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Article

Homoleptic Coinage Metal Compounds of Group(IV)heteroborates

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This article describes the synthesis and characterization of the first silver complex with the germylene $[GeB_{11}H_{11}]^{2-}$ and coinage metal complexes with the stannylene ligand $[SnB_{11}H_{11}]^{2-}$. Starting materials like CuCl, $AuCl(Me_2S)$, and $AgNO_3$ were used to give mononuclear (**3** and **4**), dinuclear (**5**), hexanuclear (**6**), and heptanuclear (**7**) coordination compounds: $[Et_4N]_5[Cu(CH_3CN)(SnB_{11}H_{11})_3]$ (**3**), $[Et_4N]_5[Ag(SnB_{11}H_{11})_3]$ (**4**), $[Et_4N]_6[\{Au(SnB_{11}H_{11})_2\}_2]$ (**5**), $[Et_4N]_6[\{Ag(GeB_{11}H_{11})\}_6]$ (**6**), and $[Et_4N]_9[Ag_7(SnB_{11}H_{11})_8]$ (**7**). In case of the oligonuclear compounds **5**−**7** silver and gold aggregation was observed under formation of metal−metal bonds. Furthermore, the germa-*closo*-dodecaborate is found in a hitherto unknown μ_3-bridging coordination mode connecting three silver atoms. The new compounds were characterized by single crystal X-ray diffraction and in the case of **3**−**6** also by NMR spectroscopy and elemental analysis.

Introduction

The synthesis of coinage metal aggregates is a field of active research with respect to the factors causing the stereochemistry and topology of these clusters.[1] An access to the formation of coinage metal clusters is the use of heavy main group element ligands with their uncommon electronic and steric effects.[2]

In our group we have an ongoing interest in the chemistry of group(IV)heteroborates $[SnB_{11}H_{11}]^{2-}$ and $[GeB_{11}H_{11}]^{2-}$.[3−5] These two dianionic nucleophiles show a great variety and flexibility in coordination chemistry with a multitude of transition metals. In case of the tin containing boron cluster many different coordination modes have been reported by our group with the tin atom coordinating at a single metal center or bridging two, three, or even four transition metals.

So far not many coordination compounds containing a silver germanium bond have been structurally characterized. The synthesis and solid state structure of $[(Me_3SiN{=}PPh_2)_2C{=}Ge(Ag)Cl]_2$ together with $[(Me_3SiN{=}PPh_2)_2C{=}Ge(Au)I]_2$ was reported recently.[6] Some examples for an unsupported silver−germanium bond were found in the case of $[HB(3,5\text{-}CF_3)_2Pz)_3]Ag\text{-}GeCl[(Me)_2ATI]$ or $[HB(3,5\text{-}CF_3)_2Pz)_3]Ag{-}Ge(OSO_2CF_3)[(Me)_2ATI]$ with $[HB(3,5\text{-}CF_3)_2Pz)_3]$ being hydrotris(3,5-bis-(trifluoromethyl)pyrazoly)borate and $(Me)_2ATI$ being *N*-methyl-2-(methylamino)troponiminate.[7] Schnepf et al. describe the synthesis of metalloid germanium clusters and their coordination chemistry with the coinage metals. Thereby a silver germanium cluster $[AgGe_{18}R_6]^-$ (R = $Si(SiMe_3)_3$) was structurally characterized exhibiting an Ag−Ge bond of 2.7641(7) Å.[8]

Ever since we isolated the first homoleptic silver cluster $[Et_4N]_8[Ag_4(SnB_{11}H_{11})_6]$[4c] we were very much interested in the analogous homoleptic gold and copper complexes and

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Table 1. Crystallographic Data of Compounds **3**−**7**

	3·$2CH_3CN$	**4**·5/2 DMF	**5**·$2CH_3CN$	**6**·$6CH_3CN$	**7**·$2CH_3CN$
formula	$C_{46}H_{142}B_{33}Cu-N_8Sn_3$	$C_{47.5}H_{154}AgB_{33}-N_{7.5}O_{2.5}Sn_3$	$C_{52}H_{170}Au_2B_{44}-N_8Sn_4$	$C_{60}H_{204}Ag_6B_{66}-Ge_6N_{12}$	$C_{76}H_{274}Ag_7B_{88}-N_{11}Sn_8$
M_r (g/mol)	1584.09	1691.55	2252.38	2890.69	3998.95
T/K			173(2)		
λ/Å			0.71073		
space group	*Pnma*	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_12_12$
a (Å)	19.8584(8)	17.1431(13)	11.1078(7)	15.3897(11)	15.8873(2)
b (Å)	29.4243(13)	17.3073(13)	26.7184(12)	15.6967(11)	28.9709(3)
c (Å)	14.1231(8)	18.9524(16)	17.1513(9)	15.7315(13)	19.5813(3)
α (deg)		74.485(6)		66.385(6)	
β (deg)		66.041(6)	100.348(5)	81.051(6)	
γ (deg)		60.101(5)		75.412(6)	
V (Å^3)	8252.4(7)	4439.7(6)	5007.4(5)	3363.3(4)	9012.7(2)
Z	4	2	2	1	2
D_c (g/cm^3)	1.274	1.265	1.494	1.427	1.474
μ/mm^{-1}	1.189	1.089	3.95	2.210	1.865
F(000)	3268	1747	2760	1452	3952
crystal size/mm	0.1 × 0.1 × 0.1	0.22 × 0.19 × 0.17	0.26 × 0.22 × 0.18	0.27 × 0.19 × 0.18	0.18 × 0.1 × 0.1
θ range /deg	5.71−26.37	5.67−26.37	3.05−26.95	5.67−25.35	3.00−26.74
limiting indices	$-23 \le h \le 24$	$-21 \le h \le 21$	$-14 \le h \le 14$	$-18 \le h \le 18$	$-20 \le h \le 20$
	$-36 \le k \le 36$	$-21 \le k \le 21$	$-33 \le k \le 33$	$-18 \le k \le 18$	$-36 \le k \le 36$
	$-12 \le l \le 17$	$-23 \le l \le 23$	$-21 \le l \le 21$	$-18 \le l \le 18$	$-24 \le l \le 24$
reflections collected/unique/R_{int}	60012/8509/0.0867	62670/17987/0.0505	69766/10649/0.0828	44710/12154/0.1122	94178/19088/0.0880
completeness (%)	98.7	98.9	97.9	98.8	99.6
data/restraints/parameters	8509/0/336	17987/5/886	10649/0/497	12154/10/577	19088/1/844
GOF on F^2	1.053	1.053	1.200	1.037	1.080
R_1, wR_2 [$I > 2\sigma(I)$]	0.0641, 0.1529	0.0352, 0.0790	0.0461, 0.0633	0.0713, 0.1707	0.0452, 0.1157
R_1, wR_2 (all data)	0.0839, 0.1640	0.0460, 0.0830	0.0643, 0.0672	0.0818, 0.1790	0.0516, 0.1191

