pyranosyl bromide **5** is obtained from **4** in 80% yield. The synthesis of the β-glucosides **6** is carried out according to the silver triflate method[13] and, without exception, leads (not optimized) to 65–80% yields. Losses arise alone by orthoester formation and associated hydrolysis (see Table 1). In no case is the α-glucoside observed.

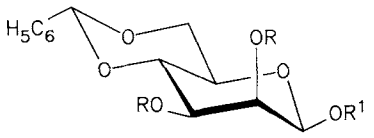
Table 1. Synthesis of β-mannosides **10** via the inversion of glycosides **6** at C-2 according to Scheme 1.

	β-Glucoside [a]			β-Mannoside **10**		
	Yield [%]	δ(C-1) [b]		Yield [%] [c]	$[\alpha]_D^{23}$ (*c*) [d]	δ(C-1) [b]
6a	40 [e]	99.7	**10a**	65	− 91.8 (0.5)	94.3
6b	65	98.8	**10b**	80	−149.3 (1.0)	92.8
6c	67	100.1	**10c**	67	− 43.3 (1.0)	95.6
6d	69	100.7	**10d**	66	− 32.9 (1.0)	94.9
6e	82	100.1	**10e**	65	− 24.5 (1.0)	96.6
			+ **11e**	10	− 14.6 (0.5)	100.01

[a] The yields (referred to **5**) were not optimized. [b] 100.1-MHz ^{13}C-NMR ($CDCl_3$). [c] Referred to **8**, which is obtained in ca. 75% yield from the respective glucoside **6**. [d] In CH_2Cl_2. [e] Using silver 4-hydroxyvalerate [14].

In particular the sluggishly reactive acceptor **12e** (with benzyl-protective groups in the 3- and 6-position), which cannot be used for direct β-mannosylation,[7] reacts with **5** to give the desired β-glucoside **6e** in 82% yield. For conversion of the β-*gluco*-compounds **6** into the β-*manno*-compounds **10/11** the *O*-acetyl groups are removed with K_2CO_3 in methanol. In the resulting sugar **7**, the 4- and the 6-hydroxy group are protected as the benzylidene acetal (→ **8**). Both reactions proceed in 85–90% yield. The free 2-hydroxy group of the β-glucosides **8** is now activated with trifluoromethanesulfonic anhydride/pyridine for the inversion of configuration to give the isolable triflates **9**, which can be converted directly into the β-mannosides **10** by heating to 75 °C in pyridine/dimethylformamide. This inversion at C-2 proceeds smoothly and without side reactions because the intramolecular attack of the carbamoyl oxygen is favored entropically. It initially affords a mixture of the 2,3-*O*-carbonyl-β-mannoside **10** in crude yields of ca. 90% and small amounts of the corresponding iminocarbonate **11**. The latter has been isolated for characterization in the case of the β-mannosylglucosamine derivative **11e**. The iminocarbonates can be easily converted into the carbonates **10** by mild hydrolysis. No carbohydrate derivatives other than the β-mannosides **10/11** are detectable in the thin-layer chromatogram of the reaction mixture. The *gluco*-configurated starting material **8** is completely converted, so a chromatographic isolation of the mannosides **10** was not really necessary. However, in these first syntheses it was carried out in order to obtain analytically pure β-mannosides. The yields of the inversion reactions after chromatographic separation are 65–80% based on the benzylidene-protected *gluco*-derivatives **8**. Thus, the disaccharide β-mannosyl-*N*-acetylglucosamine (with protecting groups: **10e**) contained in the core region of the *N*-glycoproteins is obtained in 75% yield, without having to separate side products with another configuration at C-1 or C-2.

The structure of the β-mannosides **10** has been confirmed ^{1}H-NMR and ^{13}C-NMR spectroscopically. Due to the 2,3-carbonate grouping the β-mannosides **10** show a remarkably large C-1/H-1 coupling with $J \approx 171$ Hz, signals shifted upfield to $\delta = 93$–96.5 for C-1 (see also Table 1), and a relatively large coupling constant $J_{1,2} \approx 3.5$ Hz in the ^{1}H-NMR spectrum.



