Chemistry of Heterocyclic Compounds, Vol. 43, No. 10, 2007

NEWS ITEMS

GERMANIUM-, TIN-, AND LEAD-CONTAINING HETEROCYCLES IN 2007*

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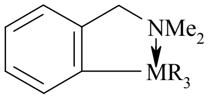
The Twelfth International Conference on the Coordination and Organometallic Chemistry of Germanium, Tin, and Lead was held from July 9 to 13 at the National University of Ireland (Galway). The conference turned out to be a memorial conference since the life of president of its organizing committee Prof. D. Cunningham unexpectedly ceased in September 2006.

Ninety seven scientists from 21 countries took part in the conference. The largest number of participants (22) represented the organizing country Ireland. Relatively large delegations came from Germany (14), Japan (9), USA (8), Great Britain (7), and France (7).

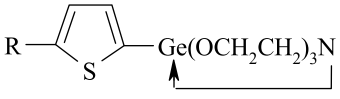
The main topics discussed at the conference related to theoretical and practical aspects of the chemistry of organic compounds of germanium and tin, the synthesis and properties of organogermanium, organotin, and organolead compounds with germanium, tin, and lead atoms of reduced or increased valence, and new derivatives of these elements containing a multiple bond.

A significant position in the program of the conference was taken up by the reports on the synthesis of new germanium-, tin-, and lead-containing heterocycles and their properties.

A large number of these heterocycles are formed as a result of additional coordination of the Ge, Sn, or Pb atom with electron-donating atoms (O, S, or N). Such heterocycles are the alkoxides and carbonates of tin and lead and also the coordination compounds with dithiocarbamate or hydroxyaldimine groups (J. R. Fulton, University of Sussex, Great Britain; L. Plasseraud, University of Burgundy, France; B. Jousseaume, University of Bordeaux, France; L. Annunziata, University of Salerno, Italy; I. Baba, University of Kebangsaan, Malaysia; A. Deák, Institute of Structural Chemistry, Budapest, Hungary). A number of these C,N-chelate compounds of tin and lead **1** were synthesized specially, using the *ortho*-organolithium derivatives of N,N-dimethylbenzylamine (A. Cristea, A. Rotar, University of Babeş-Bolay, Cluj-Napoka, Romania;



1 M = Sn, Pb



2 R = H, 2-thienyl

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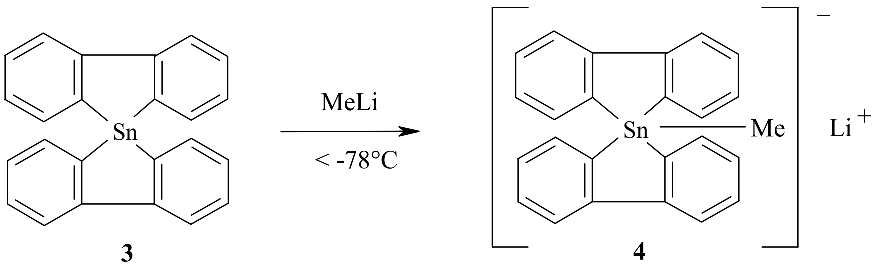
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1592-1595, October, 2007.

A. Růžička, University of Pardubice, Czech Republic). The formation of the N→M coordination bond (M = Ge, Sn, Pb) in compounds **1** and **2** and the disordering of the thiophene ring in thienylgermatranes **2** were confirmed by X-ray crystallographic investigations (L. Ignatovich, Latvian Institute of Organic Synthesis, Riga, Latvia).

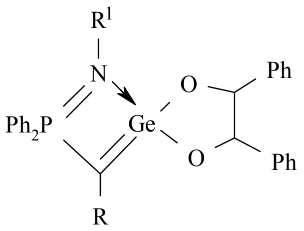
The greatest interest in this group of compounds was raised by the synthesis of the first stable pentaorganostannate **4**, which contains five (!) carbon substituents at the tin atom (M. Saito, University of Saitama, Japan). The reaction of bis(2′-bromobiphenyl)stannane with *t*-BuLi at −78°C in tetrahydrofuran took place with the elimination of aryl- or alkyllithium and led to the formation of compound **4**, which was also obtained by the addition of methyllithium to spirostannafluorene **3**.



3 **4**

The structure of compound **4** was established by X-ray crystallographic analysis and confirmed by the ^{1}H, ^{13}C, ^{7}Li, and ^{119}Sn NMR spectra.

The heterocycles of divalent germanium are also formed through a coordination bond. It was found that bisgermavinylidene in cycloaddition reactions with benzil, azobenzene, and trimethylsilyl azide acts as source of germavinylidene R_2C=Ge:, leading to various new five-membered germacycles **5**-**7** (W. P. Leung, Chinese University of Hong Kong, Chinese Peoples' Republic).