furthermore wanted to transfer these reactions to the nucleophilic germylene ligand $[GeB_{11}H_{11}]^{2-}$. Here we present the first example for copper coordination at stanna-*closo*-dodecaborate, a trigonal planar coordinated silver−tin compound, the largest silver−tin cluster with the ligand $[SnB_{11}H_{11}]^{2-}$ as a side product of the previous reported synthesis of $[Et_4N]_8[Ag_4(SnB_{11}H_{11})_6]$ and a dimeric homoleptic gold−tin compound. With the germylene ligand **2** we found a novel hexanuclear silver−germanium cluster. The substances were characterized by X-ray crystal structure analysis and salts **3**−**6** by NMR spectroscopy and elemental analysis.

Experimental Section

General Procedures. All manipulations were carried out under argon atmosphere in Schlenk glassware. Solvents were dried and purified by standard methods and were stored under argon. NMR spectra were recorded on a Bruker DRX-250 NMR spectrometer equipped with a 5 mm ATM probe head operating at 80.25 MHz (^{11}B) and 93.25 MHz (^{119}Sn) and a Bruker AV II+500 NMR spectrometer equipped with a 5 mm TBO probe head operating at 186.50 MHz (^{119}Sn). Chemical shifts are reported in δ values in parts per million (ppm) relative to external $BF_3 \cdot Et_2O$ (^{11}B) and $SnMe_4$ (^{119}Sn) using the chemical shift of the solvent ^{2}H resonance frequency. Elemental analyses were carried out with an elemental analyzer Vario EL and a Vario MICRO EL from Elementar Co. operating in CHNS modus. Starting materials CuCl, $AgNO_3$, and Me_2SAuCl were purchased commercially. $[Et_4N]_2[SnB_{11}H_{11}]$ (**1**) and $[Et_4N]_2[GeB_{11}H_{11}]$ (**2**) were prepared according to the literature method and modifications thereof.[9] X-ray data for compounds **3**−**7** were collected with a Stoe IPDS 2T diffractometer and corrected for Lorentz and polarization effects and absorption by air (Table 1). The programs used in this work were Stoe's X-Area and WinGX suite of programs including SHELXS and SHELXL for structure solution and refinement. Numerical absorption correction based on crystal-shape optimization was applied for compounds **4**−**6** with Stoe's X-Red and X-Shape.[10]

Preparation of $[Et_4N]_5[Cu(SnB_{11}H_{11})_3(CH_3CN)]$ (3). To a solution of $[Et_4N]_2[SnB_{11}H_{11}]$ (61 mg, 0.12 mmol) in acetonitrile (15 mL) CuCl (8 mg, 0.06 mmol) was added. The suspension was stirred for 40 min and after filtration through Celite, pale-yellow crystals (21 mg, 35% yield) were obtained by slow diffusion of diethylether into the acetonitrile phase at +4 °C. $^{11}B\{^1H\}$ NMR (CD_3CN, 299 K): δ −12.4 (s, 10B, B2−B11), −5.7 (s, 1B, B12). ^{119}Sn NMR (CD_3CN, 299 K): δ −491(s). Anal. Calcd for $C_{42}H_{125}B_{33}CuN_6Sn_3 \cdot 2CH_3CN$ (1584.12): C, 34.88; H, 9.04; N, 7.07. Found: C, 34.79; H, 8.92; N, 6.98.

$[Et_4N]_5[Ag(SnB_{11}H_{11})_3]$ (4). To a solution of $[Et_4N]_2[SnB_{11}H_{11}]$ (122 mg, 0.24 mmol) in dimethylformamide (DMF) (15 mL) $AgNO_3$ (13 mg, 0.08 mmol) was added. After filtration through Celite, colorless crystals (77 mg, 64% yield) were obtained by slow diffusion of diethylether into the DMF phase. $^{11}B\{^1H\}$ NMR (DMF-d_7, 299 K): δ −13.2 (s, 10B, B2−B11), −6.1 (s, 1B, B12). ^{119}Sn NMR (DMF-d_7, 299 K): δ −361(s). $^{119}Sn\{^1H\}$ NMR (DMF-d_7, 213 K): δ −352 [d, $^1J(^{119}Sn\text{-}^{107/109}Ag) = 2051$ Hz, $^2J(^{119}Sn\text{-}^{107/109}Ag\text{-}^{117}Sn) = 5062$ Hz]. Anal. Calcd for $C_{40}H_{133}B_{33}AgN_5Sn_3$ (1505.29): C, 31.92; H, 8.91; N, 4.65. Found: C, 32.21; H, 9.02; N, 5.05.

