

# Synthesis of Genuine Germyl Lithiums and the First Persistent Germyl Radicals

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Dedicated to Professor Matthias Driess

**Abstract:** The first isolated genuine germyl lithiums ( $R_3Si$ )(1-Ad)C=Ge(SiMetBu<sub>2</sub>)(Li-2 L) ( $R_3Si = tBu_2MeSi$ , L = THF (**1a**), or L = 12-crown-4 (**1b**) and  $R_3Si = tBuMe_2Si$ , L = THF (**2a**), or L = 12-crown-4 (**2b**)), were synthesized by reaction of the corresponding acyl germanes **3** and **4**, respectively, with  $tBu_2MeSiLi$  in THF at 70 °C. The novel **1a** and **2b** were characterized by NMR and UV/Vis spectroscopy, and also by X-ray crystallography ( $r(C=Ge) = 1.865 \text{ \AA}$  for **1a** and  $1.877 \text{ \AA}$  for **2b**). Nucleophilic addition reaction of **1a** with MeI and a C–H insertion reactions to the C=Ge bond of **1a**, **2a** and **2b**, are reported. Oxidation of **1a** and **2b** (toluene, 230 K) produces the first persistent germyl radicals ( $R_3Si$ )(1-Ad)C=Ge<sup>•</sup>-(SiMetBu<sub>2</sub>) ( $R_3Si = tBu_2MeSi$  (**13a**),  $R_3Si = tBuMe_2Si$  (**13b**)), which were characterized by EPR spectroscopy ( $t_{1/2} \approx 30 \text{ min}$  at 230 K,  $g = 2.029$ ,  $a_{av}(^{73}Ge)$  is 55.0G for **13a** and 60.2G for **13b**). The experimental EPR parameters and DFT calculations indicate that **13a** and **13b** have a strongly bent structure at Ge (calc.  $\angle(C=Ge-Si) = 136.7^\circ$  (**13a**),  $135.9^\circ$  (**13b**)), and that the unpaired electron has a substantial s-character.

The heavier analogs of unsaturated hydrocarbons, featuring multiple bonds between one or two heavier Group 14 elements (E), continue to attract growing attention in main-group chemistry.<sup>[1]</sup> Of special interest are metal (M) substituted heavy alkenes, ( $R_2E'=ER-M$ ), the analogues of alkenyl anions.<sup>[1i,2,3]</sup> Such compounds have great synthetic potential, including transformations which incorporate E=E' and C=E bonds into organic molecules.<sup>[2c]</sup> Several disilanyl anions (disilenes) ( $R_2Si=SiR'-M$ , M = Li, Na, K) were synthesized,<sup>[3c-g,k]</sup> and their use as precursors for more extended conjugated systems,<sup>[3b,4]</sup> functionalized heavier alkenes,<sup>[5]</sup> heterocycles<sup>[6]</sup> and E-clusters,<sup>[7]</sup> was explored. In contrast, only one example of a digermanide,<sup>[3i]</sup> ( $R_2Ge=GeR'-M$ ), and several digermanide dianions<sup>[8]</sup> were isolated. Synthesis of *hetero-nuclear* heavier alkenyl anions, consisting of two different Group 14 elements, remains challenging. Recently, the first potassium silagermanide ( $R_2Si=GeR'-K$ ) was isolated by Scheschkewitz et al. and was used for the synthesis of functional silagermenes.<sup>[3j]</sup> Metallo-silenes **I**<sup>[9]</sup> and **II**,<sup>[10]</sup> were synthesized and isolated in our

group (Figure 1). Tokitoh et al. reported the synthesis and isolation of metallo-germyl (germabenzenyl) **IIIa** and metallo-stannyl (stannabenzenyl) **IIIb** anions,<sup>[11]</sup> heavier analogs of phenyl anion (Figure 1), and also of a trimer of germaantracenyl anion **IV**.<sup>[12]</sup> Silanylidene anion **Va**<sup>[13]</sup> and germylidene anions **Vb**<sup>[13]</sup> and **VI**<sup>[14]</sup> (Figure 1), were synthesized by the groups of Roesky and Tuononen,

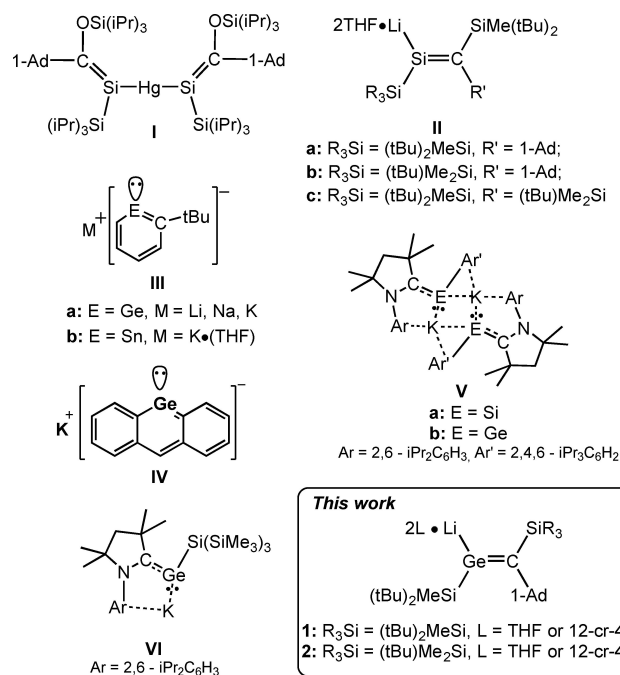


Figure 1. Isolated heavy alkenyl anions,  $R_2C=ER-M$ .

