

both the 3'-5'-coupled pyrophosphate **3f** and the 5'-5'-coupled **4** are rapidly formed in the template-independent reaction with **1f** (cf. *b*).

The results described here offer evidence that chemical self-replication is possible even in model systems in which oligonucleotides with 3'-5' pyrophosphate bonds are synthesized. Oligonucleotides with pyrophosphate backbones are increasingly being discussed as possible prebiotic "information molecules"; their template properties in nonenzymatic oligomerizations have been described recently.^[10] Further investigations into sequence dependence will presumably show to what extent the selection values of self-replicating molecules can be understood in terms of thermodynamically and kinetically controlled selectivities in the synthesis of alternative sequences. Such studies might afford insight into the question whether a self-constitution^[11] of sequential information must be considered in the later phases of chemical evolution.

Received: April 7, 1989 [Z 3280 IE]
German version: *Angew. Chem.* 101 (1989) 1259

CAS Registry numbers:

1b, 122238-09-9; **1c**, 122238-10-2; **1d**, 122238-11-3; **1e**, 122238-12-4; **1f**, 122238-13-5; **1g**, 122238-14-6; **1h**, 122238-15-7; **2b**, 122238-16-8; **3a**, 122238-25-9; **3b**, 122238-17-9; **3c**, 122238-18-0; **3d**, 122238-19-1; **3e**, 122238-20-4; **3f**, 122238-21-5; **3g**, 122238-22-6; **3h**, 122238-23-7; **4**, 122238-24-8.

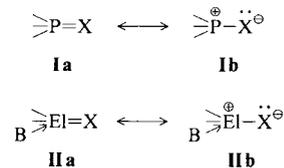
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[4] The use of an MTM protecting group instead of the previously used methyl group has, in addition to logistical advantages in the synthesis of trimers, the effect that the kinetic measurements can be carried out more exactly by HPLC. Thus, **1f** reacts with the 5'-hydroxy trimer **2a** to give a hexamer, which differs from the template used, **3a**, only in the protecting group at the 5' end, but which can be separated chromatographically from **3a**. This obviates the necessity of following the reaction by calculating differences between HPLC integrals.
[5] Equation (1) should be referred to as the "square root law", where *c'* is the concentration of the hexamer formed (here, **3f**), *c* the concentration of the added template (here, **3a**), *a* an empirical constant for the template-dependent synthesis of **3f**, and *b* the rate of the template-independent synthesis of **3f**. The constants *a* and *b* correspond to *k_a* and *k_b* in [2], *K_a* and *K_b* in [1], and *α* and *β* in [3].
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A Base-Stabilized Ge–S Double Bond

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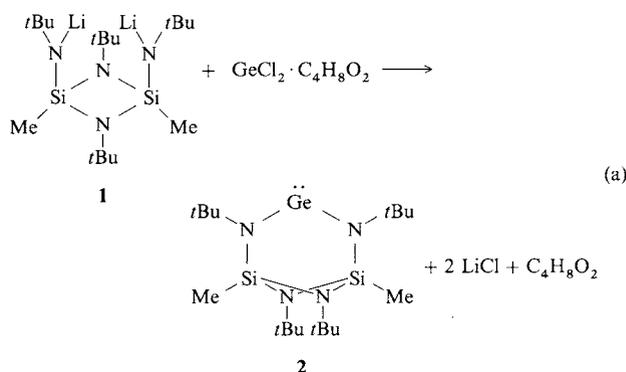
Elements of higher periods (principle quantum number *n* ≥ 3) apparently undergo multiple bonding with oxygen or sulfur when the d-orbitals can participate in the stabilization of the system or when resonance structures can be invoked in which the element in question carries a positive charge and

the chalcogen atom a negative charge. This type of bonding is particularly common in the case of phosphorus where it is generally described in terms of the resonance structures **Ia** and **Ib**.^[1] Recently, silicon-containing intermediates have also been characterized to which a structure analogous to that of the phosphorus compounds can be ascribed (Scheme 1).^[2]

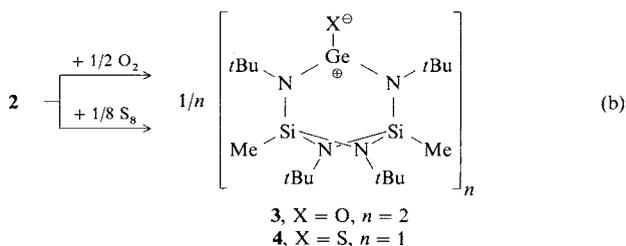


Scheme 1. X = O,S; E| = Si, Ge; B = base.

