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Anionic dicarbollyl complexes of germanium(II) and tin(II) – missing links in a series of π-complexes with Group 14 elements as central atoms

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Abstract

On the basis of the isolobal concept, comparable series of structurally different π-complexes with Group 14 elements as central atoms and with cyclopentadienyl or dicarbollyl systems as ligands can be organized. We describe for the first time anionic π-complexes in which one or two dicarbollyl ($B_9H_9C_2Me_2$) ligands are coordinated to a divalent germanium or tin centre. Thus, reaction of the phosphonium salt $Ph_3MeP^+TlB_9H_9C_2Me_2^-$ (**4**) with the element dichlorides $GeCl_2$ and $SnCl_2$, respectively, in a 1:1 ratio leads to the ionic compounds $Ph_3MeP^+ClGeB_9H_9C_2Me_2^-$ (**5**) and $Ph_3MeP^+ClSnB_9H_9C_2Me_2^-$ (**6**), respectively. In a 2:1 ratio of the same reactants, the ionic compounds $(Ph_3MeP^+)_2Ge(B_9H_9C_2Me_2)_2{}^{2-}$ (**7**) and $(Ph_3MeP^+)_2Sn(B_9H_9C_2Me_2)_2{}^{2-}$ (**8**), respectively, are formed. Some further chemistry of the starting material $Tl^+TlB_9H_9C_2Me_2^-$ is also described. The characterization of the new complexes is based on ^1H, ^{13}C, ^{11}B and ^{119}Sn NMR data and on X-ray crystal structure investigations (**5** and **7**).

Introduction

More than twenty years ago, a deprotonated carbaborane system was used for the first time as a π-ligand in the chemistry of the Group 14 elements. Todd *et al.* [1] synthesized the icosahedral metallacarbaborane $CH_3GeCHB_{10}H_{10}$ with tetravalent germanium as an integral member of the cage, whereas Rudolph *et al.* [2] prepared compounds of the type $MC_2H_2B_9H_9$ with divalent germanium, tin or lead as part of the closo-polyhedron. Some years later, cage compounds of the type $MC_2R_2B_4H_4$ with divalent lead or tin were synthesized by Wong and Grimes [3]; these compounds were characterized as pentagonal-bipyramidal systems with the metal occupying the apical site. All these compounds can be regarded as π-complexes consisting of an anionic carbollide ligand and a cationic Group 14 metal centre. Their structures have been accurately assigned on the basis of NMR, IR and mass spectroscopic data.

The first X-ray crystallographic data for a Group 14 carbaborane compound were reported in 1984 [4]. Since that time, especially the π-complex chemistry with different dicarbollyl ligands has been further developed [5]; a special review on these topics appeared only recently [6]. In the course of further investigations, different types of structures were observed. At a first approximation, the isolobal principle allows a relationship between dicarbollide and cyclopentadienide π-ligands [5]*; the latter still are the π-systems most often used in main-group chemistry [5, 8]. Having in mind the isoelectronic behaviour of a cyclopentadienide mono-anion and a dicarbollide di-anion, a series of comparable classes of π-complexes can be envisaged, as portrayed in Fig. 1.

According to qualitative MO arguments and to theoretical calculations [7], the π-ligands are η^5-bonded** in compounds of types I and VI, whereas in all other classes the π-ligands are expected to be $\eta^{2/3}$-bonded. In cyclopentadienyl chemistry, examples of the structure types Ia, IIa, IIIa and Va are already known [5]. In dicarbollyl chemistry, there exist examples of types Ib, IIb, IVb and VIb with the $C_2R_2B_9H_9{}^{2-}$ ligand, and of types Ib, IIb and VIb with the $C_2R_2B_4H_4{}^{2-}$ ligand [9–13]. In this paper we describe for the first time π-

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*Fenske–Hall and MNDO-SCF molecular orbital calculations show that cyclopentadienide and dicarbollide π-systems are not isolobal in a strong sense [7].

**Nearly all η^5-complexes show a distinct dislocation of the apical heteroatom away from the two cage carbon atoms. Calculations [7] have been used to explain the slip distortion.

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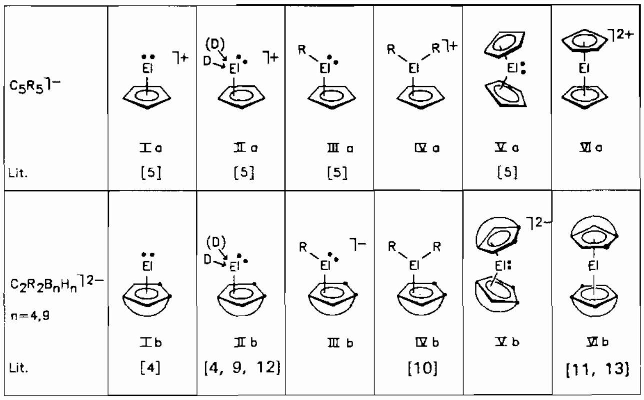
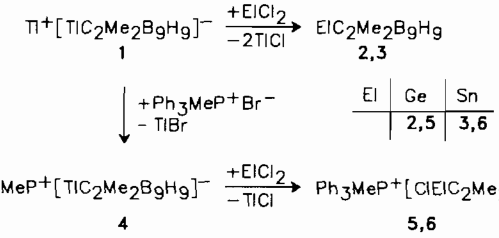


Fig. 1. Series of comparable cyclopentadienyl and dicarbollyl complexes with Group 14 elements.