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respectively. These low-valent Ge anions, stabilized by cyclic alkyl(amino) carbene (cAAC), have significant C=Ge double bond character, but the authors preferred to classify them as germylidene anions (i.e. germylene anions). *Stable germyl anions with a genuine C=Ge double bond, having substituents with mild electronic effects, have not been yet reported.*

Herein, we report the synthesis of the first stable genuine germyl anions:  $(R_3Si)(1-Ad)C=Ge(SiMetBu_2)(Li\cdot 2L)$  (**1**:  $R_3Si = tBu_2MeSi$ ,  $L = THF$  (**1a**), or  $L = 12\text{-crown-4}$  (**1b**), and **2**:  $R_3Si = tBuMe_2Si$ ,  $L = THF$  (**2a**), or  $L = 12\text{-crown-4}$  (**2b**)), obtained via metalation of the corresponding acylgermanes. Note that both **1** and **2** have an  $\alpha$ - $tBu_2MeSi$  substituent, but the *trans*- $\beta$ -silyl group in **1** is ( $tBu_2MeSi$ ), much larger than in **2** ( $tBuMe_2Si$ ). Germyl lithiums **1** and **2** were isolated and characterized by NMR and UV/Vis spectroscopy, and **1a** and **2b** also by X-ray diffraction analysis. Several reactions of **1a**, **2a** and **2b** are reported. Oxidation of **1a** or **2b** generates the corresponding first persistent ( $t_{1/2} \approx 30$  min at 230 K) germyl radicals  $(R_3Si)(1-Ad)C=Ge^\bullet-(SiMetBu_2)$ , characterized by electron paramagnetic resonance (EPR) spectroscopy and density functional theory (DFT)<sup>[15]</sup> calculations.

Reaction of colorless acyl germanes  $(R_3Si)_2GeHC(O)(1-Ad)$  (**3** or **4**) with 2.5 equivalents of  $tBu_2MeSiLi$  in THF for 2 hours at 70 °C, produces a red colored solution [Eq. (1), step a]. Replacing THF by hexane leads to a color change to orange. Germyl lithium **1a** crystallizes from hexane at room temperature as orange crystals in 71 % yield. The structure of **1a** was determined by X-ray diffraction analysis, identifying it as a germyl lithium contact ion pair (CIP) (Figure 2a). Crystallization of **2a** from hexane was not successful; therefore, 2 equivalents of 12-crown-4 were added to the reaction mixture, and subsequent crystallization from toluene yields orange crystals of **2b** in 74 % yield [Eq. (1), step b]. X-ray diffraction analysis shows that **2b** is a free germyl anion, associated by charge attraction to a lithium cation solvated by two crown ether molecules (Figure 2b).<sup>[16]</sup>

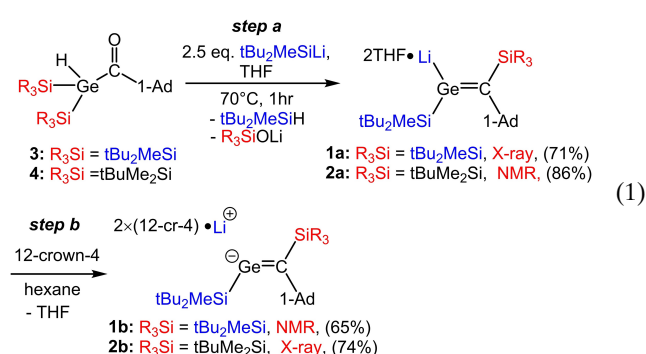
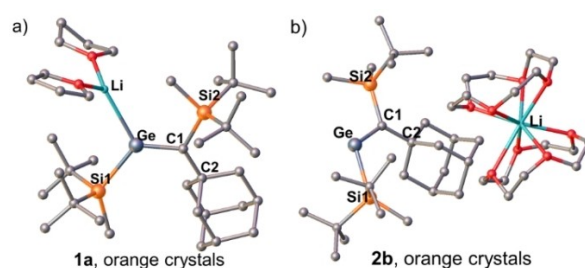


Table 1 compares the most important bond lengths and bond angles of **1a** and **2b**. In both, **1** and **2**, the  $\alpha$ -( $tBu_2MeSi$ ) and  $\beta$ -silyl substituents ( $tBu_2MeSi$  in **1a** and  $tBuMe_2Si$  in **2b**), are *trans*. There are only minor structural differences in the germyl ( $C=Ge$ ) unit between the CIP **1a** and the free germyl anion **2b**, although the  $\beta$ -silyl substituents have different size. The  $C=Ge$  double bond of **1a** (1.865 Å) and



**Figure 2.** X-ray structure (Olex drawing) of: a) CIP germyl lithium **1a**, and b) free germyl anion **2b**. Hydrogen atoms are omitted for clarity. Some structural details are given in Table 1 and full details are given in the Supporting Information.