We posed ourselves the question of just how far the "base-stabilization concept" can be extended to the homologous element germanium. All attempts to isolate compounds with "unprotected" Ge–O and Ge–S double bonds have previously failed, even with sterically demanding ligands on the germanium.^[3–5] We wanted to achieve intramolecular addition of a base at germanium and therefore used polycyclic lithium silylamide **1** (Li bridges),^[6] which apart from containing two amide nitrogen atoms also contains two amine nitrogen atoms capable of coordination.



1 reacts with the dioxane adduct of germanium(II) chloride to give the bis(amino)germanediyl **2** in high yields [Eq. (a)], which has been characterized by elemental analysis, molecular weight determination and ¹H NMR spectroscopy.^[7] **2** can be easily converted with oxygen or sulfur into the oxidation products **3** and **4**, respectively [Eq. (b)].



The ¹H NMR spectra of **3** and **4** are identical at room temperature (in each case three resonance signals are observed for the *tert*-butyl groups,^[7] indicating intramolecular chelation by one of the N-atoms of the N₂Si₂ group in solution, whereas the spectrum of **4**, in contrast to that of **3**, becomes simpler on increasing the temperature (coalescence of two *tert*-butyl signals). Apparently, in the case of **4** the

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N-Ge donor bond then rapidly opens and closes on the NMR time scale (competition between the N-atoms in the N_2Si_2 ring). The compounds also differ greatly in their solubility: **3** precipitates as main product from the solution of **2** upon the introduction of oxygen, whereas **4** is readily soluble. X-Ray crystal structure analyses of **3** and **4** confirm that **3** is present as a dimer, whereas **4** is surprisingly, monomeric, i.e. contains a singly coordinated sulfur atom (in the crystalline state **4** still contains 1/2 molecule of benzene per formula unit).

The structures of the oxidation products **3** and **4** are shown alongside each other in Figure 1. The germanium

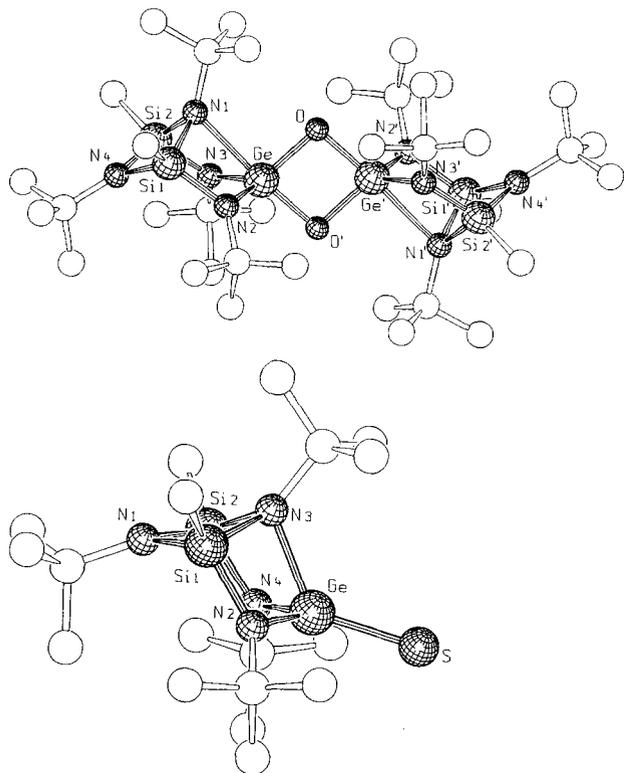


Fig. 1. The molecular structures of **3** (top) and **4** (bottom) (the carbon atoms are not labelled) [8]. Some important bond lengths [Å] and bond angles [°]: **3**: Ge-O 1.809(4), Ge-O' 1.825(4), Ge-N1 2.370(5), Ge-N2 1.880(5), Ge-N3 1.887(5), Si-N 1.744(9) (mean); N1-Ge-O 90.5(2), N1-Ge-O' 175.3(2), N2-Ge-O' 108.1(2), N3-Ge-O' 109.9(2), N2-Ge-O 119.9(2), N3-Ge-O 119.3(2), N2-Ge-N3 110.7(2), O-Ge-O' 84.8(2), Ge-O-Ge' 95.1(2). - **4**: Ge-S 2.063(3), Ge-N3 2.050(6), Ge-N2 1.882(6), Ge-N4 1.886(6), Si-N(1,2,4) 1.721(8) (mean), Si(1,2)-N3 1.831(5) (mean); N2-Ge-S 121.4(2), N4-Ge-S 123.0(2), N2-Ge-N4 110.6(3), S-Ge-N3 128.9(2), N2-Ge-N3 79.8(2), N4-Ge-N3 79.5(2).

atoms in **3** are coordinated almost trigonal-bipyramidally by two oxygen atoms and three nitrogen atoms, whereby the longer bonds are, as expected, the axial bonds in each case (to N1 and O' and N1' and O, respectively). The polycycle, with crystallographic point group $\bar{1}(C_1)$, contains two sec-onorcube units (N_4Si_2Ge), which are coupled to each other via a Ge_2O_2 four-membered ring.