Scheme 1.

complexes from germanium and tin chemistry, which belong to the classes IIIb and Vb, i.e. which possess one or two dicarbollide ligands coordinated to an :ElR^{1+} or :El^{2+} centre.

Results and discussion

Synthesis and spectroscopic characterization

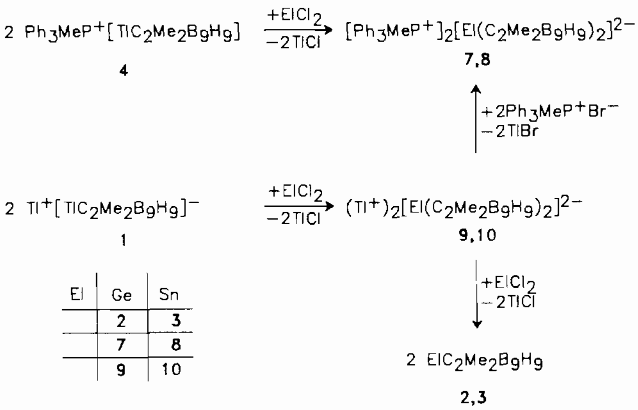
Thallium nonahydro-2,3-dimethyl-1-thalla-2,3-dicarba-closo-dodecaborate(1−) (**1**) [14] reacts with the dioxane adduct of germanium dichloride or with tin dichloride in tetrahydrofuran (THF) to give the known closo-heterocarboranes 2,3-dimethyl-1,2,3-germa-dicarba-closo-dodecaborane(9) (**2**) [10] and 2,3-dimethyl-1,2,3-stanna-dicarba-closo-dodecaborane(9) (**3**), respectively [4, 9] (Scheme 1). Basic solvents like THF form adducts with compounds **2** and **3** [9]. As a consequence, the stannacarborane **3** is isolated as a 1:1 adduct with THF. Adduct formation with the germacarborane **2** is observed only in solution, so that **2** can be isolated in pure form.

Cation exchange in **1** with methyl(triphenyl)phosphonium bromide leads to methyl(triphenyl)phosphonium nonahydro-2,3-dimethyl-1-thalla-2,3-dicarba-closo-dodecaborate(1−) (**4**) [15]. In the reaction of **4** with $GeCl_2$·dioxane or with $SnCl_2$ in a 1:1 ratio, the phosphonium salts **5** and **6**, respectively, are formed, which contain the nonahydro-1-chloro-2,3-dimethyl-1,2-3-germadicarba-dodecaborate(1−) and the respective stannadicarba-dodecaborate(1−) anion. Both compounds are isolated as colourless solids in good yields after crystallization from trichloromethane. They are moisture- and air-sensitive, easily soluble in THF and dichloromethane and moderately soluble in trichloromethane and hot toluene.

In the ^1H and ^{13}C NMR spectra of **5** and **6** the expected resonances for the phosphonium cation are observed. The protons of the methyl groups in the dicarbollyl units appear as a singlet at $\delta = 1.8$ ppm for both compounds, the carbon atoms of the $C-CH_3$ units give rise to two singlets at $\delta = 73.6$ and 26.7 ppm in **5** and $\delta = 66.0$ and 27.2 ppm in **6**. The ^{11}B NMR spectra display five doublets of 1:2:3:2:1 ratio in **5** and four doublets of 1:5:2:1 ratio in **6**; both patterns are typical of π-bonded $B_9H_9C_2Me_2$ fragments. The ^{119}Sn NMR spectrum of **6** exhibits a single resonance at $\delta = 229$ ppm.

Reaction of **4** with the element dichlorides of germanium and tin in a 2:1 ratio results in the formation of bis[methyl(triphenyl)phosphonium][commo-1,1′-germanium-bis-(nonahydro-2,3-dimethyl-1,2,3-germadicarba-dodecaborate)(2−) (**7**) and the analogous tin complex **8**, respectively (Scheme 2). The compounds are isolated as pale yellow needles after crystallization from THF/hexane in 59% and 94% yield, respectively. They are moderately stable as solids, but very sensitive in solution. They are very soluble in THF and dichloromethane and moderately soluble in trichloromethane.

The ^1H NMR spectra of **7** and **8** display singlets for the methyl groups of the dicarbollyl units at $\delta = 1.75$ in **7** and at $\delta = 1.76$ ppm in **8**. In the ^{13}C NMR spectra, the $C-CH_3$ units of the dicarbollyl fragments give rise to singlets at $\delta = 62.6$ and 26.7 ppm in **7** and $\delta = 58.7$ and 27.5 ppm in **8**. The ^{11}B NMR spectra exhibit four doublets of 3:2:3:1 ratio in **7** and three doublets of 3:5:1 ratio in **8**. These patterns are typical of π-bonded $B_9H_9C_2Me_2$ fragments; furthermore, they demonstrate the equivalence of the two dicarbollyl systems in **7** and also in **8**.



Scheme 2.

