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Stabilization of Triaryltin(IV) Cations Containing an O,C,O-Coordinating Pincer-Type Ligand. Isolation of a New $[Ag(1\text{-}CB_{11}H_{12})_3]^{2-}$ Anion

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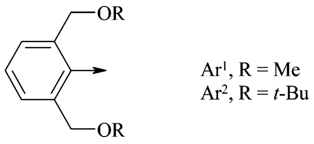
Reported is the stabilization of pincer-type triaryltin(IV) $[Ar^1SnPh_2]^+$ and $[Ar^2SnPh_2]^+$ cations (where $Ar^1 = 1\text{-}\{2,6\text{-}(MeO)_2C_6H_3\}$ and $Ar^2 = 1\text{-}\{2,6\text{-}(t\text{-}BuO)_2C_6H_3\}$) with weakly coordinating carborane anions $[1\text{-}CB_{11}H_{12}]^-$ and $[3\text{-}Co{-}(1,2\text{-}C_2B_9H_{11})_2]^-$. Treatment of Ar^1SnPh_2Cl with $Ag^+[1\text{-}CB_{11}H_{12}]^-$, depending on the molar ratio, reaction time, and solvent used (CH_2Cl_2 or THF), resulted in the isolation of the ion-pairs $[Ar^1SnPh_2]^+[1\text{-}CB_{11}H_{12}]^-$ (**1**) (yield 86%) and $[Ar^1SnPh_2]^+_2[Ag(1\text{-}CB_{11}H_{12})_3]^{2-}$ (**2**) (yield 94%). Compound **2** contains a new $[Ag(1\text{-}CB_{11}H_{12})_3]^{2-}$ anion in which the Ag^+ ion is bound to the carborane cages via six hydrogen bridges. Compounds $[Ar^1SnPh_2]^+[3\text{-}Co\text{-}(1,2\text{-}C_2B_9H_{11})_2]^-$ (**3**) and $[Ar^2SnPh_2]^+[1\text{-}Co\text{-}(2,3\text{-}C_2B_9H_{11})_2]^-$ (**4**) were prepared in yields of 97 and 95%, respectively, via metathesis of the $[Ar^1SnPh_2]^+OTf^-$ and $[Ar^2SnPh_2]^+OTf^-$ triflates with $Cs^+[1\text{-}Co\text{-}(2,3\text{-}C_2B_9H_{11})_2]^-$ in CH_2Cl_2. The products were characterized by multinuclear (^1H, ^{11}B, and ^{119}Sn) NMR and IR spectroscopy, ESI/MS, and elemental analyses, and the structures of compounds **2**, **3**, and **4** were determined by X-ray diffraction studies.

Introduction

The chemistry of icosahedral monocarbaborane anions, the most studied of which has been $[1\text{-}CB_{11}H_{12}]^-$,[1] is currently a rapidly developing area, as their weakly coordinating properties[2] are beneficial for the stabilization of highly Lewis-acidic species. This property has been justified by successful approaches to the isolation of the salts of $[1\text{-}CB_{11}H_{12}]^-$ and its substituted derivatives with several cations, ion-like or covalent species, such as R^+ (R = Me, Et, *i*-Pr, and *t*-Bu),[3,4] $C_6H_7^+$ (protonated benzene),[5] $HC60^+$ (protonized fullerene),[6] R_3Si^+,[7] R_3Sn^+,[8] $[Cu(CO)_4]^+$,[9] $[(COD)Rh(THF)_2]^+$,[10] $[(COD)Rh]^+$,[10] $[(PPh_3)_2Rh]^+$,[11] $[CpMo(CO)_3]^+$,[12] $[Ag(PPh_3)]^+$,[13] $[Ag(PPh_3)_2]^+$,[13] Cp_2ZrMe^+,[14,15] among others. There are also isolated examples when the cobaltadicarbollide anion[16] $[3\text{-}Co\text{-}1,2\text{-}C_2B_9H_1]^-$ was used as a weakly coordinating anion (WCA) for the stabilization of the Cp_2ZrMe^+ and $[(EBTHI)M(H)(NPhMe_2)]^+$ (M = Zr and Hf; EBTHI = ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)) cations.[17,18] Generally, new classes of borane-based WCAs, sometimes referred to as 3D analogue of benzene, have been

Chart 1



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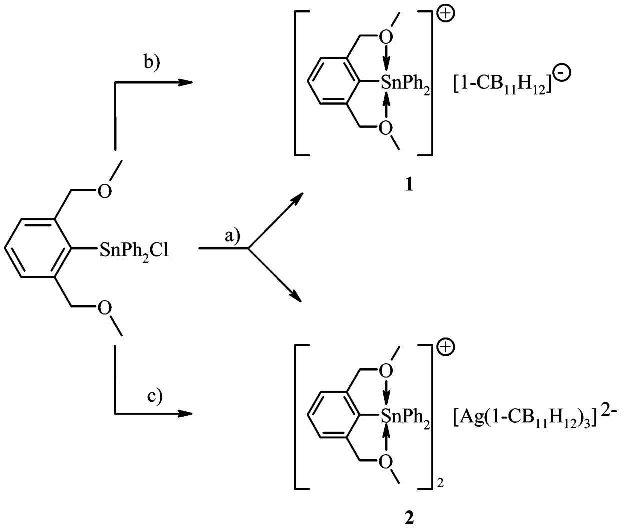
Scheme 1. Preparation of the Ion-Pairs $[Ar^1SnPh_2]^+[1\text{-}CB_{11}H_{12}]^-$ (1) and $[Ar^1SnPh_2]^+{}_2[Ag(1\text{-}CB_{11}H_{12})_3]^{2-}$ (2): Path a: Molar Ratio 1:1, CH_2Cl_2, 2 Days; Path b: Molar Ratio 1:1, THF (or CH_2Cl_2), 7 Days; Path c: Molar Ratio 2:3, CH_2Cl_2, 2 Days



