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Tetrylenes based on polydentate sulfur-containing ligands

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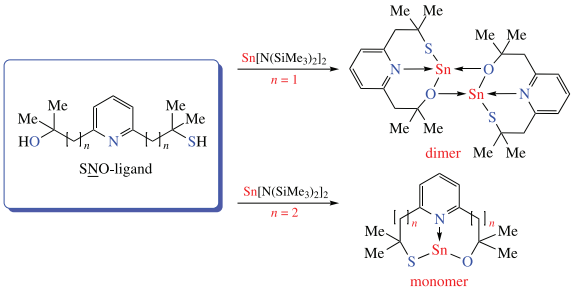
Polydentate SNO-coordinating proligands were obtained by addition of thioacetic acid to conjugated alkene, or ring-opening of thiiranes with organolithium compounds as the key stages. These SNO- and known SNS- and SOS-coordinating proligands were used for the synthesis of tetrylenes by the reaction with Lappert's tetrylenes $E[N(SiMe_3)_2]_2$ (E = Ge, Sn), giving polymeric, monomeric or dimeric species depending on the type of the ligand. The structure of stannylenes in solution was analysed by ^{119}Sn NMR spectroscopy.

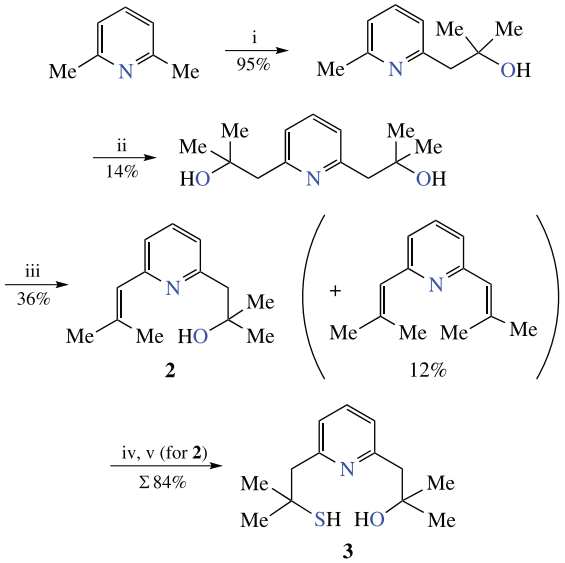


Keywords: tetrylenes, germylenes, stannylenes, organosulfur compounds, polydentate ligands, thiiranes, ring-opening, oligomerization, ^{119}Sn NMR spectroscopy.

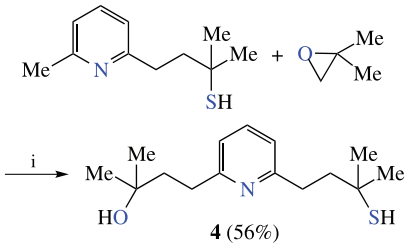
Tetrylenes are compounds of Group 14 elements (Si, Ge, Sn, Pb) with the oxidation state of E atom being II; in this case E atom has a vacant orbital and a lone electron pair. These compounds are highly reactive; there are two main ways for the stabilization of such species, including kinetic (introduction of bulky substituents) or thermodynamic (using polydentate ligands, donating electron density on E vacant orbital).[1,2] Such 'heavy' carbene analogues attract considerable attention due to their unique physical properties, reactivity, application in synthesis, catalysis,[3] activation of small molecules,[4] as ligands for transition metals[5] and even as antitumor substances.[6] Interestingly, the design of organic ligand used for tetrylene synthesis allows one to obtain highly stable compounds.