The dithallium salts **9** and **10** with the $El(C_2Me_2B_9H_9)_2^{2-}$ anions are formed in the reaction of **1** with the respective element dichlorides in THF (Scheme 2). Concentration of the resulting THF solutions leads to amorphous, pale yellow powders, which are insoluble in all other common solvents and were therefore not further characterized spectroscopically. Solutions of **9** and **10** react with methyl(triphenyl)-phosphonium bromide to give the compounds **7** and **8**, respectively; reaction with the element dichlorides of germanium and tin results in the formation of **2** and **3**, respectively (Scheme 2).

Further information about the structure of the anions in the new compounds **5**, **6**, **7** and **8** can be obtained from a comparison of their ^{11}B NMR data with those of other carboranes. In Fig. 2, the proton-decoupled ^{11}B NMR line spectra of the carborane $Me_2C_2B_{10}H_{10}$ and of some metallacarboranes are shown. Note that the closo-carborane $Me_2C_2B_{10}H_{10}$ and the closo-metallacarboranes $MC_2Me_2B_9H_9$ (**2**, **3**) exhibit resonances within a rather narrow range (*c.* 10 ppm) between −20 and −30 ppm.

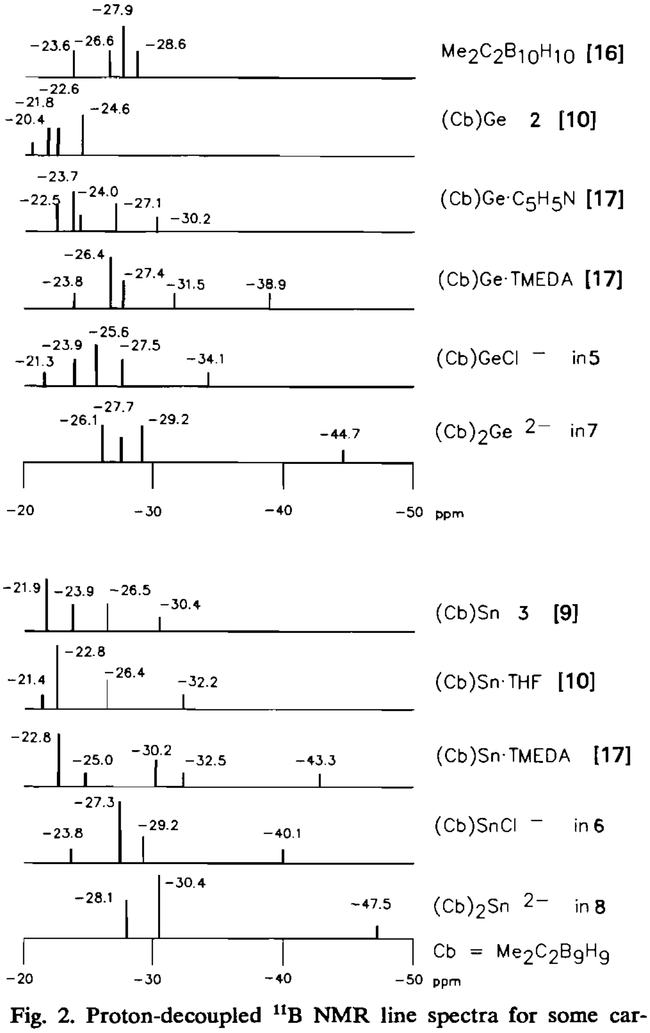


Fig. 2. Proton-decoupled ^{11}B NMR line spectra for some carbaborane systems.

The formal coordination of a chloride ion to **2** or **3**, leading to **5** or **6**, results in a characteristic change of the resonance pattern. One of the nine ^{11}B resonances is shifted drastically upfield, whereas all others remain in the narrow range expected for the closo-structures. Similar observations have been made for 1:1 and 1:2 adducts of **2** (or **3**) with neutral Lewis bases [9]. The upfield shifted ^{11}B resonance is assigned to the unique boron atom within the B_3C_2 unit and can be correlated with the extent of 'slippage' of the metal atom. This distortion is likely to have the most significant impact on the electron density at the central boron atom. This concept is supported by calculations [7]. Comparable effects should hold also for the 'chloride adducts' in **5** and **6**. From these considerations, a distorted icosahedral structure with an $\eta^{2,3}$-bonded dicarbollide π-system (see Fig. 1, type IIIb) can be anticipated for the anions in these compounds.

The ^{11}B NMR data of **7** and **8** can be discussed similarly. The effect of formal coordination of a further dicarbollide ion to **2** and **3**, leading to **7** and **8**, is evident; the resonances of the unique boron atom in each dicarbollyl unit are shifted extremely upfield (see Fig. 2). The distortion from the ideal closo-structure is likely to be more pronounced in these compounds than in **5** or **6**. As a result, a bent-sandwich structure with a weak $\eta^{2,3}$-bonding of the dicarbollyl ligands to the relevant metal centre is discussed (see Fig. 1, type Vb). A bent structure is postulated in analogy to the neutral Group 14 metallocenes, allowing the presence of a stereochemically active lone-pair.

The ^{13}C NMR shifts of the ring carbon atoms in the π-complexes **2**, **3**, **5**, **6**, **7** and **8** are given in Table 1. An upfield shift of the relevant singlets is observed on going from the dicarbollyl units in the neutral closo-metallocarboranes **2** and **3** to those in the mono-anions **5** and **6** and further on to those in the di-anions **7** and **8**. This upfield shift is consistent with an increase of negative charge at the respective ring carbon atoms.