	R	R	δ(C-1)	*J*(C-1/H-1) [Hz]
10a	−CO−		94.3	170.9
13a	H	H	98.0	157.1
10b	−CO−		92.8	172
13b	Ac	Ac	95.9	155

Removal of the CO group from **10b** under basic conditions and acetylation of the 2-OH and 3-OH groups furnishes the corresponding di-*O*-acetyl-β-mannoside **13b**, whose C-1 signal and, in particular, C-1/H-1 coupling confirm the β-mannoside structure. $J_{1,2}$ (≈ 1 Hz) in the ^{1}H-NMR spectrum of **13b** also has the small value typical for β-mannosides.

The reaction sequence shown in Scheme 1 thus enables the difficultly realizable β-mannosidic linkage to be achieved both selectively and efficiently.

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Polycyclic Silylamides of Ge^{II} and Sn^{II} with Different Structures—Bis(germanediyl) versus Distannate**

By *Michael Veith** and *Richard Lisowsky*

Dedicated to Professor Heinrich Nöth on the occasion of his 60th birthday

The differing coordination behavior of homologous elements in compounds of the same type can be due, inter alia, to differences in electronegativity and/or atomic size. We report here on the incorporation of two germanium(II) or tin(II) atoms respectively into the cyclodisilazane **1**; the

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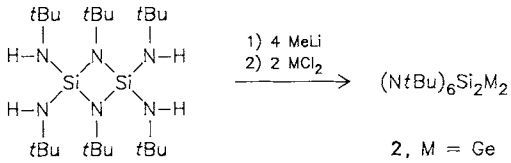
[**] Cyclic Diazastannylenes, Part 27.—Part 26: [1].

extreme differences in the structures of the products **2** and **3** are attributed to specific ring-strain effects.

Continuing on the basis of investigations into the chemistry of low valent main group elements[2] we have examined the reaction of the tetralithium salt of **1**[3] with two equivalents of the dioxane adduct of germanium dichloride and with the dichlorides of tin and lead.



1

$(NHtBu)_2(NtBu)_4Si_2Pb$ **4**

In the reaction with $PbCl_2$, a compound could be isolated in small yields which contained only one lead atom and, according to an elemental analysis, could be formulated as **4** (owing to its ready decomposition further physical-chemical characterization was not possible).

The compounds **2** and **3**, which are isolated in good yields, have analogous composition, have the expected molecular weights in benzene, and do not decompose in the gas phase under reduced pressure (mass spectra). The ^{1}H-NMR spectra of **2** and **3** consist of two singlets in the integral ratio 2:1 (Table 1).

Table 1. Some data for **2** and **3**.

	2	**3**
M_r (exp. in benzene/calc.)	620/628.08	710/720.30
^{1}H-NMR (δ values)	1.49 (18H, *t*Bu), 1.57 (36H, *t*Bu)	1.49 (36H, *t*Bu), 1.52 (18H, *t*Bu)
Crystal system	tetragonal	monoclinic
space group	$P4_2nm$	$P2_1/c$
a [pm]	957.7(9)	915.1(9)
b [pm]	957.7(9)	1931(2)
c [pm]	1753(2)	994(1)
β [°]	90	111.1(1)
V [$10^6 \cdot pm^3$]	1608	1639
Z	2	2
Measured reflections	775	1952
($F<2\sigma$)	203	341
Parameters	55	262
R (R_w)	0.056 (0.069)	0.038 (0.029)
Weighting scheme	k_1 1.000	0.7583
$W=k_1/(\sigma_F^2+k_2 \cdot F^2)$	k_2 0.01819	0.000173

The single-crystal X-ray structure analyses of **2** and **3** (Table 1) show that the structures of the two compounds are fundamentally different despite their similar composition (Fig. 1): **2** is a dispiro system with crystallographic point symmetry *mm*2 (C_{2v}) and is the first example of a species containing two isolated germanediyl units in one molecule (cf. also Refs. [4, 5]; a digermanetetrayl with both germanium atoms of formal oxidation state +1 has been described recently[6]); compound **3**, on the other hand, is a pentacycle with crystallographic point symmetry $\bar{1}$ (C_i) and with three-coordinate tin atoms. The H/Ge exchange in **1** formally proceeds with coupling of the nitrogen atoms bound to the *same* silicon atom; consequently, **2** contains two spiro centers and a linear arrangement of silicon and germanium atoms. In contrast, in the case of the formal H/Sn exchange the nitrogen atoms bridge *different* silicon atoms. The tin atoms thus come in the proximity of the nitrogen atoms N2 and N2', and, consequently, formation of an additional λ^4N-λ^3Sn bond can occur. The pentacyclic $Sn_2N_6Si_2$ skeleton can be described in terms of two face-sharing (Si_2N_2) seco-norcubane units.