In **4** the germanium atom is only four coordinate. The coordination can be described as distorted tetrahedral, or better still as trigonal-planar (N2, S, N4) with an additional bond (Ge-N3), since the sum of the angles at the germanium atom for the bonds to N2, S and N4 deviates only 5° from the ideal value of 360°. Especially striking is the difference in length (0.17 Å) between the Ge-N3 bond and the other, shorter Ge-N bonds. The Ge-S distance of 2.063(3) Å is so far the shortest germanium-sulfur distance and is about

0.2 Å shorter than the value for a Ge-S single bond.^[9] In the thio germanate ion $Ge_4S_{10}^{4-}$, which has an adamantane-like structure, the terminal Ge-S distances are 2.12(1) Å^[10] and are thus 0.06 Å longer than in **4**. According to calculations on $H_2Ge = S$ the $p\pi-p\pi$ Ge-S double bond should be 2.02 Å in length.

Accordingly, all structural data suggest that the bonding model **II** can also be applied to **4**. Compound **4** is therefore the first isolable compound with a base-stabilized double bond between sulfur and a tetravalent element of a higher period. Molecules with intramolecular base-stabilized Si-S and Ge-S bond, respectively, have recently been obtained via an entirely different route.^[12] Of interest in the importance of **4** is that a molecule isoelectronic to **4** with Ga and Cl instead of Ge and S exists^[13] (see also the corresponding methylgallium derivative).^[14]

Experimental

2: A solution of the dilithium compound **1** (385 mg, 1 mmol) in benzene was added dropwise within 30 min to a slurry of the dioxane adduct of germanium(II) chloride (232 mg, 1 mmol) in benzene (5 mL)^[6]. After 12 hours the precipitate was filtered off, the solvent removed from the filtrate by distillation, and the resulting residue sublimed at 80 °C/10⁻³ torr; this furnished 363.3 mg (82%) of colorless, crystalline **2**.

3,4: A solution of 181.1 mg (0.41 mmol) of **2** in 2 mL of toluene was treated with a stream of oxygen diluted with nitrogen, or with 13.1 mg (0.41 mmol) of sulfur. **3** precipitated as a colorless powder, which was recrystallized from benzene; **4** could first be isolated after evaporation of the solution to dryness. Yields 112.9 mg (60%) **3**; 190.6 mg (98%) **4**.

Received: April 14, 1989 [Z 3295 IE]

German version: *Angew. Chem.* 101 (1989) 1287

CAS Registry numbers:

1, 122093-34-9; **2**, 122093-35-0; **3**, [Ge^{IV}], 122093-36-1; **3**, (chelate), 122114-35-6; **4**, [Ge^{IV}], 122093-37-2; **4**, (chelate), 122093-39-4; **4** (Ge^{IV})-1/2 benzene, 122093-38-3; **4** (chelate)-1/2 benzene, 122093-40-7; GeCl₂·D, 28595-67-7.

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- [7] ¹H-NMR (toluene): **2** (290 K): δ = 0.55 (s, 6H, SiCH₃), 1.26 (s, 18H, NC(CH₃)₃), 1.41 (s, 18H, NC(CH₃)₃); **3** (290 K): δ = 0.71 (s, 6H, SiCH₃), 1.28 (s, 9H, NC(CH₃)₃), 1.57 (s, 9H, NC(CH₃)₃), 1.73 (s, 18H, NC(CH₃)₃); **4** (370 K): δ = 0.65 (s, 6H, SiCH₃), 1.34 (s, 18H, NC(CH₃)₃), 1.51 (s, 18H, NC(CH₃)₃); coalescence temperature: 307 K; **4** (290 K): δ = 0.58 (s, 6H, SiCH₃), 1.28 (s, 9H, NC(CH₃)₃), 1.39 (s, 9H, NC(CH₃)₃), 1.52 (s, 18H, NC(CH₃)₃).
- [8] Crystallographic data: **3**: triclinic, $P\bar{1}$, $a = 10.794(8)$, $b = 10.816(8)$, $c = 11.121(8)$ Å, $\alpha = 97.5(1)$, $\beta = 102.9(1)$, $\gamma = 97.8(1)^\circ$, $V = 1236$ Å³; $Z = 1$; 2064 „observed“ reflections ($2\sigma_F$), 278 parameters, $R = 0.049$. - **4**: $\frac{1}{2} C_6H_6$: orthorhombic, $Pbca$, $a = 10.619(6)$, $b = 15.834(9)$, $c = 33.84(2)$ Å, $V = 5687$ Å³; $Z = 8$; 2128 „observed“ reflections ($3\sigma_F$), 305 parameters, $R = 0.051$. - Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-53903, the names of the authors, and the journal citation.
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