The large range of ^{119}Sn chemical shift values indicates that this parameter is extremely sensitive towards changes in the coordination sphere of a tin atom [18]. Organometallic tin(II) compounds are of special interest in the context of the theory of nuclear shielding. Whereas monomeric tin(II) amides give signals at the low-field end for all known ^{119}Sn resonances, the π-cyclo-

TABLE 1. ^{13}C NMR shifts of the ring carbon atoms in the dicarbollyl units of **2**, **3**, **5**, **6**, **7** and **8**

Compound	2	3	5	6	7	8
δ (ppm)	77.8	68.6	73.6	66.0	63.4	58.7

TABLE 2. ^{119}Sn NMR shifts of $[(Me_3Si)_2N]_2Sn$, **8**, **6**, **3**, Me_5C_5SnCl, $(Me_5C_5)_2Sn$ and $Me_5C_5Sn^{1+}$

Compound	$[(Me_3Si)_2N]_2Sn$	**8**	**6**	**3**	Me_5C_5SnCl	$(Me_5C_5)_2Sn$	$Me_5C_5Sn^+$
δ (ppm)	+776 [18]	+449	+224	−379	−993 [19]	−2129 [5,20]	−2247 [20]

pentadienyl complexes of tin(II) are found at the other extreme, at very high field; an explanation has been given in terms of different contributions of the paramagnetic term as part of the nuclear screening constant [18]. An intermediate shift region is observed for tin(II) dicarbollyl complexes. In Table 2, the ^{199}Sn NMR shifts of the compounds **3**, **6** and **8** are given together with those of the corresponding (see Fig. 1) π-cyclopentadienyl complexes $Me_5C_5Sn^{1+}$, Me_5C_5SnCl and $(Me_5C_5)Sn$ and with that of the monomeric stannylene $[(Me_3Si)_2N]_2Sn$. In the cyclopentadienyl series, a significant down-field shift is observed on going from the cationic η^5-complex $Me_5C_5Sn^{1+}$ to the neutral η^3-complex Me_5C_5SnCl, whereas there is only a small shift difference between the resonances of $Me_5C_5Sn^{1+}$ and $(Me_5C_5)_2Sn$. In the dicarbollyl series, a significant down-field shift is observed on going from the neutral closo-stannacarborane **3** to the anionic complex in **6** and further on to the dianionic complex in **7**. These differences in the ^{119}Sn NMR shift remain surprising. They indicate important changes in bonding (reduced hapticity) between the dicarbollyl ligands and the tin atom.

Crystal structures of 5 and 7

Crystals of **5** suitable for an X-ray crystal structure investigation were obtained by crystallization from dichloromethane. Crystallographic data are collected in Table 3, selected bond lengths and angles are given in Tables 4 and 5. The atomic coordinates are collected in Table 6. As expected, the structure of **5** displays isolated phosphonium cations and chloro-germadicarbollyl anions; this is shown in Fig. 3. The structure of the anion in **5** is shown in more detail in Fig. 4. The most interesting feature is that the dicarbollyl unit is η^3-bonded to the germanium centre. A significant dislocation of the apical germanium atom away from the two cage carbon atoms and towards the three boron atoms is observed. Thus, the Ge–C distances of 2.54 Å are substantially longer than the Ge–B distances (2.26, 2.19, 2.28 Å).

In some other cases, the change from η^5- to η^3-bonding coincides with the non-planarity of the B_3C_2 open face of the relevant dicarbollyl fragment [21]. In the anion of **5** the interplanar angle between the $B_3B_1B_5$ unit and the $B_3C_1C_2B_5$ unit in **5** is 4.8°. Comparable values have been observed for base adducts of the stannacarborane $SnB_9H_9C_2Me_2$ [9].

TABLE 3. Crystal structure data of **5**

Empirical formula	$C_{23}H_{33}B_9PGeCl$
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimension	
a (Å)	12.121(1)
b (Å)	14.738(1)
c (Å)	16.167(1)
β (°)	103.73(1)
Volume (Å^3)	2805.5
Z	4
D_{calc} (Mg/m^3	1.292
Absorption coefficient (mm^{-1})	1.24
$F(000)$	1120
Radiation	Mo Kα(λ = 0.71069)
Temperature	r.t.
φ Range	2.21, 27.84
Absorption correction	DIFABS
Reflections collected	6679
Independent reflections	2435
Observed reflections	2176 ($F_0 > 3\sigma F_0$)
No. parameters refined	387
Weighting scheme	unit weights
Final $R(F)/(F_0)$	0.050
Final R_w	0.057

The Ge–Cl bond distance of 2.37 Å in **5** is much longer than that in Me_5C_5GeCl (2.26 Å) [22] and in $(CO)_5WGe(Cl)C_5Me_5$ (2.24 Å) [23]. This bond lengthening reflects the comparably higher negative charge at the germanium centre in **5**.

The structure of **7** is also supported by an X-ray crystal structure investigation. Due to the poor quality of the crystals, the resulting structure determination is not good enough to be discussed in detail. The expected structure of type Vb (see Fig. 1) with bent dicarbollyl fragments and a central germanium atom is present without any doubt. Another investigation with crystals of better quality is intended.

