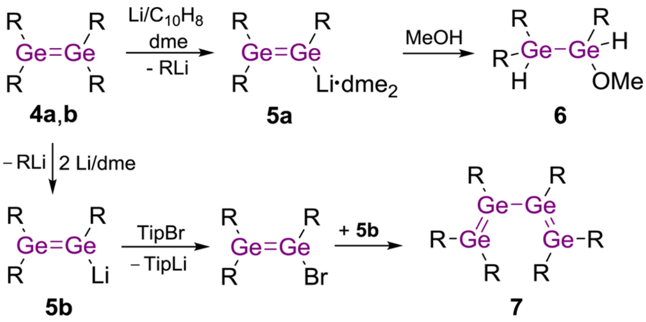


1-3

Being readily accessible in bulk quantitates, **1** and **3** have been employed in various synthetic applications. In general, the use of disilenides as Si═Si transfer reagents under retention of the Si═Si motif[4] can be distinguished from the incorporation with subsequent rearrangement to give heteronuclear double bonds,[5] heterocycles,[6] or cluster species.[7]

In contrast, much less is known about the heavier congeners, the digermenides. In 1989, Masamune and co-workers obtained a red microcrystalline product upon reduction of digermene $Dip_2Ge{=}GeDip_2$ (**4a**; Dip = 2,6-diisopropylphenyl) with an excess of lithium/naphthalene, for which they proposed the constitution of lithium digermenide **5a** on the basis of ^{1}H NMR and UV/vis spectroscopy (Scheme 2).[8] Support for the identity of **5a** in the absence of structural data in the solid state was obtained by chemical derivatization with methanol under consumption of the Ge═Ge bond: the addition of MeOH across the double bond of **5a** resulted in digermane **6**.[8] An analogous synthetic approach was later employed by the Weidenbruch group.[9] The reduction of $Tip_2Ge{=}GeTip_2$ (**4b**; Tip = 2,4,6-triisopropylphenyl) with lithium in dme was assumed to afford digermenide **5b**, which was oxidized without further analysis by the addition of TipBr to the first molecule with conjugated Ge═Ge bonds, tetragermabutadiene **7** (Scheme 2).[9,10] While neither **5a** nor **5b** could be isolated, examples of dianionic germanium species containing a Ge═Ge bond were fully characterized by the groups of Power and Aldridge.[11] In view of the momentum that disilenide chemistry gained with the isolation of the first bona fide disilenides **1** and **2**, we sought to develop a protocol for the isolation of **5b**.

Scheme 2. Suggested Digermenide Intermediates 5a,b according to Masamune and Weidenbruch (4a, 5a, 6, R = Dip = 2,6-Diisopropylphenyl; 4b, 5b, 7, R = Tip = 2,4,6-Triisopropylphenyl)[8,9]



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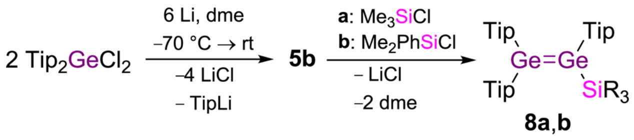
We now report on the synthesis and isolation of the first fully characterized monoanionic digermenide **5b** as well as its reactivity toward triorganochlorosilanes (Me_3SiCl, $Me_2PhSiCl$) under retention of the Ge═Ge double bond to afford the unsymmetrically substituted monosilyl triaryl digermenes.

In analogy to the well-established synthesis of disilenide **1**, we aimed to carry out the digermene synthesis and the reductive cleavage of an aryl group in a one-pot reaction with a dichlorogermane precursor. Tip_2GeCl_2 was prepared by modified literature procedures (for detailed information see the Supporting Information),[12] and reduced at −70 °C with 3.3 equiv of lithium powder in dme in the presence of a catalytic amount (0.4 mol %) of naphthalene (Scheme 3). After the deep red to black reaction mixture was warmed to room temperature, a ^1H NMR spectrum indicated the uniform conversion to a new species with chemical shifts similar to those of disilenide **1**.[3a] A dilute pentane solution afforded red crystals of **5b** in 45% yield after 14 h at −26 °C (mp 135−138 °C; isolated yields in repeat experiments 36−48%). The UV/vis spectrum in hexane shows the longest wavelength absorption in the typical region for heavier alkene homologues at λ_{max} 435 nm (ε = 11800 L mol^{-1} cm^{-1}), which despite the similarity of substituents (**5a**, R = Dip; **5b**, R = Tip) is remarkably blue shifted from the value reported for digermenide **5a** (λ_{max} 458 nm). This discrepancy may indicate the presence of unknown contaminations of the UV/vis sample used by the Masamune group.[8] The extinction coefficient is much larger for **5b** than for disilenide **1** (ε = 760 L mol^{-1} cm^{-1}),[3a] suggesting that a $\pi-\pi^*$ rather than a $n-\pi^*$ transition is responsible for the absorption in the case of the former.