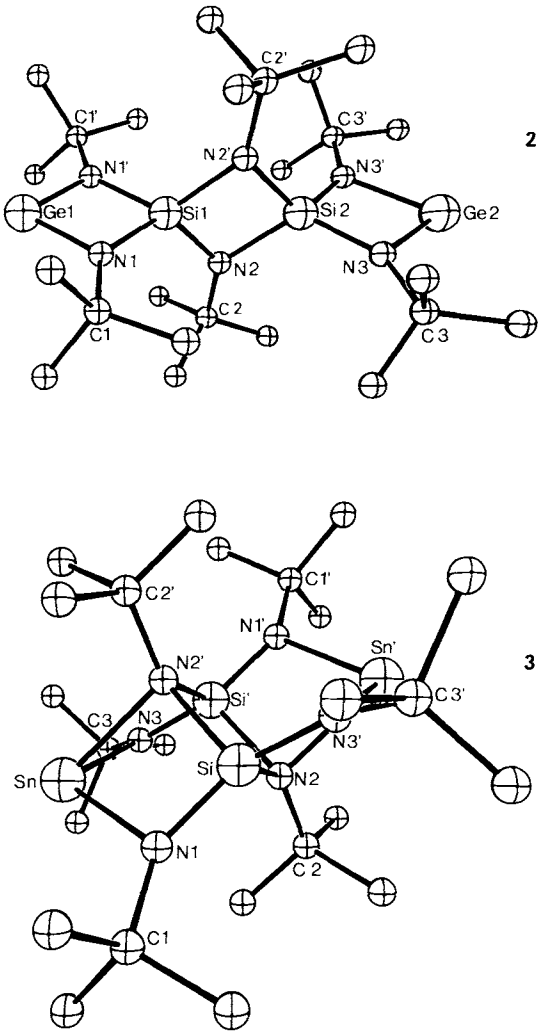


Fig. 1. Molecular structures of compounds **2** and **3**. Some (mainly averaged) bond lengths [pm] and angles [°]: **2**: N-Ge 185.6(6), N1,3-Si 173.4(3), N2-Si 174.9(1); N-Ge-N 80.9(3), N1,3-Si-N1',3' 88.0(2), N2-Si-N2' 85.9(1).—**3**: N-Sn 224.7(9), N1,3'-Si 166.8(1), N2,2'-Si 181.0(4); N1-Sn-N3 110.8(2), N1,3-Sn-N2 70.7(2), N2-Si-N2' 86.7(3), N1-Si-N3' 142.2(9) [10].

With regard to the bond lengths and angles in **2** and **3** the following special features are noteworthy (cf. Fig. 1):

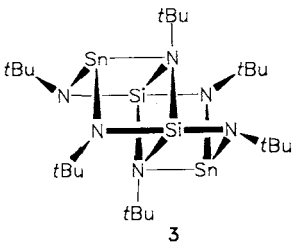
1) The Si–N distances in the central Si_2N_2 four-membered ring are, as expected, shorter in **2** than in **3**, corresponding to the different coordination numbers of N2 in **2** (three, sp^2 hybridization) and in **3** (four, sp^3).