The compounds **5**–**10** are the first examples where anionic dicarbollyl π-complexes with divalent germanium or tin are realized. It is evident from spectroscopic data that part of the negative charge remains concentrated on the π-bonded dicarbollyl ligands. Examples of the stabilization of positively charged species by π-complexation have already been given [5].

In contrast to the chemistry of Group 14 cyclopentadienyl complexes, the chemistry of the corresponding dicarbollyl complexes has so far not been investigated, very much [6]. Future work will determine whether the

TABLE 4. Selected bond lengths (Å) in 5

Cl(1)–Ge(1)	2.366(5)	C(1)–Ge(1)	2.542(12)
C(2)–Ge(1)	2.543(14)	B(1)–Ge(1)	2.197(12)
B(3)–Ge(1)	2.265(16)	B(5)–Ge(1)	2.280(15)
C(2)–C(1)	1.547(17)	B(3)–C(1)	1.672(17)
C(3)–C(1)	1.537(15)	B(4)–C(1)	1.707(19)
B(9)–C(1)	1.672(20)	C(4)–C(2)	1.532(19)
B(4)–C(2)	1.674(20)	B(5)–C(2)	1.691(17)
B(6)–C(2)	1.682(19)	B(2)–B(1)	1.721(20)
B(3)–B(1)	1.738(17)	B(5)–B(1)	1.725(19)
B(8)–B(1)	1.724(22)	B(5)–B(2)	1.702(21)
B(6)–B(2)	1.732(22)	B(7)–B(2)	1.746(21)
B(8)–B(2)	1.729(24)	B(8)–B(3)	1.738(20)
B(9)–B(3)	1.758(23)	B(6)–B(4)	1.702(20)
B(7)–B(4)	1.723(18)	B(9)–B(4)	1.735(22)
B(6)–B(5)	1.773(23)	B(7)–B(6)	1.753(22)
B(8)–B(7)	1.751(23)	B(9)–B(7)	1.766(20)
B(9)–B(8)	1.743(21)	C(10)–P(1)	1.782(10)
C(11)–P(1)	1.762(6)	C(21)–P(1)	1.775(7)
C(31)–P(1)	1.783(8)	C(12)–C(11)	1.395(9)
C(16)–C(11)	1.395(8)	C(13)–C(12)	1.395(7)
C(14)–C(13)	1.395(8)	C(15)–C(14)	1.395(9)
C(16)–C(15)	1.395(7)	C(22)–C(21)	1.395(9)
C(26)–C(21)	1.395(8)	C(23)–C(22)	1.395(7)
C(24)–C(23)	1.395(8)	C(25)–C(24)	1.395(9)
C(26)–C(25)	1.395(7)	C(32)–C(31)	1.395(8)
C(36)–C(31)	1.395(9)	C(33)–C(32)	1.395(9)
C(34)–C(33)	1.395(9)	C(35)–C(34)	1.395(8)
C(36)–C(35)	1.395(9)		

TABLE 5. Selected bond angles (°) in 5

B(1)–Ge(1)–Cl(1)	92.1(4)	B(5)–C(2)–C(1)	110.5(9)
B(3)–Ge(1)–Cl(1)	110.3(4)	B(3)–C(1)–C(2)	109.8(8)
B(5)–Ge(1)–Cl(1)	119.0(4)	B(1)–B(3)–C(1)	108.7(9)
B(3)–Ge(1)–B(1)	45.8(4)	C(3)–C(1)–B(3)	121.6(11)
B(5)–Ge(1)–B(1)	45.3(4)	B(5)–C(2)–C(4)	122.1(12)
B(5)–B(1)–B(3)	102.8(9)	C(3)–C(1)–C(2)	117.5(11)
B(1)–B(5)–C(2)	107.9(9)	C(4)–C(2)–C(1)	117.2(10)

chemistry of dicarbollyl systems has analogies or differences to the chemistry of cyclopentadienyl systems.

Experimental

Synthesis of 2 and 3 by reaction of 1 with ElCl$_2$

A suspension of 1.89 g (3.32 mmol) 1 in 40 ml THF is treated dropwise with a solution of 0.78 g (3.37 mmol) GeCl$_2$·dioxane in 20 ml THF at −60 °C. After stirring for 30 min at −60 °C, for 1 h at 20 °C and filtration, the colourless solution is concentrated *in vacuo*. The remaining compound 2 is sublimed at 100 °C in vacuo.

2: 0.70 g (90%); m.p.>300 °C ^{11}B, ^{1}H, ^{13}C NMR data are consistent with literature data [10]. *Anal.* Calc. for $C_4H_{15}B_9Ge$ (233.0): C, 20.61; H, 6.49. Found: C, 20.39; H, 9.5%.