Scheme 3. Synthesis of Digermenide 5b and Silyl Digermenes 8a,b



The X-ray analysis confirms the molecular structure of lithium digermenide **5b** as a contact ion pair (Figure 1). The distorted-square-pyramidal coordination sphere of the lithium cation is completed by two dme molecules as in the case of lithium disilenide **1**.[3a] The Ge═Ge moiety in **5b** is slightly more twisted (τ = 19.9°) than in $Tip_2Ge═GeTip_2$ (**4b**)[13] (τ = 14°). In contrast, the trans-bent angles ($\theta(GeTip_2)$ = 7.1°; $\theta(GeTipLi)$ = 12.8°) are almost identical with those of **4b** ($\theta(GeTip_2)$ = 12°) and much smaller than those of the less bulkily substituted $Mes_2Ge═GeMes_2$ ($\theta(GeMes_2)$ = 33°).[14] Despite the much less pronounced trans-bending, the Ge1−Ge2 double-bond length of 2.284(6) Å is close to the value of $Mes_2Ge═GeMes_2$ (2.286 Å) and significantly longer than that of neutral **4b** (2.213 Å).[13,14] The lengthening of the double bonds of heavier homologues of vinyl anions is a common feature, which is also backed by computations.[15] The distances between germanium and carbon (1.986(3)−2.031(4) Å) are slightly shorter than in Power's Ge dianion (2.060 Å).[11a] The Ge−Li bond length is, at 2.842(7) Å, in the typical range (2.55−2.91 Å).[16]

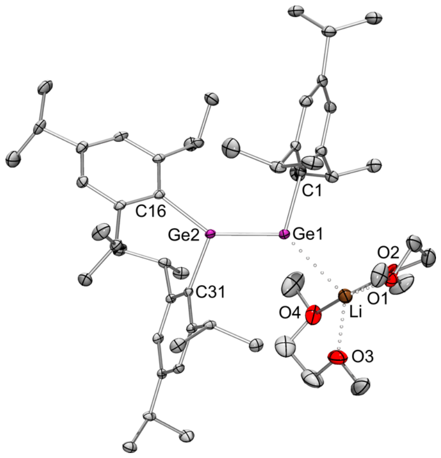


Figure 1. Molecular structure of **5b**·2dme in the solid state (ellipsoids at 30% probability, hydrogen atoms omitted for clarity). Selected bond lengths (Å): Ge1−Ge2 2.2840(6), Ge1−C1 2.031(4), Ge1−Li 2.842(7), Ge2−C16 2.003(3), Ge2−C31 1.986(3).

In order to confirm the frontier orbital sequence suggested by the UV/vis data of **5b**, DFT calculations at the B3LYP/6-31G(d,p) level of theory were carried out on the all-Dip-substituted **5a**. The optimized structure of **5a** is very similar to the experimental structure of **5b** with only minor variations such as a slightly longer Ge═Ge bond of 2.298 Å. The double bond of **5a** is nearly planar with trans-bent angles of $\theta(GeDip_2)$ = 1.69° and $\theta(GeDipLi)$ = 2.81° and a twist angle of 5.78°.

Indeed, as expected on the basis of the strong longest wavelength UV/vis absorption observed for **5b**, the HOMO and the LUMO of **5a** are identified as the π and π^* orbitals of the Ge═Ge bond (Figure 2). The mostly nonbonding HOMO-1 corresponds to the Ge−Li bond and shows relatively high s character ($sp^{0.43}$), which is in line with the electropositive character of lithium. The UV/vis spectrum of **5a** was simulated by TD-DFT, and the comparison to the measured spectra of **5a**,**b** corroborates the orbital sequence, although the calculated values are slightly red shifted in comparison to those experimentally determined for **5b**.

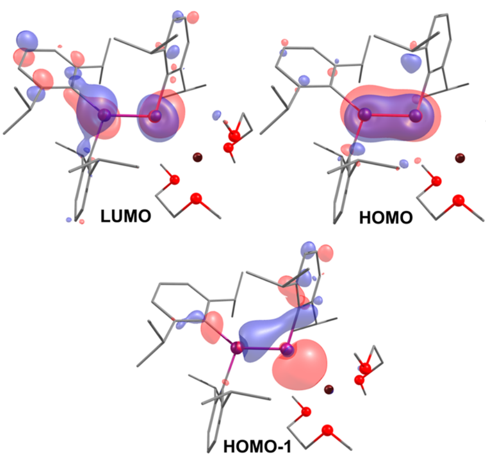


Figure 2. Plots of selected canonical MOs of **5a**·2dme calculated at the B3LYP/6-31G(d,p)-level.

An intense longest wavelength absorption band at 458 nm is ascribed to two transitions at 464 and 427 nm, which both originate in the HOMO and branch out in contributions to the LUMO and LUMO+1. The high intensity of the band is diagnostic for $\pi-\pi^*$ transitions, which gives further evidence for the energetic orbital sequence. A minor band in the simulated spectrum at 356 nm stems from a HOMO-1 → LUMO transition from the n orbital into the π^* orbital and can also be found in the UV−vis spectra of **5a** (λ 378 nm) and **5b** (λ 356 nm, ε = 5600 L mol^{-1} cm^{-1}). The low intensity is typical for n → π^* transitions.