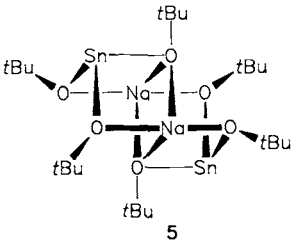
2) The Si1–N1 and Si2–N3 distances in **2** are longer than Si–N1 and Si–N3' in **3**. It can therefore be concluded that the neighboring Sn–N bond is more polar than the neighboring Ge–N bond, consistent with the higher electronegativity of the germanium compared to the tin.[7]

3) The Ge–N bond in **2** is short compared to that in the likewise monomeric bis(2,2,6,6-tetramethylpiperidino)germanium (188.5 pm);[4] this can be explained by additional p$\pi \rightarrow$pπ bonding (N$\rightarrow$Ge). All the Sn–N bonds in **3** are

about the same length; their length compares very well with those of typical λ^3Sn-λ^4N bonds such as are found in $Sn_4(NtBu)_4$ (Sn–N = 220.2 pm).[8]

The N1-Si-N3′ bond angle in **3** (Fig. 1) is extremely large for a four-coordinate silicon atom, thus indicating large steric constraints. **3** is isoelectronic and isostructural with sodium *tert*-butoxystannate **5**.[9] However, whereas





sodium as electropositive element can cope relatively well with the imposed strain in **5** (O-Na-O angle: axial 177.9(2)°, equatorial 103.3(2)°), the electronegative silicon in **3** would prefer a tetrahedral geometry (for comparison: N1-Si-N3′ 142.2°, N2-Si-N2′ 86.7°).

The different structures of **2** and **3** may be directly related to the aforementioned constraints. Since the germanium atom has a smaller radius than the tin atom, the distortion at the silicon atom in **3** should increase on formal exchange of Sn by Ge. The system is apparently no longer stable and changes to the dispiro compound **2**, even though the germanium thereby achieves the electronically less favorable coordination number two.

Experimental

A solution of **1** (1.8 g, 3.7 mmol) [3] in 20 mL hexane/20 mL diethyl ether was treated dropwise with 9.9 mL (15 mmol) of a 1.5 M solution of methyllithium in diethyl ether. After heating under reflux for 3 h the solution was cooled to −78 °C and treated with 1.7 g (7.4 mmol) of germanium dichloride-dioxane adduct, [11] 1.4 g (7.4 mmol) of anhydrous tin(II) chloride or 2.06 g (7.4 mmol) of lead(II) chloride, respectively. The reaction mixture was then warmed to room temperature and stirred for a further 4 h. In all three cases the solvent was removed under high vacuum and the resulting residue recrystallized from toluene. Yields: 1.86 g (71%) pale yellow crystals of **2** (150 °C, decomp.), 1.63 g (61%) orange-yellow crystals of **3** (decomp. 200 °C), and 0.38 g (15%) deep-red crystals of **4**.

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The Enzymic Interconversion of Isobutyryl and *n*-Butyrylcarba(dethia)-Coenzyme A: A Coenzyme-B_{12}-dependent Carbon Skeleton Rearrangement**

By *Günther Brendelberger, János Rétey,* Doreen M. Ashworth, Kevin Reynolds, Frances Willenbrock,* and *John A. Robinson**

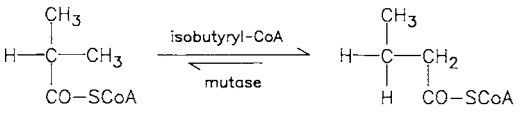
Dedicated to Professor Theodor Wieland on the occasion of his 75th birthday

Coenzyme B_{12} has one of the most complex structures[1] amongst the known coenzymes and in association with various proteins is able to promote several rearrangement reactions that until recently were without clear chemical precedence. Amongst these are three well known carbon skeleton rearrangements[2] in which an organic moiety and a hydrogen atom exchange positions on adjacent carbon atoms [Eq. (a)]. The mechanism of these rearrangements is

(a)

R = CO–SCoA methylmalonyl-CoA mutase
R = $CHNH_2$–COOH glutamate mutase
R = C(=CH_2)–COOH methyl itaconate mutase

still incompletely understood. Recently, evidence was presented for the existence of a novel rearrangement, occurring in the polyether antibiotic producing organism *Streptomyces cinnamonensis*, which involves the interconversion of isobutyryl-CoA **1** and *n*-butyryl-CoA **2**[3] [Eq. (b)]. We describe here evidence that this represents a new type of coenzyme-B_{12}-dependent enzymic rearrangement.



(b)

1 2

It was shown recently that synthetic methylmalonyl-dethia(carba)-coenzyme A (with CH_2CoA partial structure) is an excellent substrate for methylmalonyl-CoA mutase from *Propionibacterium shermanii*.[4] Such CH_2-CoA

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