

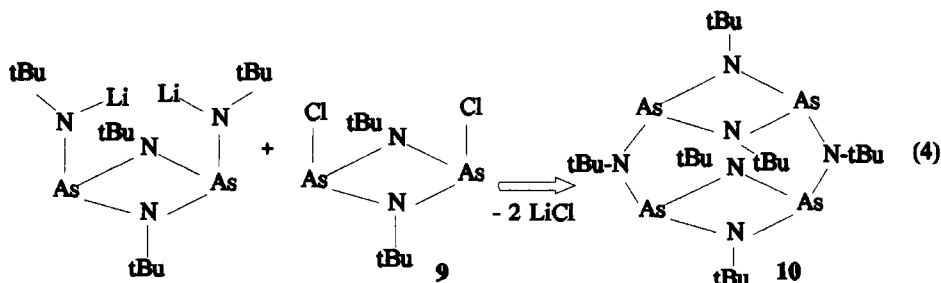
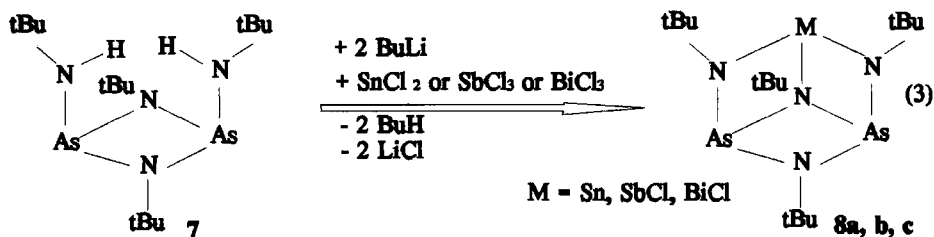
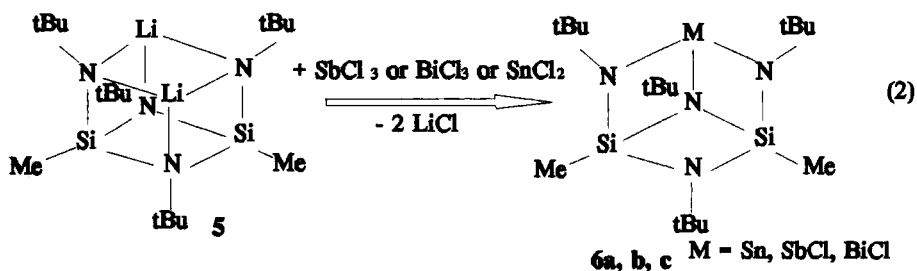
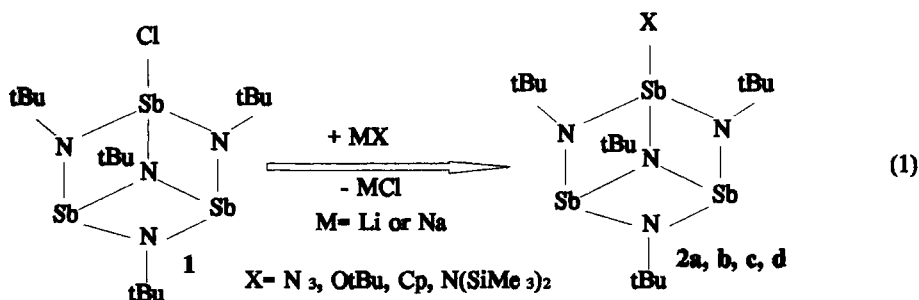
POLYCYCLIC AMIDES AND SILYLAMIDES OF Ge, Sn, As, Sb AND Bi

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Abstract Polycyclic compounds with nitrogen, (silicon, carbon) and metallic main group elements like Ge, Sn, As, Sb and Bi forming the skeleton have been synthesized by two different ways. By a first route the components of the compounds are put together by classical salt elimination reactions while by the second procedure a Lewis acidic center in the molecule (Ge) serves as target for an intramolecular attack of a nitrogen base. If this nitrogen atom has an trimethylsilyl substituent a trimethylsilyl migration to the electronegative end of the Ge=X bond (X=O, N-SiMe₃, S) is observed parallel to the Ge-N bond formation; if the nitrogen atom is substituted by tert-butyl, an intramolecularly N-coordinated Ge=X system is isolated as a crystalline compound.

POLYCYCLES WITH A METAL TRICAPPED N₄-TETRAHEDRON

As we have shown several years ago the tricyclic Sn₃(NtBu)₄H₂ can be described as a distorted N₄-tetrahedron three of the faces being capped by tin atoms.¹ This compound also shows unique bond fluctuations.² We have been interested in the synthesis of similar compounds, in order to study the parameters more closely which could be responsible for such properties. In equations (1) - (4) our attempts are summarized. All products (50-85% yield) show correct analytical and spectroscopic (IR, NMR) data. The chlorine substituent in 1 (which originates from the reaction of SbCl₃ and tert-butylamine besides other products) can be displaced by several ligands to yield 2a, 2b, 2c and 2d. Treatment of 1 with AlCl₃ or SnCl₂ is followed by chloride abstraction from the polycycle yielding the ionic Sb₃(NtBu)₄⁺ AlCl₄⁻ (3) and Sb₃(NtBu)₄⁺ SnCl₃⁻ (4). While in 1, 2, 3 and 4 three