The scope of tetrylenes stabilized by sulfur containing ligands is narrow and limited to several examples including $RN(CH_2CH_2S)_2Sn$ (R = Bu^t,[7] Me),[8] $MeN(CH_2CH_2CH_2S)_2Sn$,[9] $O(CH_2CH_2S)_2Sn$,[8] $S(CH_2CH_2S)_2Sn$,[8] $RP(CH_2CH_2S)_2Sn$ (R = Bu^t,[10] Ph[11,12]), $[Me_2NCHCMe_2S]_2E$ (E = Ge,[13] Sn[14]). Therefore, the synthesis and study of the properties and structure of stannylene and germylene based on such ligands are an actual subject. In continuation of our research,[15–17] in this work we report the syntheses of novel tetrylenes and the relationship between the ligand type and the degree of their oligomerization. For tetrylenes we designed the family of new proligands (becoming ligands after deprotonation) including 2,6-Py$(CH_2CH_2CH_2SH)_2$ (**1a**), 2,6-Py$(CH_2CH_2CH_2SH)_2$ (**1b**), 2,6-Py$(CH_2CMe_2SH)CH_2CMe_2OH$ (**3**), 2,6-Py$(CH_2CH_2CMe_2OH)CH_2CH_2CMe_2SH$ (**4**), O[2-$C_6H_4SH]_2$ (**5**) by variation of: (1) nature of donor atoms (N-/O-, OH-/SH-type); (2) the size of the substituents at C atoms near the donor atoms; (3) the length of carbon chain between donor atom and pyridine ring; (4) the type of SH groups (mercaptane or thiophenol). Proligands **3** and **4** are new; compounds **1a**,**b**,[18] and **5**[19] were synthesized according to described procedure.

Individual approach has to be applied to access particular type of ligand due to specific chemical properties of SH groups (ability to oxidation, high acidity and nucleophilicity). Symmetric mercaptane proligands of SNS-type **1a**,**b** (donor atom coordinatively bonded to E atom is underlined) are synthesized using our procedure[18] where the key stage consists in ring-opening of the thiirane ring by generated *in situ* stabilized organolithium reagents. To obtain ligand with short 'arms' (less CH_2 groups between donor atoms), different synthetic strategy has been employed. Thus, SNO-coordinating proligand **3** was obtained in five steps including two-step successive addition of lithiated lutidine to acetone,



Scheme 1 *Reagents and conditions*: i, BuLi (1 equiv.), Et_2O, then Me_2CO, –40 °C; ii, BuLi (2 equiv.), Et_2O, then Me_2CO, –40 °C; iii, H_3PO_4, 130 °C; iv, MeC(O)SH, PhMe, 110 °C; v, KOH, EtOH, then AcOH.

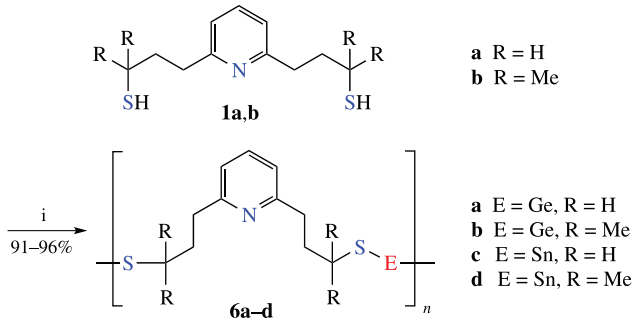


Scheme 2 *Reagents and conditions*: i, BuLi (2 equiv.), Et_2O, then 2,2-dimethyloxirane, –40 °C to room temperature.

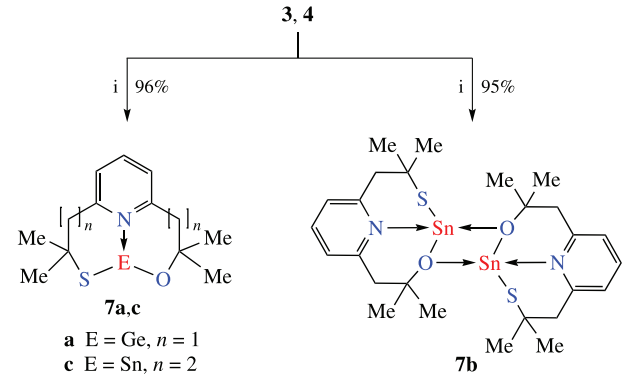
dehydratation, addition of thioacetic acid to alkene and basic hydrolysis (Scheme 1).

Proligand **4** was obtained in two steps using subsequent ring-opening of thiirane (for details, see ref. 18) and then oxirane (Scheme 2).