**Table 1:** Selected geometrical parameters of germyl lithiums **1a** and **2b**.

| Entry | Parameter                                     | <b>1a</b> | <b>2b</b> |
|-------|---|-----------|-----------|
| 1     | $r(\text{Ge}-\text{C1})$ , [Å]                | 1.865     | 1.877     |
| 2     | $r(\text{Ge}-\text{Li})$ , [Å]                | 2.611     | 8.240     |
| 3     | $r(\text{Ge}-\text{Si1})$ , [Å]               | 2.469     | 2.502     |
| 4     | $r(\text{C1}-\text{Si2})$ , [Å]               | 1.901     | 1.825     |
| 5     | $r(\text{C1}-\text{C2})$ , [Å]                | 1.549     | 1.576     |
| 6     | $\Sigma \angle (\text{Ge})$                   | 359.5     | 360.0     |
| 7     | $\Sigma \angle (\text{C1})$                   | 360.0     | 359.9     |
| 8     | $\angle (\text{C1}-\text{Ge}-\text{Si1})$     | 121.7     | 119.5     |
| 9     | $\angle (\text{Si2}-\text{C1}-\text{Ge})$     | 110.2     | 109.2     |
| 10    | $\angle (\text{Si2}-\text{C1}-\text{C2})$     | 125.3     | 125.7     |
| 11    | $(\text{Si1}-\text{Ge}-\text{C1}-\text{Si2})$ | 10.1      | 13.8      |

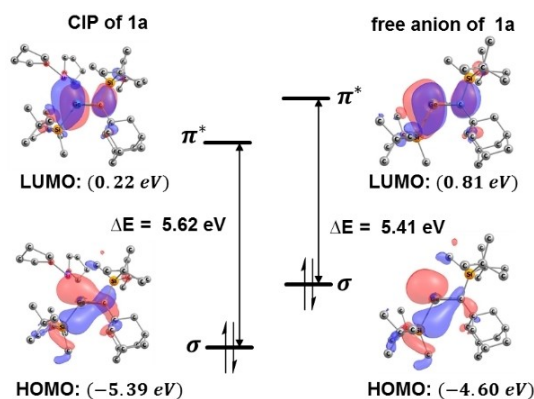
**2b** (1.877 Å) are similar to that in germylidene anions **Vb** and **VI** (Figure 1) (1.872 Å<sup>[13]</sup> and 1.879 Å,<sup>[14]</sup> respectively), but are somewhat longer than previously reported C=Ge double bonds (1.772–1.859 Å)<sup>[1d,f]</sup> (e.g., 1.808 Å in 2-Ad=Ge( $SiMe_2tBu$ )<sub>2</sub>,<sup>[17]</sup> 1.859 Å in a norbornene endocyclic germene<sup>[18]</sup>). Elongation of double bonds of heavy analogues of alkenyl anions relative to their neutral analogues, by 0.03–0.07 Å, was previously reported for  $Tip_2E=E(Tip)-Li$  ( $E = Si, Ge$ ;  $Tip = 2,4,6\text{-iPr}_3C_6H_2$ )<sup>[3d,i]</sup> and  $(tBu_2MeSi)(R)C=Si(SiR'_3)-Li$  ( $R = tBuMe_2Si, 1\text{-Ad}$ ;  $R'_3Si = tBu_2MeSi, tBuMe_2Si$ )<sup>[10]</sup> and is also supported by calculations<sup>[19]</sup> (by 0.046 Å for **1a**, in comparison to the corresponding H–Ge=C germene<sup>[20]</sup>). The calculated C=Ge Wiberg bond index (WBI) in **1a** of 1.456<sup>[21]</sup> is consistent with a C=Ge double bond (1.472 in  $(tBu_2MeSi)(1-Ad)C=Ge(SiMetBu_2)(Me)$ , and 1.553 in  $Me_2C=GeMe_2$ ). The calculated WBI in **2b** of 1.375 is somewhat smaller, in line with its longer C=Ge bond. Interestingly, germylidene anions **Vb** and **VI** (Figure 1) have similar WBI of 1.396<sup>[13]</sup> and 1.442,<sup>[14]</sup> respectively, although they were classified as germylidene anions.<sup>[13,14]</sup> The geometry around the C=Ge bond in both **1a** and **2b** is essentially planar (sum of bond angles around either the Ge or C atoms is nearly 360°). Twisting around the C=Ge double bonds is small (the  $\angle Si1-Ge=C1-Si2$  dihedral angles are 10.1° (**1a**) and 13.8° (**2b**)).<sup>[22]</sup> **1a** and **2b** exhibit a strongly bent geometry at Ge;  $\angle C1=Ge-Si1$  is 121.7° in **1a** and 119.5° in **2b**, consistent with a  $sp^2$ -type anion. The significantly longer C1–Si2 bond in **1a** (1.901 Å) vs. **2b** (1.825 Å), by 0.076 Å, results from steric repulsions in

