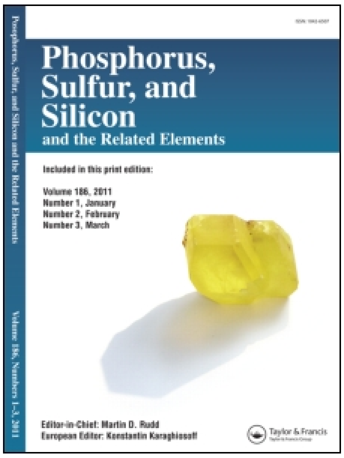

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Polycyclic Amides and Silylamides of Ge, Sn, As, Sb and Bi

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

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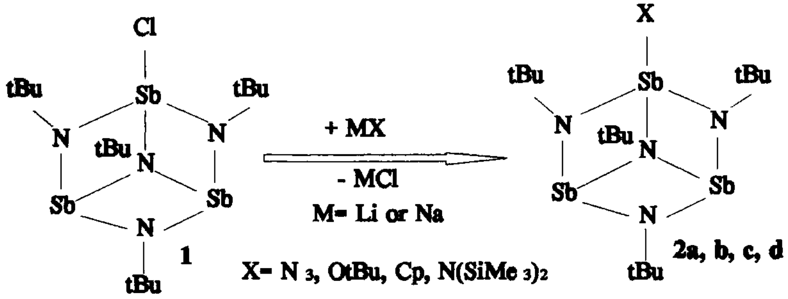
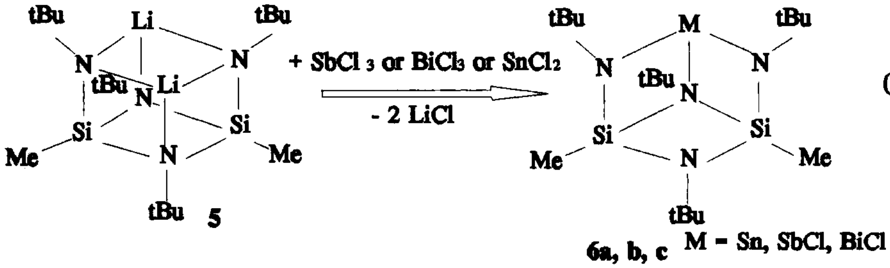
Abstract Polycyclic compounds with nitogen, (silicon, carbon) and metallic main group elements like Ge, Sn, As, Sb and Bi forming the skeleton have been synthesized by two different ways. By a first route the components of the compounds are put together by classical salt elimination reactions while by the second procedure a Lewis acidic center in the molecule (Ge) serves as target for an intramolecular attack of a nitogen base. If this nitrogen atom has an trimethylsilyl substituent a trimethylsilyl migration to the electronegative end of the Ge=X bond (X=O, N-SiMe$_3$, S) is observed parallel to the Ge-N bond formation; if the nitorgen atom is substituted by tert-butyl, an intramolecularly N-coordinated Ge=X system is isolated as a crystalline compound.

POLYCYCLES WITH A METAL TRICAPPED N_4-TETRAHEDRON

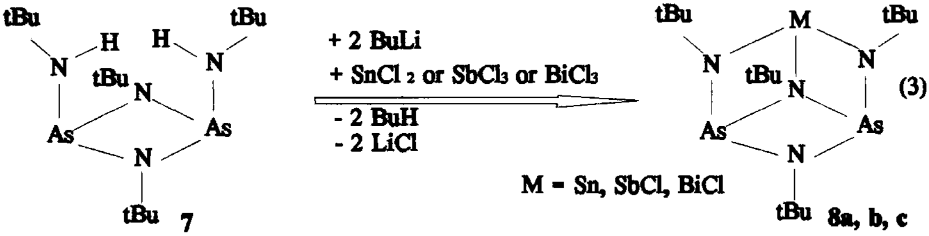
As we have shown several years ago the tricyclic $Sn_3(NtBu)_4H_2$ can be described as a distorted N_4-tetrahedron three of the faces being capped by tin atoms.[1] This compound also shows unique bond fluctuations.[2] We have been interested in the synthesis of similar compounds, in order to study the 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 $SbCl_3$ and tert-butylamine besides other products) can be displaced by several ligands to yield **2a**, **2b**, **2c** and **2d**. Treatment of **1** with $AlCl_3$ or $SnCl_2$ is followed by chloride abstraction from the polycycle yielding the ionic $Sb_3(NtBu)_4^+$ $AlCl_4^-$ (**3**) and $Sb_3(NtBu)_4^+$ $SnCl_3^-$ (**4**). While in **1**, **2**, **3** and **4** three



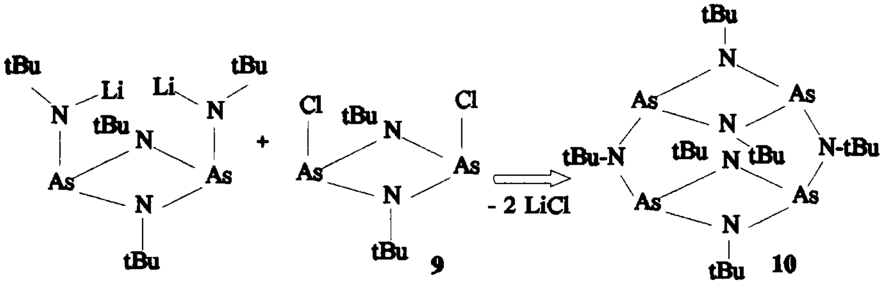
(1)



