Synthesis and Structure of the Disilagmerimane GeCl₂ + 2(Me₅Si)₂SiLi(thf)₃ \rightarrow \text{GeLi(thf)₃}  \big\downarrow \text{GeCl₂} + 2\text{Me₅SiLi} + 3\text{thf}

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Up until the beginning of the 1980s three-membered ring systems of the heavier elements of group 14 were considered unobtainable, and in fact even today not many of these compounds are known. However, the use of very bulky ligands stabilizes these tricyclic systems kinetically and protects the reactive center with an organic layer. This prevents further reaction and dimerization. In 1981 Masumune et al.\[11\] isolated the unprecedented hexakis(2,6-dimethylphenyl)cyclosilirane by reduction of dichlorobis(2,6-dimethylphenyl)silane with lithium atom over all three ring positions; however the disorder could be solved and refined reasonable well. The site occupation factor of the Ge atom converged at 1/3. As expected the two exocyclic Ge–Si distances (235.6 pm) are shorter than the endocyclic Ge–Si distances (239.1 pm). This is also valid for the Si–Si distances (236.6 pm exocyclic, 237.7 pm endocyclic). The Si – Si and Si – Ge distances in the three-membered ring are consistent with the results of recently published ab initio calcula-
The most remarkable structural feature in the anion of 2 is the Si-Ge-Si angle (average of 101.6°; Ge1, Si1, and C2 lie on a crystallographic mirror plane, so that there are only two independent angles). This angle is more acute than the Si-Si-Si angle in the tris(trimethylsilyl)silyllithium derivatives R3SiLi(thf) (102.1°) [15] and R3SiLi(dme)1.5 (104°) [16] (R = SiMe3, dme = dimethylethane), which both crystallize as contact ion pairs. The reason for this is the increasing energetic separation of ns and np orbitals for the heavier elements of the group. This decreases the participation of electrons in σ orbitals in σ bonds. Therefore, in the [Ge(SiMe3)3] anion the three orthogonal p orbitals are chiefly used for bonding to the three MeSi3 substituents, whereas the lone pair possesses mainly s character.

Recent investigations on Ph5SnLi(thf) [17] and Ph5PbLi(thf) [18] (pmeta = (Me5NCH2CH2)NMe) show that with increasing atomic number this effect becomes more pronounced (C-E-C angle in Ph5E-Li: E = Sn: 96.1° and for E = Pb: 94.3°). The reduction in the Si-Ge-Si angle in the [Ge(SiMe3)3] anion is even more remarkable, because the steric demand of a thfLi group such as in (Me2Si)2SiLi(thf) on the Si-Si-Si angle is even smaller for these reasons. In Ge(pz)3Na(thf) (pz = pyrazol-1-yl) the germam group is likewise not coordinated by the alkali metal, because the sodium atom is coordinat-
ence peak and hole: 310 e mm$^{-1}$, R$_1$ (F > 4σ(F)) = 0.040 and wR$_2$ = 0.095 (all data); R values as defined above. Data of both structures were collected on a Stoe-Siemens-AED diffractometer. The intensities of the rapidly cooled crystal-
as in an oil drop [27] were collected by the $2\theta$ω method. Both structures were solved by direct methods (SHELXS-90) [28] and refined by full-matrix least-squares on F$^2$ [29]. The silicon/germanium disorder in 1, which is caused by symmetry could be resolved. The refinement of occupancy for the central silicon atoms and the germanium atom resulted in values of 2/3 and 1/3, respectively. The refinement in the space group C2/c was not successful. Due to the disorder of the crown ether molecule caused by the mirror plane, two crown ether molecules with an occupancy of 1/2 each were refined. 1–2 and 1–3 distances of chemically equivalent bonds were refined by using distance restraints. Further details of the crystal structure investigations are available on

One of the insights obtained from quantum chemical calculations of 3b and its reaction with R'Li$^{[7]}$ was that the N–O bond in 3b is bridged by Li and longer than the related bond in its nonlithiated counterpart 3a. This would explain the relatively facile cleavage of the N–OCH$_3$ bond in 3b$^{[6]}$ and the N–X bonds in other nitrenoids such as 1a,b. In 1991 Genet, Mallart, Greek, and Piveteau showed that nitrenoids of type 6 are also suited for the electrophobic amination of R'Li to give 7$^{[9]}$. The corresponding Boc-protected primary amine is obtained from protonation of 7.

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We report here on the crystal structure of N-lithium N-mesitylsulfonyloxy-tert-butylcarbamate (6b), which crystallizes as a dimer with three equivalents of THF, and we compare this structure to that of the dimer of the nonlithiated N-toluene-
sulfonyloxy-tert-butylcarbamate (8). Compound 6b is the first nitrenoid characterized by X-ray structure analysis.$^{[10]}$

The two anions in [(6b)$_2$(thf)$_3$] (Fig. 1) are linked by two Li cations, such that Li1 (Li1A) is bound to N1A (N1) and O4 (O4A). The strong donor O4A prevents the bridging of, for example, the N1–O3 bond by Li1A. The two Li centers are tetra-coordinate; each interacts with two terminal (O6, O6A) and one shared THF molecule (O7), an unusual type of THF coordination. It is amazing that the oxygen atoms O1 (O1A) and O2 (O2A) of the sulfonyloxy unit are not bound to lithium, considering their excellent donor properties.$^{[13]}$ The shortening of the N1–C10 bond in [(6b)$_2$(thf)$_3$] to 133.1(4) pm relative to the analogous bond in (8)$_2$ (N1–C8, 140.6(7) pm, Fig. 2) and the lengthening of the C10–O4 bond in [(6b)$_2$(thf)$_3$] (123.9(4) vs. 120.6(7) pm for C8–O4 in (8)$_2$) are as expected. In [(6b)$_2$(thf)$_3$], C10 has planar coordination, in (8)$_2$ (C8, sum of angles 360.0, 359.8°, respectively). O3 in [(6b)$_2$(thf)$_3$] is almost in the plane formed by N1, C10, O4, and O5 (torsion

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Nitrenoids I and their reactions have been known for a very long time. In 1872 Lossen described compounds of type 1a$^{[1]}, 2a, b)$ which like compounds $2b^{[2a, b, 3]}$ prepared by Hofmann in 1881, are converted into isocyanates 2a by the shift of the R group to the N atom and x elimination of NaX.

![Diagram](attachment:image.png)

The observation made by Schverdina and Kotscheschkov in 1938 was particularly remarkable and long not understood: in the amination of organolithium compounds R'Li the elec-

trophilic species is not O-methylhydroxylamine (3a) but rather the N-lithiated species 3b. Primary amines 5 are then obtained via 4$^{[8]}$. The dimerization of a nitrenoid$^{[5]}$, which proceeds analogously, and its x elimination to provide a nitrene$^{[6]}$ were

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