TABLE 6. Fractional atomic coordinates (×10^4) and equivalent isotropic temperature factors (Å^2×10^3)

	x	*y*	*z*	*U*
Ge(1)	4226(1)	7481(1)	1202(1)	60(1)
Cl(1)	5794(2)	6646(2)	974(2)	72(1)
C(1)	2427(6)	7553(8)	1749(5)	65(3)
C(2)	3046(9)	8474(7)	1949(6)	70(4)
B(1)	4655(9)	7160(8)	2568(6)	64(4)
B(2)	4423(11)	7836(12)	3377(7)	102(7)
B(3)	3345(10)	6704(8)	2069(8)	71(5)
C(3)	1481(9)	7486(12)	929(8)	144(7)
C(4)	2642(16)	9253(10)	1324(9)	155(11)
B(4)	2179(10)	8184(10)	2572(8)	77(6)
B(5)	4434(10)	8311(9)	2420(8)	76(5)
B(6)	3450(12)	8688(9)	3000(9)	88(7)
B(7)	3029(11)	7726(10)	3484(7)	86(6)
B(8)	3741(12)	6801(10)	3171(9)	93(7)
B(9)	2337(11)	7014(10)	2641(9)	87(6)
P(1)	6111(2)	3876(2)	1634(1)	45(1)
C(11)	6294(5)	3917(4)	2748(2)	46(3)
C(12)	5744(5)	4581(4)	3117(2)	56(3)
C(13)	5871(5)	4596(4)	3997(2)	64(4)
C(14)	6548(5)	3949(4)	4509(2)	75(4)
C(15)	7098(5)	3285(4)	4140(2)	81(5)
C(16)	6971(5)	3269(4)	3259(2)	71(4)
C(21)	6137(5)	2723(3)	1325(3)	46(3)
C(22)	7160(5)	2316(3)	1279(3)	61(4)
C(23)	7182(5)	1402(3)	1056(3)	81(5)
C(24)	6181(5)	896(3)	881(3)	88(5)
C(25)	5158(5)	1303(3)	927(3)	84(5)
C(26)	5136(5)	2216(3)	1150(3)	70(4)
C(31)	7214(4)	4482(3)	1315(3)	46(3)
C(32)	7962(4)	5038(3)	1885(3)	61(4)
C(33)	8764(4)	5556(3)	1604(3)	76(5)
C(34)	8818(4)	5519(3)	752(3)	77(5)
C(35)	8070(4)	4963(3)	182(3)	76(4)
C(36)	7268(4)	4445(3)	463(3)	56(3)
C(41)	4779(7)	4359(6)	1114(5)	55(3)

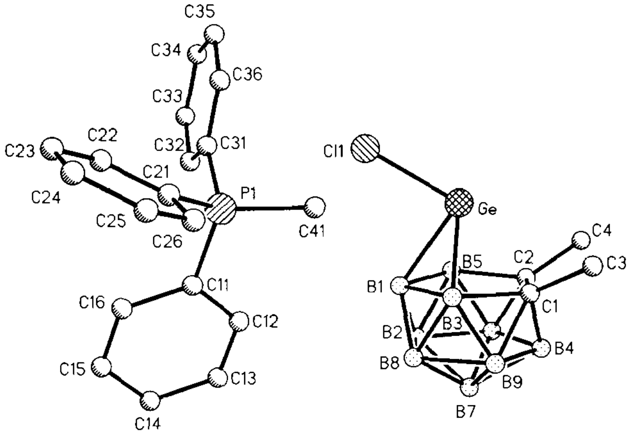


Fig. 3. Solid-state structure of 5.

Analogously, compound 3 is synthesized from 2.18 g (3.83 mmol) 1 in 60 ml THF and from 0.73 g (3.85 mmol) SnCl$_2$ in 20 ml THF.

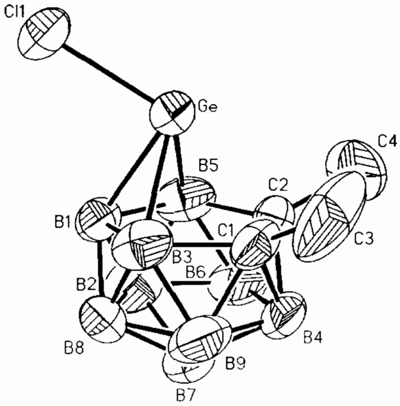


Fig. 4. Solid state structure of the $ClGe(Me_2C_2B_9H_9)^-$ anion in **5**.

3·THF: 0.71 g (53%); m.p. 135–137 °C (dec.). ^{11}B, ^{1}H and ^{13}C NMR data are consistent with literature data [9]. *Anal.* $C_8H_{23}B_9OSn$ Calc. for (351.3): C, 27.36; H, 6.60. Found: C, 27.16; H, 46.50%.

Synthesis of 5 and 6 by reaction of 4 with ElCl$_2$

With exclusion of light, a solution of 0.39 g (1.64 mmol) of $GeCl_2$·dioxane in 20 ml THF is added with stirring at −50 °C to a solution of 1.04 g (1.62 mmol) of **4** in 60 ml THF. After reaction at −50 °C for 1 h, further reaction at 20 °C for 16 h and filtration, the remaining solution is concentrated *in vacuo*. The residue is crystallized from 10 ml of hot $CHCl_3$, and **5** is obtained as colourless crystals.