(2)



(3)

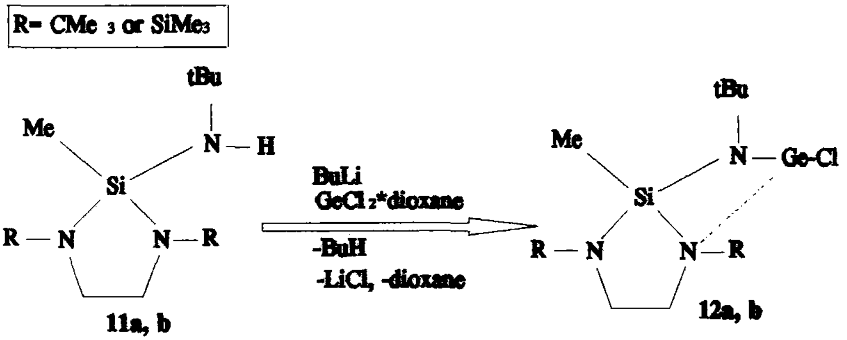


(4)

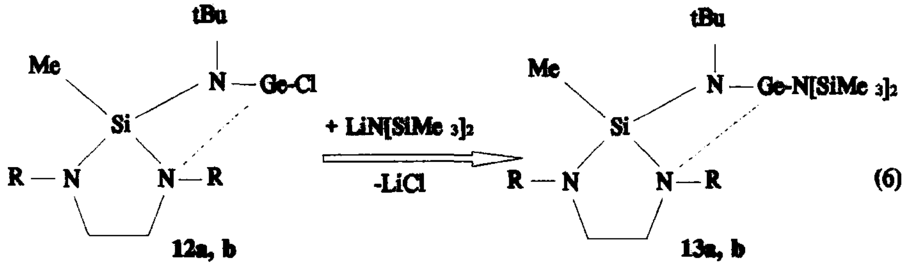
antimon atoms together with the nitrogen atoms form the polycyclic skeleton, in **6** and **8** two of the elctropositive sites are occupied by Me-Si or As, which are introduced by the precursors **5**[3] and **7**[4] [see equations (2) and (3)]. A remarkable tricyclic compound **10**, which displays parallel As_2N_2 rings, is obtained in reaction (4), when the ring compound **9**[5] 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)$_2$N(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

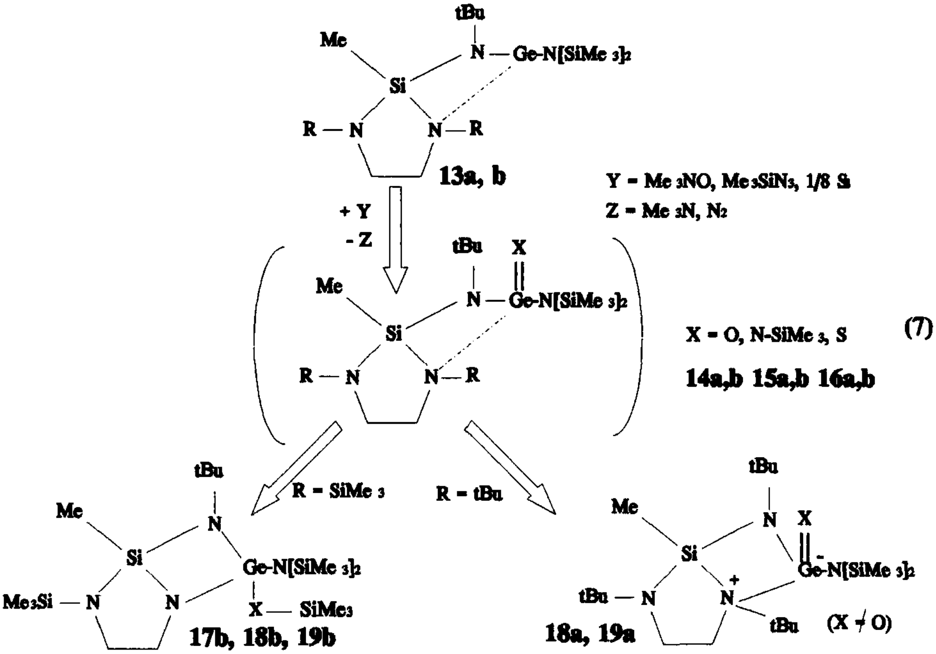


(5)



(6)

hexamethyldisilzyl 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 nitogen 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_3 and elementary sulfur as oxidants



(7)

versus germanium(II). The transient intermediates **14**, **15** and **16** behave differently with respect to the ligand at the ring nitrogen atoms. If R = tBu the Ge=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 = $SiMe_3$ a migration of the trimethylsilyl group is observed to the electronegative end of the Ge-X-bond while at the same time a SiN_2Ge four membered cycle is formed (**17b**, **18b**, **19b**). All compounds **12** - **19** show high fluctional mobility as well as a unique stereochemistry at N, Si and Ge.

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