**1a**, between the bulky  $t\text{Bu}_2\text{MeSi}$  substituent at C1 and Li·2THF, repulsions which are absent in **2b**. The C1–C2 bond in **2b** is longer than in **1a** by 0.027 Å, due to  $\sigma$ -Ge lone pair– $\sigma^*$ (C1–C2) hyperconjugation. Germyl lithium **1a** is the heavier analogue of the previously reported silenyl lithium **IIa** (Figure 1).<sup>[10a]</sup> The structures of **1a** and **IIa** are very similar, except for the much shorter  $r(\text{C}=\text{Si})$  of 1.773 Å (in **IIa**) vs.  $r(\text{C}=\text{Ge})$  of 1.865 Å (in **1a**), due to the smaller atomic covalent radius of Si vs. Ge ( $r_{\text{cov}}(\text{Si})=1.169$  Å,  $r_{\text{cov}}(\text{Ge}) 1.223$  Å).<sup>[23]</sup>

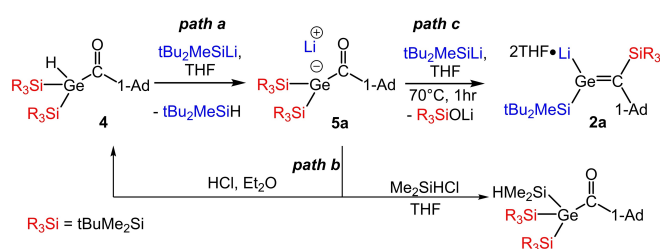
In the  $^{13}\text{C}$ -NMR spectrum<sup>[24]</sup> (in THF), the doubly-bonded carbon atoms of **1** and **2** resonate at  $\approx 195$  ppm, shielded relative to the alkenyl carbon of 2-Ad=Ge-(SiMe<sub>2</sub>tBu)<sub>2</sub> (208.6 ppm),<sup>[17]</sup> and of germylidene anions **Vb** and **VI** (212 ppm and 226 ppm, respectively).<sup>[13,14]</sup> The alkenyl carbon of the analogous silenyl anion **IIa** resonates at 175 ppm.<sup>[10a]</sup> Similarly, for the isostructural 2-Ad=E-(SiMe<sub>2</sub>tBu)<sub>2</sub> (E=Si, Ge), substitution of Si by Ge causes a downfield shift of the alkenyl carbon (198 ppm for E=Si, 208.6 ppm for E=Ge).<sup>[17]</sup> In the  $^{29}\text{Si}$ -NMR spectrum, two peaks, at –6.0 and 13.2 ppm for **1**, and at –6.8 and 10.2 ppm for **2**, were observed, corresponding to the silyl substituents bonded to the C=Ge atoms, respectively (based on DFT calculations, see Supporting Information).

The visible spectrum of **1a** in THF (most likely a free anion) shows a wide absorption with a peak at 495 nm ( $\epsilon=85.7\text{ M}^{-1}\text{ cm}^{-1}$ ), red-shifted by 38 nm relative to that in benzene ( $\lambda=457$  nm,  $\epsilon=403.5\text{ M}^{-1}\text{ cm}^{-1}$ ). A similar shift of the absorption between THF and benzene (585 and 526 nm, respectively) was reported for silenyl lithium **IIc**, corresponding to free-anion $\rightleftharpoons$ CIP transformation, controlled by THF $\rightleftharpoons$ benzene solvent change.<sup>[10b]</sup> The visible absorption spectra of free anion **1a** (in THF) and CIP **1a** (in benzene), are reasonably well reproduced by TD-DFT calculations (at M062X/def2svp//M062X/6-311+G(d,p) (for H, C, Si, O, Li), SDD (Ge)),  $\lambda(\text{THF})=495$  nm,  $\epsilon=125\text{ M}^{-1}\text{ cm}^{-1}$ ;  $\lambda(\text{benzene})=448$  nm,  $\epsilon=333\text{ M}^{-1}\text{ cm}^{-1}$ ). The observed absorptions are attributed to a forbidden HOMO-LUMO transition, with calculated energy gaps of 5.62 eV for CIP **1a**, and 5.41 eV for free anion **1a**, explaining the observed red shift for free anion **1a** (observed in THF) relative to CIP **1a** (observed in benzene). In both species the HOMO is the in-plane Ge  $\sigma$ -anionic lone pair orbital ( $s^{72.5\%} p^{27.5\%}$  hybridization) and the LUMO is the  $\pi^*(\text{C}=\text{Ge})$  orbital (Figure 3). Upon dissociation of CIP **1a** both the HOMO and the LUMO shift to higher energy, but the change is larger for the HOMO (see Supporting Information), resulting in a smaller HOMO-LUMO gap in the free anion (Figure 3). The UV spectra of **1a** in THF and in benzene also show a wide peak at 355 nm ( $\epsilon(\text{THF})=6496\text{ M}^{-1}\text{ cm}^{-1}$ ,  $\epsilon(\text{benzene})=18636\text{ M}^{-1}\text{ cm}^{-1}$ ), attributed to a forbidden  $\pi(\text{C}=\text{Ge})$  (HOMO-1)–LUMO transition (see Supporting Information).