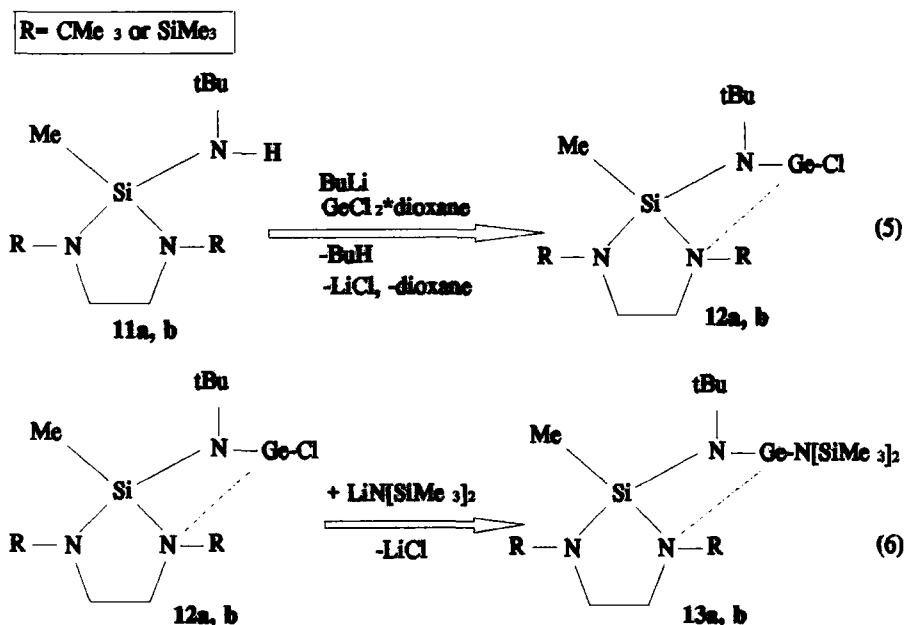


antimon atoms together with the nitrogen atoms form the polycyclic skeleton, in 6 and 8 two of the electropositive sites are occupied by Me-Si or As, which are introduced by the precursors 5³ and 7⁴ [see equations (2) and (3)]. A

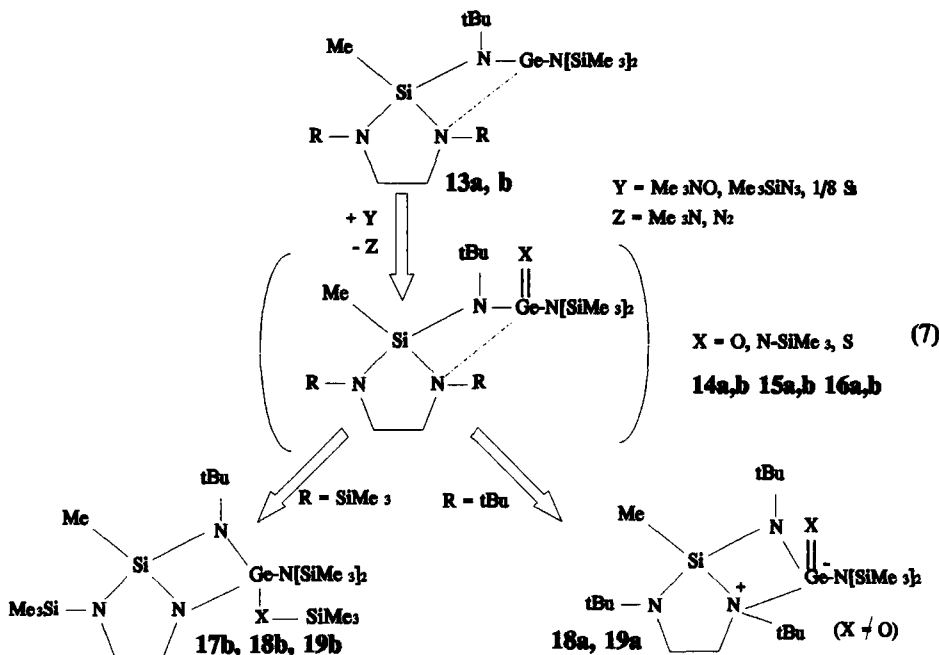
remarkable tricyclic compound **10**, which displays parallel As_2N_2 rings, is obtained in reaction (4), when the ring compound **9⁵** is used as starting material. X-ray structure analyses have made of **1**, **2a**, **4**, **6b*** $SnCl_2$, and **10**.

INTRAMOLECULAR NITROGEN COORDINATION TO UNSATURATED Ge

The ring compounds **11a** ($R = tBu$) and **11b** ($R = SiMe_3$) can be synthesized from $Me-Si(Cl)_2N(tBu)H$ and $R-N(H)-CH_2CH_2-N(H)-R^6$ by standard techniques. The amino hydrogen atom is then displaced by $Ge-Cl$ following the route described in equation (5) yielding **12a,b**. The sterically very demanding



hexamethyldisilyl ligand is introduced at the germanium atom [**13a,b** equation (6)] to protect it from immediate polymerisation when the germanium(II) compound is oxidized. X-ray structure determination of **12a** reveals a donor acceptor bond from one of the nitrogen atoms in the five membered ring to Ge. All oxidation reactions performed with **13a,b** are summarized in reaction scheme (7), in which we have used Me_3NO , Me_3SiN , and elementary sulfur as oxidants



versus germanium(II). The transient intermediates 14, 15 and 16 behave differently with respect to the ligand at the ring nitrogen atoms. If $R = \text{tBu}$ the $\text{Ge}=\text{X}$ bond is substantially maintained by coordination of the nitrogen base to the electrophilic germanium center (see also lit.⁷) forming 18a and 19a (X-ray structures). If $R = \text{SiMe}_3$, a migration of the trimethylsilyl group is observed to the electronegative end of the $\text{Ge}-\text{X}$ -bond while at the same time a SiN_2Ge four membered cycle is formed (17b, 18b, 19b). All compounds 12 - 19 show high fluxional mobility as well as a unique stereochemistry at N, Si and Ge.

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