5: 0.59 g (67%); m.p. 190–193 °C. ^{11}B NMR ($CDCl_3$): $\delta = -21.3$ (1B), −23.9 (2B), −25.6 (3B), −27.5 (2B), −34.1 ($^1J(BH) = 159$ Hz), 1B). ^1H NMR (CD_2Cl_2): $\delta = 1.82$ (s, 6H, $C_2B_9H_9(C\mathit{H}_3)_2$), 2.89 (d, $^2J(HP) = 3$Hz, 3H, $(C\mathit{H}_3)(C_6H_5)_3P$), 7.55–7.81 (m, 15H, $(CH_3)(C_6\mathit{H}_5)_3P$). ^{13}C NMR (CD_2Cl_2): $\delta = 10.7$ (d, $^1J(CP) = 59$ Hz, $(\mathit{C}H_3)(C_6H_5)_3P$), 26.7 (s, $C_2B_9H_9(\mathit{C}H_3)_2$), 73.6 (br. s, $\mathit{C}_2B_9H_9(CH_3)_2$), 119.1 (d, $^1J(CP) = 89$ Hz, Ph–C1), 131.1 (d, $^3J(CP) = 13$ Hz, Ph–C3,C5), 133.5 (d, $^2J(CP) = 10$ Hz, Ph–C2,C6), 136.0 (s, Ph–C4). ^{31}P NMR (CD_2Cl_2): $\delta = 21.5$ (s). *Anal.* Calc. for $C_{23}H_{33}B_9ClPGe$: C, 50.61; H, 6.09. Found: C, 50.74; H, 6.08%.

Analogously, compound **6** is obtained from 0.23 g (1.21 mmol) of $SnCl_2$ in 10 ml THF and 0.77 g (1.20 mmol) of **4** in 50 ml THF. Compound **6** is crystallized from 30 ml $CHCl_3$ and 20 ml hexane.

6: 0.38 g (53%); m.p. 166–169 °C (dec.). ^{11}B NMR (CD_2Cl_2): $\delta = -23.8$ (1B), −27.3 (5B), −29.2 (2B), −40.1 ($^1J(BH) = 139$ Hz, 1B). ^{11}B NMR (THF): $\delta = -25.8$ (1B), −27.4 (4B), −28.7 (3B), −41.3 ($^1J(BH) = 145$ Hz, 1B). ^1H NMr ($CDCl_3$): $\delta = 1.85$ (s, 6H, $C_2B_9H_9$ $(C\mathit{H}_3)_2$), 2.87 (d, $^2J(HP) = 13$ Hz, $(C\mathit{H}_3)(C_6H_5)_3P$), 7.55–7.81 (m, 15H, $(CH_3)(C_6\mathit{H}_5)_3P$). ^{13}C NMR (CD_2Cl_2): $\delta = 10.7$ (d, $^1J(CP) = 59$ Hz, $\mathit{C}H_3)(C_6H_5)_3P$), 27.2 (s, $C_2B_9H_9(\mathit{C}H_3)_2$), 66.0 (br.s, $\mathit{C}_2B_9H_9(CH_3)_2$), 119.1 (d, $^1J(CP) = 89$ Hz, Ph–Cl), 131.1 (d, $^3J(CP) = 13$ Hz, Ph–C3,C5), 133.5 (d, $^2J(CP) = 10$ Hz, Ph–C2, C6), 136.0 (s, Ph–C4). ^{31}P NMR (CD_2Cl_2): $\delta = 21.5$ (s). ^{119}Sn NMR (CD_2Cl_2): $\delta = 224$ Hz (s, $\nu_{1/2} \approx 560$ Hz). *Anal.* Calc. for $C_{23}H_{33}B_9ClPSn$ (591.9): C, 46.67; H, 5.62. Found: C, 46.92; H, 5.83%.

Synthesis of 7 and 8 by reaction of 4 with ElCl$_2$

With exclusion of light, a solution of 0.21 g (0.91 mmol) of $GeCl_2$·dioxane in 20 ml THF is added at −50 °C with stirring to a solution of 1.13 g (1.76 mmol) of **4** in 60 ml THF. After stirring for 1 h at −50 °C and for 2 h at 20 °C and after filtration, the yellow solution is concentrated to half of the volume and treated with 15 ml hexane. After 4 days at −60 °C, a light yellow oil has separated. The oil is dissolved in 20 ml THF and treated with 5 ml hexane. After 12 h at 20 °C compound **7** can be isolated as light yellow needles.

7: 0.49 g (59%); m.p. 157 °C. ^{11}B NMR (CH_2Cl_2): $\delta = -25.6$ (2×3B), −27.0 (2×2B), −28.7 (2×3B), −44.3 ($^1J(BH) = 132$ Hz, 2×1B); ^1H NMR (CD_2Cl_2): $\delta = 1.75$ (s, 2×6H, $C_2B_9H_9(C\mathit{H}_3)_2$), 2.86 (d, 2×3H, $^2J(HP) = 13$ Hz, $(C\mathit{H}_3)(C_6H_5)_3P$), 7.59–7.84 (m, 2×15H, $(CH_3)(C_6\mathit{H}_5)_3P$). ^{13}C NMR ($CDCl_3$): $\delta = 9.6$ (d, $^1J(CP) = 57$ Hz, $(\mathit{C}H_3)(C_6H_5)_3P$), 26.7 (s, $C_2B_9H_9(\mathit{C}H_3)_2$), 62.6 (brs. $\mathit{C}_2B_9H_9(CH_3)_2$), 118.6 (d, $^1J(CP) = 89$ Hz, Ph–C1), 130.4 (d, $^3J(CP) = 12$ Hz, Ph–C3,C5), 132.7 (d, $^2J(CP) = 10$ Hz, Ph–C2,C6), 134.9 (s, Ph–C4). ^{31}P NMR ($CDCl_3$): $\delta = 19.6$. *Anal.* Calc. for $C_{46}H_{66}B_{18}GeP_2$ (948.2): C, 58.27; H, 7.02. Found: C, 58.57; H, 7.30%.