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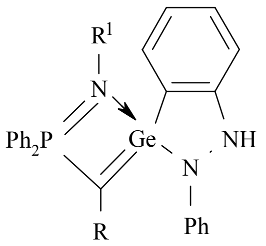

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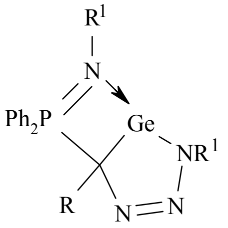

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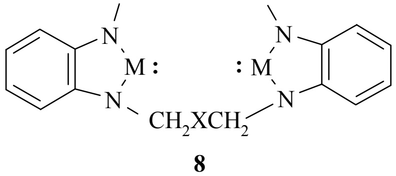
R = Ph_2P=NR^1, R^1 = Me_3Si

Heterocycles of divalent germanium of a different type were obtained by the reaction of the dioxane complex of $GeCl_2$ with N, N',N'',N'''-tetralithium-substituted tetraamines or by direct transamination of tetraamines with germylene or stannylene $[(Me_3Si)_2N]_2M$: (A. V. Zabula, University of Münster, Germany):



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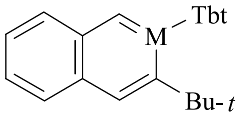
M = Ge, Sn; R = Me, Me_3CCH_2, $Me_2NCH_2CH_2$;
X = CMe_2, $(CH_2)_n$, n = 2, 3; *o*-, *m*-C_6H_4, 2,6-C_5H_3N

The stabilizing action of the bulky 2,4,6-tris[(trimethylsilyl)methyl]phenyl (Tbt) and 2,6-bis-[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt) substituents was used for the first time in the synthesis of a series of stable germa- and stannaaromatic compounds: 2-germa(stanna)naphthalene **9**, 9-germaanthracene **10**, 9-germa(stanna)phenanthrene **11** (N. Tokitoh, University of Kyoto, Japan):



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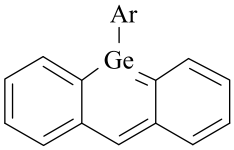
M = Ge, Sn



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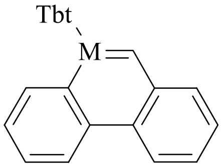
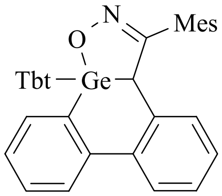
Ar = Tbt, Bbt



11

M = Ge, Sn

The ^{1}H and ^{13}C NMR spectra indicate that there are ring currents in these aromatic systems, while X-ray crystallographic analysis confirms the planarity of the rings. At the same time 9-germaphenanthrene **11** (M = Ge) enters into cycloaddition with 2,3-dimethyl-1,3-butadiene, mesitylnitrile oxide, and sulfur at the Ge=C bond like germene. Here new condensed germacycles such as **12** and **13** are formed.



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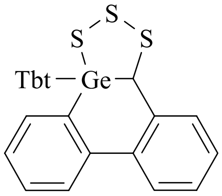
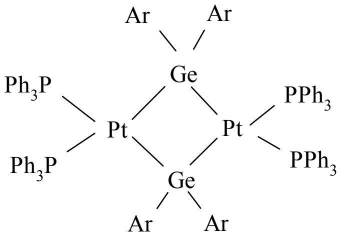


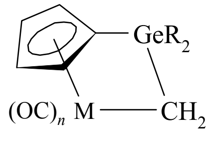
13

Numerous metallaheterocycles, containing one or more heteroatoms in the ring in addition to germanium or tin, have been synthesized. They include Ge–Pt rings **14**, formed during the reaction of the platinum complex $Pt(\eta^2\text{-}C_2H_2)(PPh_3)_2$ with tetraaryldigermanes (A. Noda, Gakushin University, Tokyo, Japan), germametallacycles **15** based on cyclopentadiene derivatives of iron, molybdenum, and tungsten (K. H. Pannell, University of Texas, El Paso, USA), and silastannacycloalkanes **16** with various ratios of silicon and tin atoms in the ring and ring sizes from four- to 12-membered (F. Uhlig, Technical University of Graz, Austria).



14

Ar = Ph, MeC_6H_4



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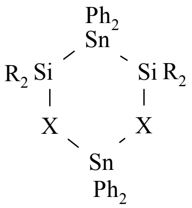
M = Fe, Mo, W



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X = $(R_2Si)_n$, $(CH_2)_m$

The 13th Conference on the Coordination and Organometallic Chemistry of Germanium, Tin, and Lead will be held in Graz (Austria) in 2010.