$[Et_4N]_6[Au_2(SnB_{11}H_{11})_4]$ (5). To a solution of $[Et_4N]_2[SnB_{11}H_{11}]$ (122 mg, 0.24 mmol) in acetonitrile (15 mL) Me_2SAuCl (35 mg, 0.12 mmol) was added under exclusion of light. After filtration through Celite colorless light stable crystals (93 mg, 72% yield) were obtained by slow diffusion of diethylether into the acetonitrile phase at +4 °C. $^{11}B\{^1H\}$ NMR (CD_3CN, 299 K): δ −14.1 (s, 10B, B2−B11), −7.2 (s, 1B, B12). $^{119}Sn\{^1H\}$ NMR (CD_3CN, 299 K): δ −9.3 [s, $^2J(^{119}Sn\text{-}Au\text{-}^{117}Sn) = 4832$ Hz]. $^{119}Sn\{^1H\}$ NMR (DMF-d_7, 223 K): δ 2, −28. Anal. Calcd for $C_{48}H_{164}B_{44}Au_2N_6Sn_4 \cdot CH_3CN$ (2211.38): C, 27.16; H, 7.61; N, 4.43. Found: C, 27.08; H, 7.42; N, 4.40.

$[Et_4N]_6[\{Ag(GeB_{11}H_{11})\}_6]$ (6). $AgNO_3$ (37 mg, 0.22 mmol) was dissolved in acetonitrile (4 mL). $[Et_4N]_2[GeB_{11}H_{11}]$ (100 mg,

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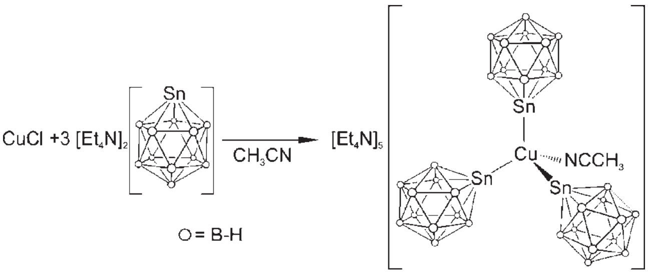
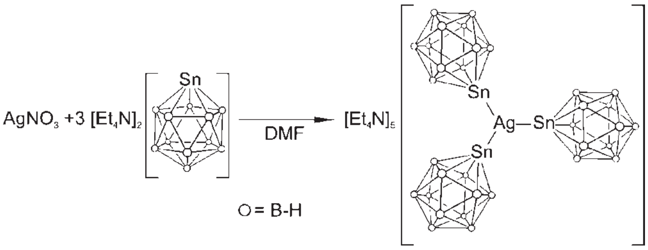
Scheme 1. Synthesis of the Copper Complex $[Et_4N]_5[Cu(CH_3CN)(SnB_{11}H_{11})_3]$ (**3**)



Scheme 2. Formation of Silver Compound $[Et_4N]_5[Ag(SnB_{11}H_{11})_3]$ (**4**)



0.22 mmol) in acetonitrile (10 mL) was added dropwise via syringe under exclusion of light. The resulting green-brownish suspension was stirred for an additional hour and filtered afterward. The resulting green solution was carefully layered with diethylether. After several days pale green crystals were obtained (24 mg, 25% yield). $^{11}B\{^1H\}$ NMR (CD_3CN, 299 K): δ −3.5 (1B, B12), −12.1 (10B, B2−B11). Anal. Calcd for $C_{48}H_{186}Ag_6B_{66}Ge_6N_6$: C, 21.80; H, 7.09; N, 3.18. Found: C, 21.98; H, 6.86; N, 3.17.

$[Et_4N]_9[Ag_7(SnB_{11}H_{11})_8]$ (7). Few brown crystals were obtained as a side product of the previously reported synthesis of $[Et_4N]_8[Ag_4(SnB_{11}H_{11})_6]$.[4c]

Results and Discusssion

Syntheses and Solid-State Structures. From the reaction of 1 equiv of CuCl with 3 equiv of tin ligand **1** in acetonitrile the mononuclear Cu(I) complex $[Et_4N]_5[Cu(SnB_{11}H_{11})_3(CH_3CN)]$ (**3**) was isolated in moderate yields by crystallization from CH_3CN/Et_2O (Scheme 1) at +4 °C. The fourth position of the tetrahedrally coordinated copper complex is occupied by an acetonitrile ligand.

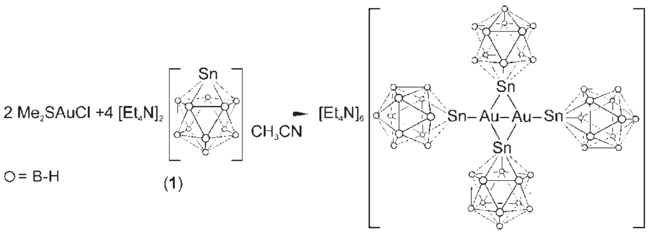
From the reaction of 1 equiv $AgNO_3$ with 3 equiv of the heteroborate salt $[Et_4N]_2[SnB_{11}H_{11}]$ (**1**) in DMF solution we obtained the silver(I) complex $[Et_4N]_5[Ag(SnB_{11}H_{11})_3]$ (**4**) in 64% yield (Scheme 2). The trigonal planar coordinated silver complex was isolated after crystallization, which was carried out by slow diffusion of ether into the filtered reaction mixture.

The reaction of $[Me_2SAuCl]$ with the tin nucleophile **1** in CH_3CN yields the gold dimer $[Et_4N]_6[Au_2(SnB_{11}H_{11})_4]$ (**5**) in 72% yield (Scheme 3).