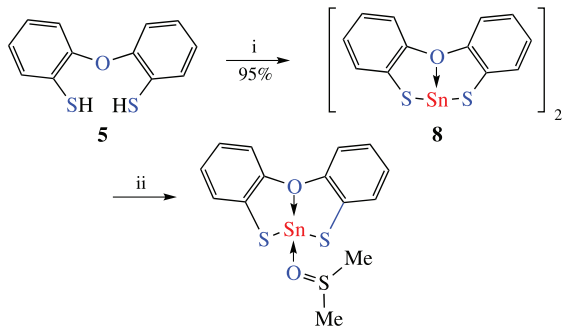
Tetrylenes **6a–d**, **7a–c**, **8** were obtained in high yields by treatment of Lappert's tetrylenes with proligands **1a**,**b** (Scheme 3), **3** and **4** (Scheme 4) and **5** (Scheme 5) (for details, see Online Supplementary Materials). Main advantage of this method is simplicity of the procedure; the sole byproduct is



Scheme 3 *Reagents and conditions*: i, $E[N(SiMe_3)_2]_2$, toluene, room temperature.



Scheme 4 *Reagents and conditions*: i, $E[N(SiMe_3)_2]_2$, toluene, room temperature.



Scheme 5 *Reagents and conditions*: i, $Sn[N(SiMe_3)_2]_2$, toluene, room temperature; ii, DMSO.

volatile $HN(SiMe_3)_2$. Extremely low solubility of tetrylenes **6a–d** based on SNS-coordinating proligands **1a**,**b** in common organic solvents (PhMe, $CHCl_3$, DMSO, pyridine) presumably indicates their linear polymeric structure; the presence and type of coordination of the N atom with the E atom requires additional research. Germylene **6a** reacts with bromine[20,21] giving insoluble materials, which further confirms the absence of coordination polymers with chelate cycles.

Tetrylenes **7a–c** are sparingly soluble in non-coordinating solvents (C_6D_6, $CDCl_3$), whereas compound **8** is soluble only in coordinating DMSO-d_6. In the last case, presumably, DMSO solvate is formed (see Scheme 5). According to XRD data for related tin(IV)[22] and tin(II)[23–27] compounds reveal these being dimers as a result of intermolecular O → Sn interactions. Alcoholate oxygen atoms have a higher donor capacity than thiolate sulfur atoms. The difference in tetrylene structure (polymeric **6a–d** *vs.* molecular **7a–c**, **8**) may be explained by the stability of S–N–S (7,7-) < S–O–S (5,5-) ≈ S–N–O (7,7-, 6,6-membered) chelate rings formed.

For stannylenes, the ^{119}Sn NMR chemical shift is sensitive to the coordination environment (coordination number)[28] and the substitution pattern (type of atoms attached to the tin center; see Table S1, Online Supplementary Materials). From these data the degree of oligomerization (association) of stannylenes can be derived. It is known that stannylenes based on 2,6-bis(oxyalkyl)-pyridine ONO-ligands tend to form dimers in solution, while for the polydentate S-ligands monomers are favorable. From ^{119}Sn NMR data we concluded that **7b** is dimer in solution (δ –228.0 ppm, SNOO-coordination) at room temperature, whereas **7c** is monomer (δ 26.3 ppm, SNO-coordination). However, monomer–dimer equilibrium[7,8] could not be excluded in both cases and should be studied further by NMR spectroscopy at variable temperature. Based on these results and on literature data (in a series of related germylenes and stannylenes based on sterically bulky ligands, Ge derivatives are monomeric),[21,29] we concluded that germylene **7a** is monomeric.

In conclusion, we obtained a series of tetrylenes based on S-containing SNS-, SNO- and SOS-coordinating polydentate ligands. For stannylenes according to ^{119}Sn NMR spectroscopy in solution, the type of donor ligand atoms and length of the carbon chain determine the degree of oligomerization. Mercaptoalkyl SNS-coordinating ligands with long ligand arms form linear polymers; thiophenolic SOS-coordinating ligands give dimers instead. For SNO-coordinating ligands, the length of the carbon (alkyl) chain also determines the oligomerization degree of stannylenes; a ligand with short chains provides dimers, whereas a ligand with long chains results in monomers. Future works will be devoted to investigate the complexation properties of the tetrylenes reported in this manuscript.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.11.027.

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