Reaction of acyl germane **3** with only one equivalent of  $t\text{Bu}_2\text{MeSiLi}$  in THF at room temperature also produces **1a**, but only in 30 % yield, after 18 h. In contrast, reaction of the less bulky acyl germane **4** with one equivalent of  $t\text{Bu}_2\text{MeSiLi}$  (THF, room temperature), yields in a few minutes quantitatively, acyl germyl lithium/germenolate<sup>[25]</sup> **5a** (Scheme 1,



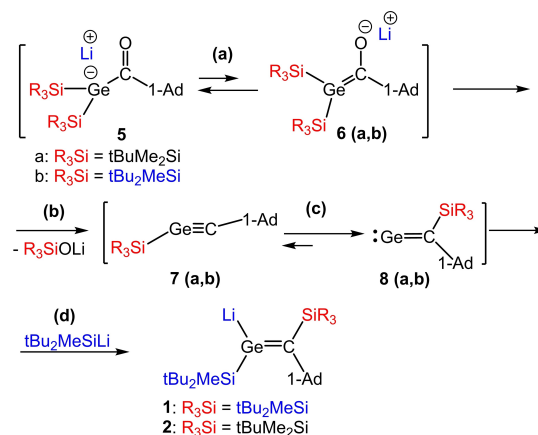
**Figure 3.** Calculated frontier molecular orbitals of CIP-**1a** and free anion of **1a**.



**Scheme 1.** Synthesis of acyl germyl lithium **5a** and its reactions with electrophiles (path b) and with  $t\text{Bu}_2\text{MeSiLi}$  (path c).

path a). The formation of **5a** was confirmed by NMR spectroscopy, and by reactions with HCl and  $\text{Me}_2\text{SiHCl}$  that produce the expected substitution products (Scheme 1, path b) (for details see Supporting Information). Heating **5a** with 1.5 equivalents of  $t\text{Bu}_2\text{MeSiLi}$  in THF for an hour at  $70^\circ\text{C}$  yields germyl lithium **2a** (Scheme 1, path c).

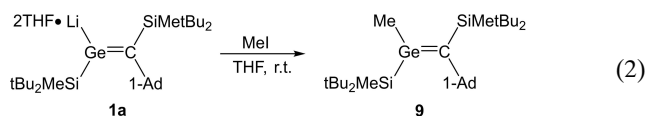
The proposed mechanism for the formation of germyl lithium **1** and **2** (equation 1) is presented in Scheme 2. It is analogous to the previously described mechanism for formation of the analogous silenyl lithiums **II**,<sup>[10a]</sup> and it is supported by DFT calculations (see Supporting Informa-



**Scheme 2.** Proposed mechanism for the formation of **1** and **2**.

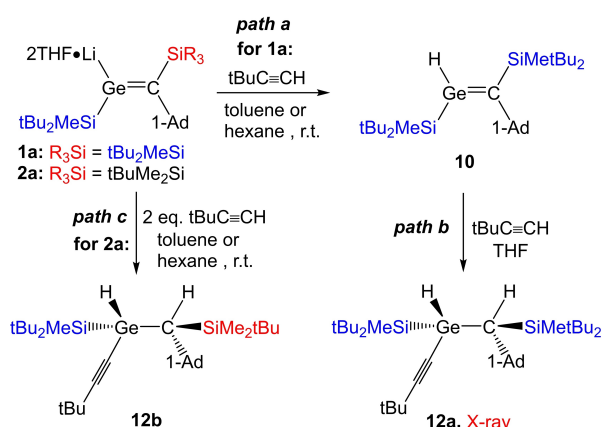
tion). Acyl germynyl lithium **5a** (observed) or **5b** (not observed) undergo interconversion to the isomeric germylenolate **6a** or **6b**, respectively (Scheme 2, step a). Elimination of  $R_3SiOLi$  from **6a** or **6b** yields germyne **7a** or **7b**, respectively (Scheme 2, step b), which isomerizes by silyl group migration to the more stable germylidene **8a** or **8b**, respectively (Scheme 2, step c). Insertion of germylidene **8a** or **8b** into the Si–Li bond of  $tBu_2MeSiLi$  yields germylenyl lithiums **1** or **2**, depending on the identity of the  $\beta$ - $R_3Si$  group (Scheme 2, step d). The fact that reaction of acylgermane **4** (or **5a**) with  $tBu_2MeSiLi$ , produces **2b**, in which the  $tBuMe_2Si$  group is bonded to C and the  $tBu_2MeSi$  group to Ge, supports the mechanism in Scheme 2. Only the E-isomers of **1** and **2** are produced in Equation (1), probably due to smaller steric repulsions in the insertion transition state of **8(a,b)** with  $tBu_2MeSiLi$ , leading to the E-isomer (Scheme 2, step d). Similarly, only the E-isomer is produced in the analogous reaction producing silenyl lithiums **II**.<sup>[10a]</sup> Elimination of  $R_3SiOLi$  from **6a** occurs at 70 °C, while for **6b** with the bulkier  $\beta$ - $tBu_2MeSi$  substituent, elimination occurs at room temperature, apparently because of a more favorable release of steric strain (see Supporting Information). This is consistent with the fact that reaction of  $tBu_2MeSiLi$  with **4** stops at **5a** (Scheme 1, path a), while reaction with the bulkier **3** proceeds directly to **1a** [Eq. (1), step a], and **5b** was not observed.