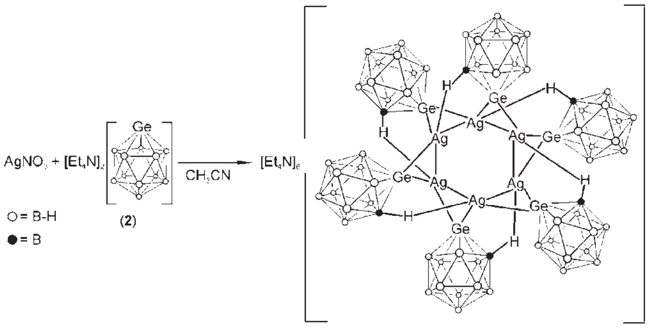
From the reaction of silver nitrate with 1 equiv of the germanium nucleophile $[Et_4N]_2[GeB_{11}H_{11}]$ (**2**) in acetonitrile solution a hexanuclear 1:1 coordination compound could be isolated in moderate yield of 25% after crystallization, which was carried out by layering the filtered reaction mixture with ether (Scheme 4).

The silver germanium coordination compound $[Et_4N]_6[\{Ag(GeB_{11}H_{11})\}_6]$ (**6**) is very sensitive toward light and air and decomposes rapidly when not stored under argon and exclusion of light.

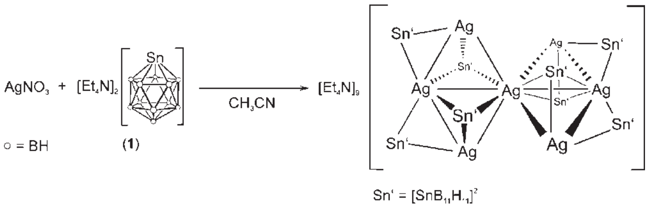
Scheme 3. Synthesis of the Dimeric Gold Complex $[Et_4N]_6[Au_2(SnB_{11}H_{11})_4]$ (**5**)



Scheme 4. Syntheses of Silver Aggregate **6**



Scheme 5. Formation of $[Et_4N]_9[Ag_7(SnB_{11}H_{11})_8]$ (**7**)



An even larger aggregate was found for silver(I) with the tin heteroborate **1** forming a heptanuclear silver core which is surrounded by eight molecules of the tin nucleophile (Scheme 5). Few brown crystals of $[Et_4N]_9[Ag_7(SnB_{11}H_{11})_8]$ (**7**) could be isolated as a side product of the previously reported synthesis of $[Et_4N]_8[Ag_4(SnB_{11}H_{11})_6]$.[4c]

All new coinage metal compounds were investigated using single crystal X-ray diffraction.

The molecular structure of the tetrahedral copper complex **3** together with selected interatomic distances and bond angles is depicted in Figure 1.

The copper tin coordination compound crystallizes in the orthorhombic space group *Pnma* with only one-half of the complex **3** and one molecule of acetonitrile in the asymmetric unit. The copper tin bond is rarely described in the literature. The interatomic separations of 2.6037(8) and 2.5928(5) Å are rather long compared to the reported values in, for example, $(IPr)CuSnPh_3$ [2.469(5) Å] with IPr being 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene,[11] or in the tris(pyrazolyl)borate complex $[MeB(3-(CF_3)Pz)_3]Cu-Sn(Cl)[(Bn)_2ATI]$ [2.4540(4) Å] with $[(Bn)_2ATI]$ = *N*-benzyl-2-(benzylamino)-troponiminate.[12]

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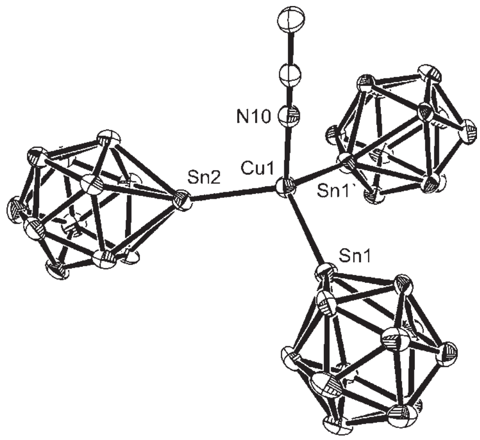

Figure 1. Molecular structure of the pentaanion of $[Et_4N]_5[Cu(SnB_{11}H_{11})_3(CH_3CN)]$ (**3**). The counter cations and hydrogen atoms have been omitted, ellipsoids at 50%. Interatomic distances [Å] and bond angles [deg]: Sn2−Cu1 2.6037(8), Sn1−Cu1 2.5928(5), Cu1−N10 2.058(5), Sn1−Cu1−Sn2 112.840(19), N10−Cu1−Sn2 106.76(15), Sn1−Cu1−Sn1′ 112.87(3).

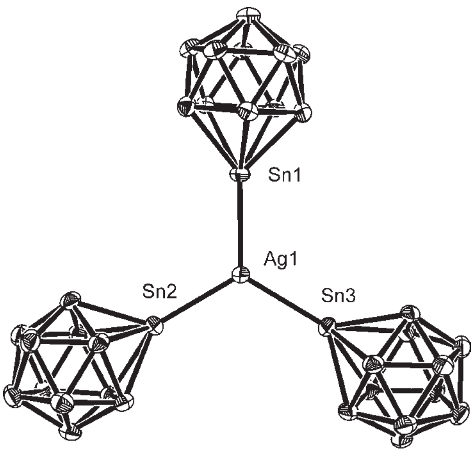

Figure 2. Molecular structure of the pentaanion of $[Et_4N]_5[Ag(SnB_{11}H_{11})_3]$ (**4**). The counter cations and hydrogen atoms have been omitted, ellipsoids at 50%. Interatomic distances [Å] and bond angles [deg]: Sn1−Ag1 2.6751(3), Sn2−Ag1 2.6749(3), Sn3−Ag1 2.6687(4), Sn3−Ag1−Sn2 118.306(12), Sn3−Ag1−Sn1 119.475(12), Sn2−Ag1−Sn1 120.970(11).

The molecular structure of **4** together with selected interatomic distances and bond angles is shown in Figure 2.