The suitability of digermenide **5b** as a precursor for functionalized Ge═Ge bond containing systems was investigated by the reactions of **5b** with chlorosilanes. Treatment of **5b** with Me_3SiCl leads to clean conversion into a single product with a ^{29}Si NMR signal at δ 1.87 ppm. The slight downfield shift in comparison to the silicon analogue (δ −8.3 ppm)[3a] may be due to the higher electronegativity of germanium vs silicon. The ^{1}H NMR spectrum of the reaction mixture is similar to that of the analogous silicon species and thus in line with the silyl-substituted digermene **8a** (Scheme 3). Unfortunately, all attempts to crystallize the anticipated product, digermene **8a**, failed. In the expectation that a phenyl-substituted silyl group might confer better crystallization properties, $Me_2PhSiCl$ was employed as an electrophile toward digermenide **5b**. The addition of the phenyl-substituted chlorosilane to **5b** induced a slow change in color from red to dark red in hexane at room temperature. A ^{29}Si NMR spectrum indicates a clean product with a single resonance at δ 0.25 ppm, which is in line with the targeted silyl digermene **8b** and similar to the corresponding chemical shifts of analogous silyl-substituted disilenes.[3a,17] Indeed, orange single crystals suitable for X-ray diffraction were obtained from a concentrated toluene solution after 3 days at room temperature. Although the X-ray structure analysis confirms the connectivity of silyl digermene **8b** in the solid state (Figure 3) without ambiguity, the statistical presence of cocrystallized hydrolysis product, digermane **9**, in an approximate 3:1 ratio (see the Supporting Information) precludes the discussion of the geometrical parameters of **8b** (and **9**).

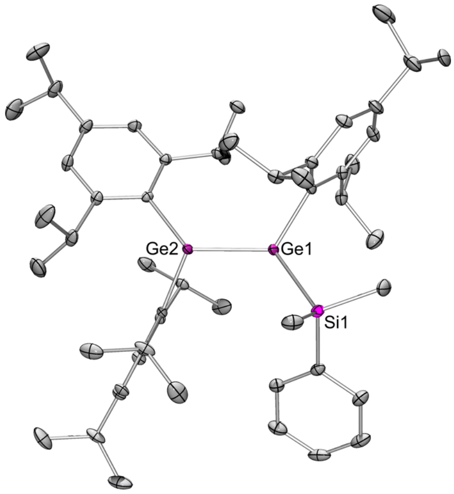


Figure 3. Molecular structure of digermene **8b** in the solid state (ellipsoids at 30% probability, hydrogen atoms of Tip and phenyl substituents as well as the randomly cocrystallized hydrolysis product **9** omitted for clarity).

Deliberate addition of degassed water to a sample of **8b** leads to clean formation of digermane **9** in solution (for detailed information see the Supporting Information). Nonetheless, as a further indication for the constitution of **8b** a UV/vis spectrum clearly proves the presence of a Ge═Ge bond with the value λ_{max} 424 nm (ε = 12500 L mol^{-1} cm^{-1}), which is slightly red shifted in comparison to digermene **4b** (λ_{max} 418 nm).[8]

As a clear indication of the decreased stability of the Ge═Ge bond in digermenide in comparison to the corresponding silicon species, **5b** readily decomposes into digermene **4b** and unidentified decomposition products (in solution after 1 week at room temperature or upon melting at 135−138 °C). Apparently, the Ge═Ge bond of **5b** is cleaved into its constituting germylene fragments with subsequent recombination to the homoleptic digermene **4b** and plausibly to a dilithiated digermene species akin to those reported by the groups of Power and Aldridge.[11] With the less bulky Tip substituents, however, the dilithio digermene cannot be observed and likely decomposes to unknown products. The comparably low stability of the Ge═Ge bond is in line with its known tendency to dissociate in germylene fragments.[18]

In summary, we have developed a straightforward synthesis of $Tip_2Ge{=}Ge(Tip)Li$ (**5b**), which allowed for the first isolation of a monoanionic digermenide and thus for the structural characterization of a germanium analogue of a vinyllithium species in the solid state. Digermenide **5b** is formed upon reduction of Tip_2GeCl_2 with Li powder and a catalytic amount of naphthalene in dme and can be isolated in acceptable yields of about 50%. The substitution reaction with electrophilic chlorosilanes provides proof of principle for the nucleophilic reactivity of **5b**. The potential of digermenide **5b** in various applications in the synthesis of low-valent germanium compounds derives inspiration from the well-developed disilenide chemistry and is currently being investigated in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00470.

NMR spectra for new compounds, UV/vis spectra, and computational details (PDF)

Cartesian coordinates of calculated structures (XYZ)

Accession Codes

CCDC 1554459−1554460 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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