Several reactions of germylenyl lithiums **1a** and **2a** were studied. Addition of iodomethane to **1a** in THF at room temperature yields germene **9** [Eq. (2)] in 80% yield. The  $^{13}C$ -NMR spectrum of **9** shows a characteristic peak of the alkenyl carbon atom at 178.6 ppm (calculated 180 ppm<sup>[26]</sup>), upfield shifted in comparison with that of **1a** (195 ppm) and of  $2-Ad=Ge(SiMe_2tBu)_2$  (208.6 ppm<sup>[17]</sup>).<sup>[27]</sup> Germene **9** was also characterized by high-resolution mass spectrometry.



Addition of *tert*-butylacetylene to **1a** (in hexane or toluene) produces hydrido germene **10** in 97% yield (Scheme 3, path a). **10** exhibits a characteristic alkenyl  $^{13}C$ -NMR signal at 187 ppm (calculated 191 ppm<sup>[26]</sup>), slightly downfield shifted in comparison to germene **9**. The alkenyl hydrogen of **10** absorbs at 6.66 ppm, in the range of known hydrido digermenes,  $L(H)Ge=Ge(H)L$  ( $L = C_6H_3-2,6(C_6H_3-2,6-iPr_2)_2$ ,<sup>[28]</sup>  $N(Ar)[Si(iPr)_3]$ ,  $Ar = 2,6-[C(H)Ph_2]_2-4-iPrC_6H_2$ <sup>[29]</sup>), (5.87 and 8.21 ppm, respectively). For comparison, the resonances of the alkenyl carbon and hydrogen of the analogous hydrido silene  $(tBu_2MeSi)(1-Ad)C=Si(H)(SiMetBu_2)$  (**11**) are at 165 ppm and 5.03 ppm, respectively,<sup>[30]</sup> upfield shifted compared to **10**.<sup>[31]</sup> A characteristic  $\nu_{GeH}$  stretch at 2062  $cm^{-1}$  is observed in the IR spectrum of **10**, slightly higher than for  $Ge^{II}$ <sup>[28,29]</sup> and  $Ge^{IV}$ <sup>[32]</sup> hydrides (1900–2000  $cm^{-1}$ ).

Germene **10** does not react with an additional equivalent of *tert*-butylacetylene in toluene or hexane.<sup>[33]</sup> However, changing the hydrocarbon solvent to THF promotes addition of the acetylenic C–H bond across the  $Ge=C$  bond of