Compound **4** crystallizes in the triclinic space group $P\overline{1}$ with 5/2 molecules of the solvent DMF in the asymmetric unit. Single crystal X-ray diffraction reveals that silver is trigonal planar coordinated by three tin ligands. The Ag−Sn distances are in the close range of 2.6687(4)−2.6751(4) Å. The determined values are again rather long distances between these two elements. Not many examples are reported in the literature comprising a terminal silver−tin bond. In complexes $[HB(3,5\text{-}(CF_3)_2\text{-}Pz)_3]Ag{-}Sn(Cl)[(n\text{-}Pr)_2ATI]$ and $[HB(3,5\text{-}(CF_3)_2\text{-}Pz)_3]Ag{-}Sn(I)[(n\text{-}Pr)_2ATI]$ silver tin separations of 2.5863(6) Å and of 2.5880(10) Å were reported.[13]

The molecular structure of compound **5** is depicted in Figure 3.

The gold dimer **5** crystallizes in the monoclinic space group $P2_1/n$ with two additional molecules of acetonitrile in the asymmetric unit. Thereby two tin ligands are bridging the gold dimer [gold−gold separation 2.6208(4) Å] in a μ_2-coordination mode and two additional stannaborate units are coordinated terminally at the gold centers establishing a nearly linear Sn−Au−Au−Sn geometry. A similar linear arrangement was reported for $[(MeSi\{Me_2SiN(p\text{-}tol)\}_3Sn)_2Au_2(CH_2PPh_2CH_2)_2]$.[14] The gold−gold separation is even slightly shorter than the one reported for the similar $[Bu_3HN]_2[\{Au(PPh_3)(SnB_{11}H_{11})\}_2]$ [2.625(1) Å] also investigated by our group.[4a] This complex features the same structural motif as the anion of **5**, with the two terminal tin ligands being replaced by two PPh_3 ligands. The interatomic Sn−Au distances are for the terminal coordinating ligands 2.5730(4) Å and 2.7669(4)−2.7740(4) Å for the μ_2-briding ones. The short Au−Sn bond is the shortest bond in the stanna-*closo*-dodecaborate chemistry[4a,b] and comparable to gold−tin coordination complexes in the literature.[13,14]

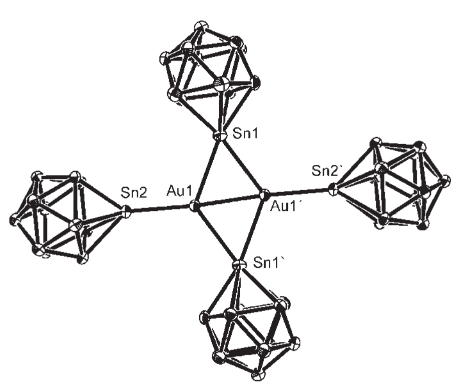

Figure 3. Molecular structure of the hexaanion of $[Et_4N]_6[Au_2(SnB_{11}H_{11})_4]$ (**5**). The counter cations and hydrogen atoms have been omitted, ellipsoids at 50%. Interatomic distances [Å] and bond angles [deg]: Au1−Sn2 2.5730(4), Au1−Au1′ 2.6208(4), Au1−Sn1′ 2.7669(4), Au1−Sn1 2.7740(4), Au1′−Sn1−Au1 56.457(10), Sn2−Au1−Sn1 114.466(13), Sn1′−Au1−Sn1 123.543(10), Sn2−Au1−Au1′, Au1−Au1′−Sn2′ 175.97(1).

Pale green crystals of $[Et_4N]_6[\{Ag(GeB_{11}H_{11})\}_6]$ (**6**) suitable for single crystal structure analysis could be obtained by layering a solution of **6** in acetonitrile with ether under exclusion of light. The molecular structure of the hexanuclear silver compound is depicted in Figures 4 and 5.

The hexaanion lies on a center of symmetry and crystallizes in the triclinic space group $P\overline{1}$. One half of the silver−germanium aggregate and three molecules of acetonitrile are included in the asymmetric unit and the counter cations show a severe disorder in the solid state. The cluster of **6** is built up of an opened octahedral silver core that is surrounded by an octahedron of six germa-*closo*-dodecaborate nucleophiles (Figure 4). The core structure of **6** together with selected interatomic distances and bond angles is depicted in Figure 6.

The silver−silver interatomic distances of the six membered silver cycle (Figure 4 left, Figure 6) lie between 2.7046(8) and 2.7619(9) Å. They are comparable to a large variety of reported values for silver aggregates: carbene, phenyl or methylpyridine bridged Ag−Ag complexes for example.[15−17] The coordination compound $[Ag_{12}(bpy)_4(C{\equiv}CBu^t)_6(CF_3CO_2)_6]$ exhibits a similar octahedral