Analogously, compound **8** is obtained from 0.17 g (0.90 mmol) of $SnCl_2$ in 10 ml THF and 1.16 g (1.81 mmol) of **4** in 60 ml THF. The separating oil crystallizes at −30 °C within 14 h. Compound **8** is recrystallized from THF/hexane as yellow needles.

8: 0.84 g (94%); m.p. 170–180 °C (dec). ^{11}B NMR (CH_2Cl_2): $\delta = -28.1$ (2×3B), −30.4 (2×5B), −47.5 ($^1J(BH) = 133$ Hz, 2×1B). ^1H NMR (CD_2Cl_2): $\delta = 1.76$ (s, 2×6H, $C_2B_9H_9(C\mathit{H}_3)_2$, 2.84 (d, $^2J(HP) = 13$ Hz, 2×3H, $(C\mathit{H}_3)(C_6H_5)_3P$), 7.58–7.83 (m, 2×15H, $(CH_3)(C_6\mathit{H}_6)_3P$). ^{13}C NMR (CD_2Cl_2): $\delta = 10.5$ (d, $^1J(CP) = 58$ Hz, $(\mathit{C}H_3)(C_6H_5)_3P$), 27.5 (s, $C_2B_9H_9(\mathit{C}H_3)_2$), 58.7 (brs, $\mathit{C}_2B_9H_9(CH_3)_2$), 119.3 (d, $^1J(CP) = 89$ Hz, Ph–C1), 131.0 (d, $^3J(CP) = 12$ Hz, Ph–C3,C5), 133.6 (d, $^2J(CP) = 10$ Hz, Ph–C2,C6), 135.8 (s, Ph–C4). ^{31}P NMR (CD_2Cl_2): $\delta = 21.7$ (s). ^{119}Sn NMR (CD_2Cl_2): δ 449 (s, $\nu_{1/2} \approx 1000$ Hz). *Anal.* Calc. for $C_{46}H_{66}B_{18}P_2Sn$ (994.3): C, 55.57; H, 6.69. Found: C, 55.80; H, 6.93%.

Synthesis of 9 and further reaction to 2 and 7

With exclusion of light, a solution of 0.13 g (0.56 mmol) of $GeCl_2 \cdot$dioxane in 10 ml THF is added at −50 °C with stirring to a suspension of 0.65 g (1.14 mmol) of **1** in 50 ml THF. After warming to 20 °C, stirring for further 20 h and filtration, a light yellow solution is obtained, which is used for further reactions.

Compound **9**: ^{11}B NMR (THF): $\delta = -26.2$, -27.4 (8B), -43.8 (1B).

Compound **2**: in an NMR experiment, part of the solution is treated with excess $GeCl_2 \cdot$dioxane. **2** can be characterized by its typical ^{11}B NMR spectrum (THF):$\delta = 22.9$ (6B), -25.6 (2B), -27.4 (1B). The pure compound **2** shows an identical spectrum in THF as solvent.

Compound **7**: a solution of **9**, prepared from 0.27 g (1.17 mmol) of $GeCl_2 \cdot$dioxane and 1.38 g (2.42 mmol) of **1** in 50 ml THF, is treated with a suspension of 0.92 g (2.58 mmol) of $Ph_3MeP^+Br^{-1}$ in 40 ml THF. After stirring for 3 h, filtration and evaporation of the solvent, the remaining residue is washed with $CHCl_3$. **7** is obtained as a light yellow solid. **7**: 0.35 g (31%). ^{11}B and ^1H NMR data are identical with those described in this paper.

Synthesis of 10 and further reaction to 3 and 8

With exclusion of light, a solution of 0.16 g (0.84 mmol) $SnCl_2$ in 10 ml THF is added at −50 °C to a suspension of 0.95 g (1.67 mmol) **1** in 50 ml THF. After warming to 20 °C, stirring for a further 20 h, and filtration, a yellow solution is obtained, which is used for further reactions. Compound **10**: ^{11}B NMR(THF): $\delta = -25.6$, -29.3 (8B), -46.5 (1B).

Compound **3**: in an NMR experiment, part of the solution is treated with excess $SnCl_2$. Compound **3**·2 THF can be characterized by its typical ^{11}B NMR spectrum (THF): $\sigma = -23.8$ (1B), -26.5 (2B), -27.5 (2B), -28.5 (3B), -39.7 ($^1J(BH) = 139$ Hz, 1B). The pure compound **2** shows an identical spectrum in THF as solvent.

Compound **8**: a solution of **10**, prepared from 0.14 g (0.74 mmol) of $SnCl_2$ and 0.83 g (1.46 mmol) of **1** in 35 ml THF is treated with a suspension of 0.57 g (1.59 mmol) of $Ph_3MeP^+Br^-$ in 30 ml THF. After stirring for 14 h and filtration, the yellow solution is concentrated and treated with 15 ml hexane. Compound **8** crystallizes as yellow needles. **8**: 0.39 g (54%). ^{11}B, ^1H, ^{13}C, ^{31}P and ^{119}Sn NMR data are identical with those described in this paper.

Supplementary material

Details of the structure determination are deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftliche Information mbH, D-7514 Eggenstein-Leopoldshafen 2, under the number CSD 56149, the names of the authors, and the name of the journal.

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