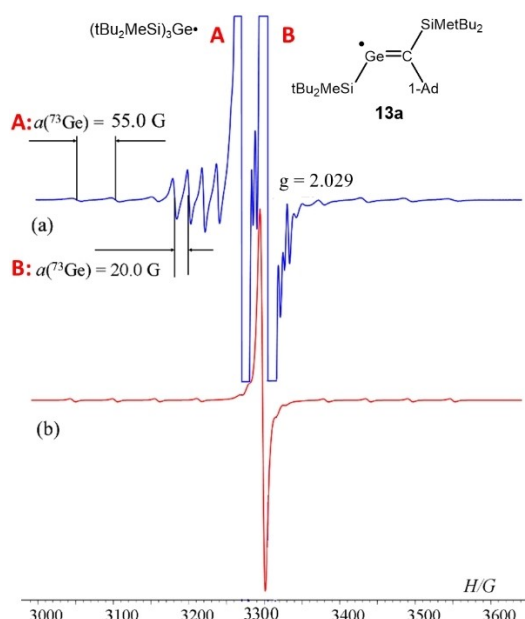


**Scheme 3.** Reactions of germylenyl lithiums **1a** and **2a** with *tert*-butylacetylene.

**10**, producing germynylacetylene **12a**, as a single ( $R^*,S^*$ )-diastereoisomer in 98% yield (according to NMR analysis, see Supporting Information) (Scheme 3, path b). The *anti*-( $R^*,S^*$ ) stereochemistry of the silyl groups in **12a** was determined by X-ray diffraction analysis (see Supporting Information). C–H insertion reactions of germene  $Me_2Ge=CH(CH_2tBu)$  with several aryl-, silyl- and alkyl-substituted alkynes, were previously reported, and the reaction mechanism was elucidated.<sup>[34]</sup> According to these studies, C–H insertion of *tert*-butylacetylene to the  $Ge=C$  bond probably proceeds through a chain reaction,<sup>[34]</sup> initiated by trace amounts of acetylenide,  $tBu-C \equiv C^-$  (present as a byproduct from the synthesis of germene **10** (Scheme 3, path a)). Addition of acetylenide anion to  $Ge$  of the  $Ge=C$  bond of **10** yields a carbanion intermediate, which can then abstract a proton, probably from *tert*-butylacetylene, producing **12a** (and the acetylenide). The observed high *anti*-stereoselectivity in the addition of *tert*-butylacetylene to the  $Ge=C$  bond in **10** is surprising, as calculations show that the barrier for rotation around the  $Ge-C$  bond in the carbanion intermediate is only ca. 1 kcal mol<sup>-1</sup> (see Supporting Information). Additional studies are required to unravel the reasons for the observed stereospecific *anti*-addition of  $tBuC \equiv CH$  to **10**. Interestingly, the smaller **2a** reacts with one equivalent of *tert*-butylacetylene (in toluene or hexane), but the reaction does not stop at the germene, producing directly a single diastereoisomer of germynylacetylene **12b** (Scheme 3, path c), according to NMR spectroscopy (see Supporting Information), by analogy probably also with *anti*-stereochemistry of the silyl groups.

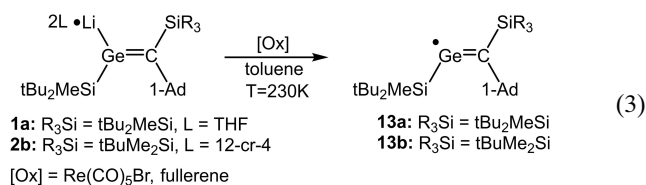
Reaction of **1a** with  $Re(CO)_5Br$  or fullerene ( $C_{60}$ ) in toluene at 230 K [Eq. (3)] produces the EPR spectrum shown in Figure 4, exhibiting a superposition of two signals: Signal A, of the known  $(tBu_2MeSi)_3Ge^\bullet$  radical ( $g = 2.0229$ ,  $a(^{73}Ge) = 20.0G$ ,  $a(^{29}Si_\beta) = 8.0G$ ),<sup>[35]</sup> probably a byproduct obtained from  $(tBu_2MeSi)_3GeLi$  in the synthesis of **1a** [Eq. (1)].<sup>[36]</sup> Signal B, corresponds to the novel germylenyl radical, **13a**. Radical **13a** is persistent at 230 K, having a half-life of about 30 min.<sup>[37]</sup> The  $g$ -value of **13a** is 2.029, slightly higher than the reported range of  $Ge$ -centered



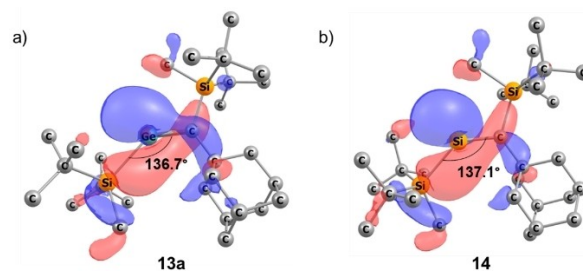


**Figure 4.** a) Experimental EPR spectrum of the reaction mixture [Eq. (3)] (230 K, toluene): A) signal of  $(\text{tBu}_2\text{MeSi})_3\text{Ge}^\bullet$ ; B) signal of germyl radical **13a**; b) simulated EPR spectra of germyl radical **13a**.<sup>[40]</sup> (For details see Supporting Information.)