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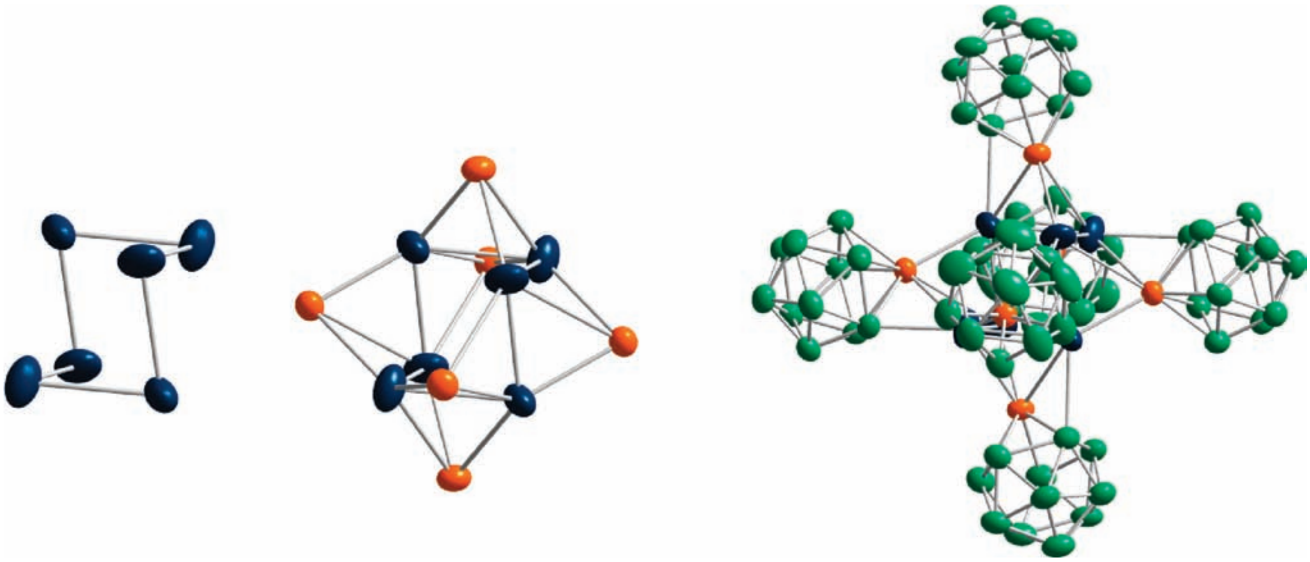

Figure 4. (left) Silver cluster; (middle) silver and germanium atoms; (right) complete anionic cluster showing the octahedral arrangement of the borates. (blue, silver; orange, germanium; green, boron).

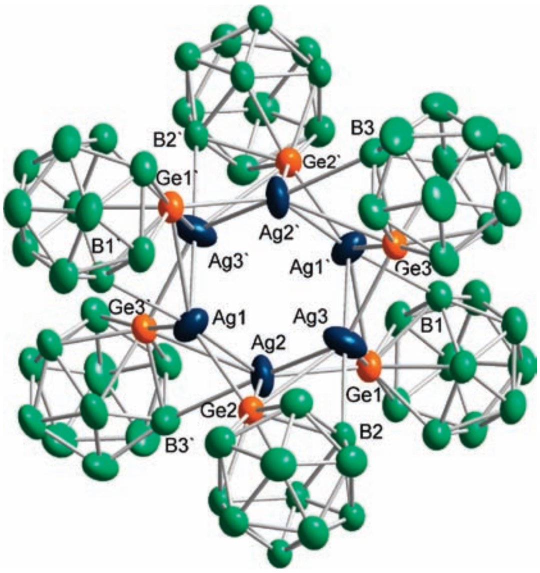

Figure 5. Molecular structure of the hexaanion of $[Et_4N]_6[\{Ag(GeB_{11}H_{11})\}_6]$ (**6**). The counter cations and hydrogen atoms have been omitted, ellipsoids at 50% (blue, silver; orange, germanium; green, boron).

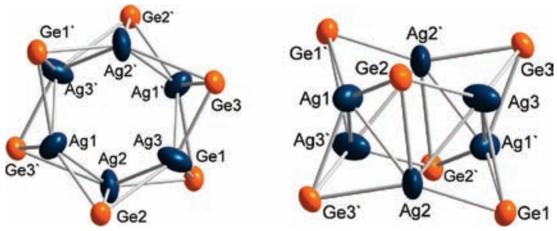

Figure 6. Cluster core of the hexaanion of **6**. Ellipsoids at 50%. Interatomic distances [Å] and bond angles [deg]: Ag1−Ag2 2.7374(9), Ag1−Ag2′ 3.3647(10), Ag1−Ag3 3.3772(10), Ag1−Ag3′ 2.7046(8), Ag2−Ag3 2.7619(9), Ag1−Ge1′ 2.8207(9), Ag1−Ge2 2.4868(8), Ag1−Ge3′ 2.7526(9), Ag2−Ge1 2.4941(9), Ag2−Ge3′ 2.8277(9), Ge1−Ag3 2.9397(10), Ge3−Ag3 2.5191(9), Ge2−Ag3 2.7121(10); Ag3′−Ag1−Ag2 79.72(3), Ag1−Ag2−Ag3 75.78(3), Ag2−Ag3−Ag1 51.78(2).

Ag_6-core structural motif with Ag−Ag distances in the range of 2.8474(6)−3.3337(7) Å.[18]

The six germa-*closo*-dodecaborate clusters (Figure 7) exhibit one coordination mode in the hexaanion of **6**. Each germanium is coordinated at one silver atom with a short Ag−Ge bond [2.4868(8), 2.4941(9), 2.5191(9)] and at another silver atom with a long interatomic distance [2.7526(9), 2.9397(10), 3.0468(10)]. Furthermore each cluster coordinates at a third silver atom via a BH−Ag interaction (Figure 7). The silver−germanium distances lie between 2.4868(8) and 3.047(1) Å. Bonds between silver and germanium are known in the literature from a small number of compounds and range between 2.44 and 2.76 Å.[7,8,13] The found short Ag−Ge interatomic distances are comparable with the literature examples. The silver−boron distances of the boron atoms involved in B−H−Ag three center two electron bonds lie between 2.570(7) and 2.635(8) Å and are typical for such a coordination mode.[19,20]

From the reaction of silver nitrate with stanna-*closo*-dodecaborate as the $[Et_4N]_2[SnB_{11}H_{11}]$ salt we isolate in 72% yield green crystals of the tetranuclear silver cluster $[Et_4N]_8[Ag_4(SnB_{11}H_{11})_6]$.[4c] In this reaction mixture a very small amount of brown crystals were found and characterized by single crystal structure solution. These crystals show the biggest silver cluster in this chemistry, a heptanuclear silver aggregate coordinated by eight stanna-*closo*-dodecaborate ligands $[Et_4N]_9[Ag_7(SnB_{11}H_{11})_8]$ (**7**). The heptanuclear silver aggregate crystallizes in the orthorhombic space group $P2_12_12$ with only one-half of the aggregate in the asymmetric unit. In Figure 8 and