radicals, 1.9991–2.0107.<sup>[38]</sup> The Ge signal is expected to show splitting to 10 satellite lines, due to coupling with the  $^{73}\text{Ge}$  nucleus ( $I=9/2$ ), but due to overlap, only 7 signals (3+4) are observed, with a hyperfine coupling constant (hfcc) of  $a_{\text{av}}(^{73}\text{Ge})=55.0\text{G}$  (Figure 4, Table S8 in Supporting Information). This  $a(^{73}\text{Ge})$  hfcc is somewhat smaller (55.0G vs 68.4–173G) in comparison to previously reported alkyl- and aryl-tri-substituted germyl radicals having a pyramidal structure at Ge.<sup>[38]</sup> However,  $a(^{73}\text{Ge})$  of **13a** is significantly larger than that of planar  $(\text{tBu}_2\text{MeSi})_3\text{Ge}^\bullet$  ( $a(^{73}\text{Ge})=20.0\text{G}$ )<sup>[35]</sup> and planar cyclotrigermeryl radical,  $(\text{GeC}_6\text{H}_3\text{mes}_2\text{-}2,6)_3^\bullet$ , ( $a(^{73}\text{Ge})=16.0\text{G}$ ).<sup>[39]</sup> Thus,  $a(^{73}\text{Ge})$  of **13a** indicates a significant s-character in the singly occupied orbital and a bent structure at the Ge atom. Reaction of **2b** with fullerene ( $\text{C}_{60}$ ) in toluene at 230 K produces the analogous germyl radical **13b** [Eq. (3)], characterized by EPR spectroscopy ( $a(^{73}\text{Ge})=60.2\text{G}$ ,  $t_{1/2}\approx 30$  min at 230 K) (Figure S3 in Supporting Information).



Additional insight is provided by quantum-mechanical calculations.<sup>[41]</sup> The calculated EPR hfcc for **13a** ( $a(^{73}\text{Ge}_v)=54.3\text{G}$ ) is in good agreement with the experimental hfcc (Table S8 in Supporting Information). **13a** is calculated to have a strongly bent structure at Ge with a  $\angle\text{Si-Ge=C}$  bond angle of  $136.7^\circ$  (Figure 5a, Table S8 in Supporting Informa-



**Figure 5.** Calculated SOMOs of a) germyl radical **13a**; b) silenyl radical **14**. Hydrogen atoms were omitted for clarity.

tion), by  $15^\circ$  larger than that in corresponding germyl lithium **1a** ( $121.7^\circ$ ). The calculated C=Ge bond in **13a** is  $1.835\text{Å}$ , by  $0.03\text{Å}$  and  $0.068\text{Å}$  shorter than in **1a** ( $1.865\text{Å}$ ) and in free anion **1a** (calculated  $1.903\text{Å}$ ), respectively. The C=Ge bond in **13a** is slightly twisted, by  $12.4^\circ$ , similarly to **1a** ( $10.1^\circ$ ). Natural bond orbital (NBO) analysis<sup>[42]</sup> indicates that the SOMO of **13a** has  $s^{54\%} p^{46\%}$  hybridization with occupancy of 0.9 electrons, consistent with the large  $a(^{73}\text{Ge})$  value.

Comparison of **13a** with the analogous silenyl radical  $(\text{tBu}_2\text{MeSi})(\text{1-Ad})\text{C}=\text{Si}^\bullet(\text{SiMetBu}_2)$  (**14**)<sup>[43]</sup> is of interest (Figure 5, Table S8 in Supporting Information). Silenyl radical **14** ( $t_{1/2}\approx 30$  min at 300 K) is significantly more stable kinetically than germyl radical **13a** ( $t_{1/2}\approx$  ca. 30 min at 230 K).<sup>[44]</sup> Replacing Si by Ge elongates the C=E bond by  $0.094\text{Å}$ , decreasing steric protection by the substituents at the radical center, explaining the lower kinetic stability of **13a** compared with **14**.<sup>[44]</sup> The  $\angle\text{C=E-Si}$  angles in **13a** and **14** are similar ( $136.7^\circ$  and  $137.1^\circ$ , respectively) (Figure 5), indicating a similar s-contribution to the orbital of the unpaired electron in these radicals (see Supporting Information, Table S8).

In conclusion, we report the synthesis, isolation, and spectroscopic characterization, including X-ray crystallography of **1a** and **2b**, the first genuine stable germyl lithiums. These germyl lithiums have substituents with a mild electronic effect, in contrast to **Vb** and **VI** having a perturbing nitrogen-substituent at the alkenyl carbon, compounds, which are better described as germanylidene anions.<sup>[13,14]</sup> The potential of **1a** and **2a** for the synthesis of new germanium compounds is demonstrated by their reactions with MeI and *tert*-butylacetylene. Oxidation of **1a** or **2b** yields the first persistent germyl radicals **13a** or **13b**, respectively ( $t_{1/2}\approx 30$  min at 230 K), which however are kinetically significantly less stable than the analogous silenyl radical **14**. EPR spectroscopy of radicals **13a** and **13b** points to significant s-character of the Ge-centered singly occupied orbital ( $a(^{73}\text{Ge})$  is  $55.0\text{G}$  for **13a** and  $60.2\text{G}$  for **13b**), in agreement with their calculated strongly bent structures at Ge ( $\angle\text{Si-Ge=C}=136.7^\circ$  (**13a**),  $135.9^\circ$  (**13b**)). Reactions of germyl lithiums **1** and **2** with other electrophiles and with small molecules such as CO and  $\text{CO}_2$ , as well as the chemistry of germenes **9** and **10**, are being currently explored in our group.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

**Keywords:** Anions · DFT calculations · EPR Spectroscopy · Germanium · Germyl Radicals

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