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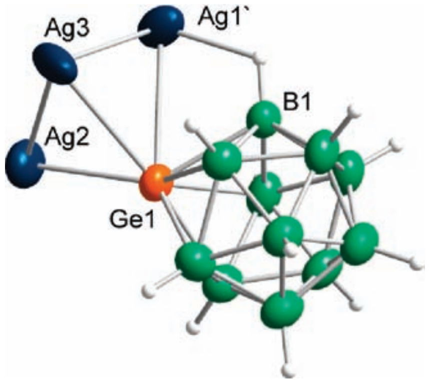

Figure 7. Detailed picture of the germa-*closo*-dodecaborate coordination. Short Ag−Ge bonds: Ag1−Ge2 2.4868(8), Ag2−Ge1 2.4941(9), Ag3−Ge3 2.5191(9); long Ag−Ge interaction: Ag1−Ge3′ 2.7526(9), Ag2−Ge2 3.0468(10), Ag3−Ge1 2.9397(10); B−H−Ag coordination: B2−Ag3 2.570(7), B3−Ag2′ 2.635(8), B1−Ag1′ 2.598(7), Ag1−Ge1′ 2.8207(9), Ag2′−Ge3 2.8277(9), Ag3−Ge2 2.7121(10) Å.

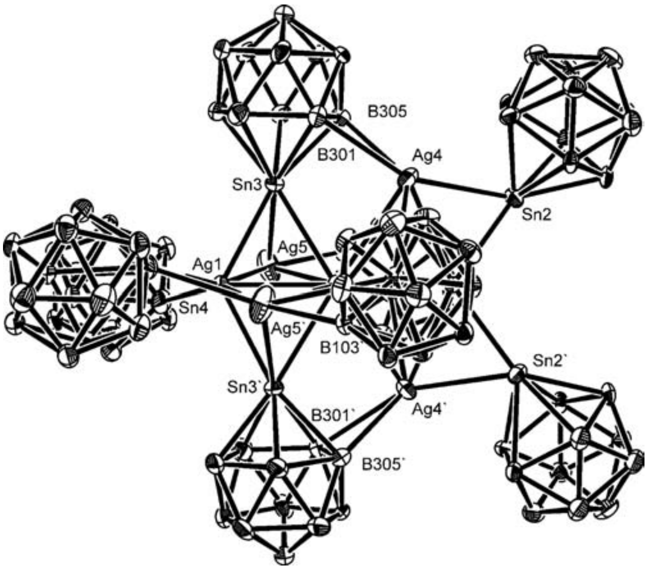

Figure 8. Structure of the anion of $[Et_4N]_9[Ag_7(SnB_{11}H_{11})_8]$.

Figure 9 the structure is depicted. The interatomic silver distances show a group of short values between 2.785 and 2.852 Å (Ag1−Ag2, Ag2−Ag3, Ag1−Ag5/Ag5′, Ag3−Ag4/Ag4′) and longer distances (Ag2−Ag5/Ag5′, Ag2−Ag4/Ag4′: 3.0800, 3.1473 Å). These Ag−Ag distances lie in the range of literature examples of stannaborate silver complexes.[4c,d] The shorter Ag−Ag interatomic distances are comparable with the short silver−silver interactions found in carbene bridged metal interactions.[21,22] Four clusters (Sn2, Sn2′, Sn4, Sn4′) show a μ_2 coordination mode and the other four clusters (Sn1, Sn1′, Sn3, Sn3′) bridge three Ag Atoms via tin coordination. Like in the already published examples the μ_2-coordinated clusters show shorter Ag−Sn bonds than the μ_3-coordinated tin ligands.[4c,d] Furthermore the clusters Sn3 and Sn3′ coordinate with two BH units each the silver atoms Ag4, Ag4′. The clusters Sn1, Sn1′show coordination of one BH unit at the silver atom Ag5, Ag5′. The found distances between the boron atoms and the silver atoms of the BH−Ag [2.5827(6), 2.6470(8), 2.6097(8) Å] units are comparable with silver−borane coordination compounds in the literature.[19,20]

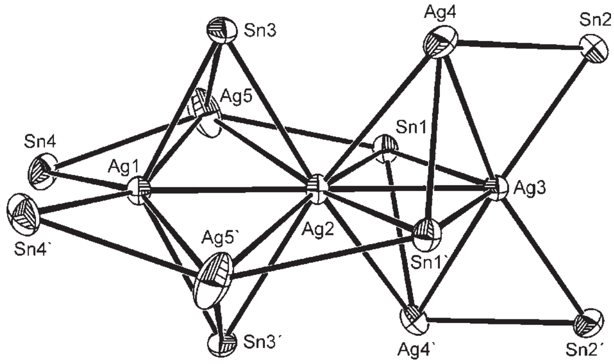

Figure 9. Core structure of $[Et_4N]_9[Ag_7(SnB_{11}H_{11})_8]$. Interatomic distances [Å] and bond angles [deg]: Ag3−Sn2 2.6701(6), Ag3−Ag2 2.8283(10), Ag3−Sn1 2.8318(5), Ag3−Ag4 2.8520(6), Ag2−Ag1 2.7846(10), Ag2−Sn1 2.7858(5), Ag2−Sn3 2.9032(5), Ag2−Ag5 3.0800(8), Ag2−Ag4 3.1473(7), Ag4−Sn2 2.9077(7), Ag4−Sn1 2.9924(7), Ag1−Sn4 2.6684(6), Ag1−Ag5 2.7890(6), Ag1−Sn3 2.8068(5), Ag5−Sn4 2.8608(8), Ag5−Sn3′ 2.9862(8), Ag5−Sn1 3.1327(8), Sn1′−Ag4′ 2.9924(7); Ag1−Ag2−Ag3 180.0.

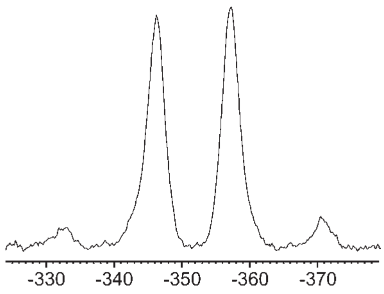

Figure 10. $^{119}Sn\{^1H\}$ NMR spectrum of silver compound **4** at −60 °C.

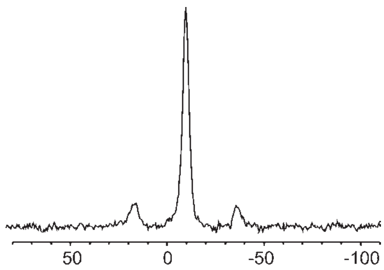

Figure 11. $^{119}Sn\{^1H\}$ NMR spectrum of gold dimer **5** in CH_3CN.

The core structure of the nona-anionic silver−tin aggregate together with selected interatomic distances is depicted in Figure 9.

NMR Spectroscopy. We tried to investigate the structures of complexes **4** and **5** in solution by ^{11}B and ^{119}Sn NMR methods. Signals in the $^{11}B\{^1H\}$ NMR spectrum of silver complex **4** at −6.1(1B) and −13.2(10B) ppm are a good proof of coordination of the heteroborate **2** at the coinage metal [$^{11}B\{^1H\}$ NMR spectrum of the uncoordinated $SnB_{11}H_{11}^{2-}$: −5.1(1B), −10.6(5B), −11.9(5B); because of isochronism the signal at −13.2 ppm is the resonance for the two B5 belts of the cluster]. At room temperature only one broad single signal in the $^{119}Sn\{^1H\}$

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Table 2. NMR Data for Compounds **1**, **3**, **4**, and **5**

compound	^{11}B{^{1}H} [ppm]	^{119}Sn{^{1}H} [ppm] (299 K)	solvent
1	−5.1(1B), −10.6(5B), −11.9(5B)	−546	CD_3CN
3	−5.7(1B), −12.4(10B)	−491	CD_3CN
4	−6.1(1B), −13.2(10B)	−361	DMF-d_7
5	−7.2(1B), −14.1(10B)	−9 [$^{2}J(^{119}\text{Sn}-\text{Au}^{117}\text{Sn})$ = 4832 Hz]	CD_3CN

NMR spectrum at −361 ppm was found. Recording the spectrum at −60 °C results in the observation of a doublet which can be assigned to the $^{1}J(^{119}\text{Sn}-^{107/109}\text{Ag} = 2051$ Hz) coupling (Figure 10). Additional splitting of this doublet because of the $^{107/109}$Ag isotopes (both $I = 1/2$) is not observed; this could be due to the signal line width of 564 Hz. Satellites due to the $^{119}\text{Sn}^{117}\text{Sn}^{107/109}\text{Ag}$ isotopomer with $^{2}J(^{119}\text{Sn},^{117}\text{Sn}) = 5062$ Hz support the coordination of silver by three stannaborate ligands. However, because of the low signal-to-noise ratio of the ^{119}Sn NMR spectrum the relative intensities of the two satellites results in an imprecise ratio of the measured isotopomers (calculated ratio 1/13/13/1; integrated 1/9/9.1/1.2; peak heights 1/10.6/11/0.8). Peak heights can also be used for quantitative analysis and show in this case a better agreement with the calculation.[23] Although crystalline material of **4** was dissolved for NMR spectroscopy the measured satellites indicate a higher coordination number. The observed $^{1}J(^{119}\text{Sn}-^{107/109}\text{Ag})$ coupling constant is smaller than the previously by Lappert et al. reported one of the Ag−Sn complex $[(\text{Ag(SCN)}\{\text{Sn(CHR}_2)_2\}(\text{thf}))_2]$ (R = $SiMe_3$), $^{1}J(^{119}\text{Sn}-^{107/109}\text{Ag}$: 4632/4063 Hz).[24]

The ^{11}B{^{1}H} NMR spectrum of dimer **5** shows two signals at −7.2(1B) and −14.1(10B) ppm (the signals for the two B5 belts show coincidence). According to the structure in the solid state two signals (one for the bridging and one for the terminal bonded ligand) in the ^{119}Sn{^{1}H} NMR spectrum of gold complex **5** were expected. However, only one signal with satellites was observed at room temperature (Figure 11). These satellite signals can be assigned to the $^{2}J(^{119}\text{Sn}-\text{Au}-^{117}\text{Sn})$ coupling with 4830 Hz. The intensity of these satellites is an indicator for the coordination of tin ligands (calculated intensity 1/8/1; integrated 1.6/12/1; peak heights 1.2/10/1). However, the low signal-to-noise ratio results in a discrepancy in the integrals of the two satellites and therefore the coordination of four ligands is only roughly verified. Recording the spectrum at −50 °C results in the observation of the expected two signals at 2 and −28 ppm. A summary of the collected boron and tin NMR data is shown in Table 2.

Deduced from ^{11}B NMR spectroscopy, in solution the germaborate silver **6** salt shows coordination of the boron clusters. Because of the small amount of crystalline material of cluster **7** we were not able to record the NMR spectra in solution.

Summary and Conclusion

In summary, we present homoleptic coinage metal complexes of silver and gold with the tin ligand stanna-*closo*-dodecaborate, together with the first copper complex in this chemistry. Furthermore, the first coinage metal complex with the germanium ligand germa-*closo*-dodecaborate was characterized. With this hexanuclear silver cluster we found the first example for silver−silver bond formation caused by the germanium nucleophile $[\text{GeB}_{11}\text{H}_{11}]^{2-}$.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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