increasingly receiving attention as suitable counteranions for multipurpose cationic catalysis and other practical uses.[19]Many groups have recently been interested in the development of the chemistry of organotin(IV) cations (OTC),[20] which are believed to play an important role in cytotoxic activity of organotin compounds[21] or in catalytic applications in the area of organic chemistry.[22] The known methods for their preparation consist in using either donor atoms[23] or so-called Y,C,Y-chelating ligands as stabilizing functionalities.[24] Just recently, we have reported on the preparation of triorganotin compounds contaning the O,C,O-chelating aryl ligands, specifically Ar^1 and Ar^2 (Ar^1 = 2,6-bis(methoxymethyl)-1-phenyl and Ar^2 = 2,6-bis(*tert*-butoxymethyl)-1-phenyl), and found that the $CF_3SO_3^-$ (OTf) counteranion had to be employed to successfully generate the Ar^1- and Ar^2-containing OTC.[25] Following our interest in Ar^1- and Ar^2-containing OTC, we report in this work experiments aimed at using cluster-carborane anions[1,16] $[1\text{-}CB_{11}H_{12}]^-$ and $[3\text{-}Co\text{-}(1,2\text{-}C_2B_9H_{11})_2]^-$ as effective counteranions for the stabilization of the $[Ar^1SnPh_2]^+$ and $[Ar^2SnPh_2]^+$ triaryltin cations. Reported is also the isolation of a new $[Ag(1\text{-}CB_{11}H_{12})_3]^{2-}$ dianion, another component of equilibria with the previously reported $[Ag_2(1\text{-}CB_{11}H_{12})_4]^{2-}$ anion.[26]

Results and Discussion

Syntheses. As shown in path a of Scheme 1, treatment of Ar^1Ph_2SnCl[27] with $Ag^+[1\text{-}CB_{11}H_{12}]^-$ [28] (molar ratio 1:1) in CH_2Cl_2 over a period of 2 days led to a mixture of the anticipated compound $[Ar^1SnPh_2]^+[1\text{-}CB_{11}H_{12}]^-$ (**1**) with an unexpected product that was characterized as $[Ar^1SnPh_2]^+{}_2[Ag(1\text{-}CB_{11}H_{12})_3]^{2-}$ (**2**). Further insights into the reaction system showed, however, a straightforward time and solvent dependence of the reaction. Prolongation of the reaction time (7 days) or the use of a coordinating solvent (THF) resulted in exclusive formation of the expected compound **1** in 86% yield (see path b of Scheme 1).

A change in the stoichiometry of the starting compounds (molar ratio 2:3, CH_2Cl_2, 2 days; path c of Scheme 1) resulted in clean and high-yield (94%) formation of compound **2**. It is evident that the formation of the new $[Ag(1\text{-}CB_{11}H_{12})_3]^{2-}$ dianion (structurally similar to closely related variants)[29] results from incomplete AgCl elimination and self-condensation of the starting $Ag^+[1\text{-}CB_{11}H_{12}]^-$ salt in the absence of a coordinating solvent that would otherwise coordinate the ion Ag^+.[30] The condensation can be reasonably supposed to proceed in two steps, outlined in Scheme 2.

The proposed condensation sequence involves the formation the earlier reported[26] $[Ag_2(1\text{-}CB_{11}H_{12})_4]^{2-}$ anion as the first condensation intermediate. This anion is then supposed to interact with excess $Ag^+[1\text{-}CB_{11}H_{12}]^-$ to generate $[Ag(1\text{-}CB_{11}H_{12})_3]^{2-}$, the final product of the condensation process in which the Ag^+ ion adopts the maximum coordination number with respect to the $[1\text{-}CB_{11}H_{12}]^-$ ligation. It is also seen that, in both steps, the self-condensation results in the generation of free Ag^+ ions, which are quickly removed from the reaction environment by eliminating AgCl via reactions with the triaryltin chloride. Naturally, AgCl elimination is then a reason the equilibrium is shifted in favor of compound **2**.

In this context, it should also be noted that compound **2**, though reasonably stable in the solid state, is unstable in solution

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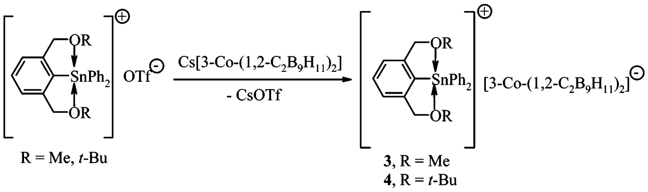
Scheme 2. Proposed Formation of the $[Ag(1\text{-}CB_{11}H_{12})_3]^{2-}$ Anion

$$4\ Ag^+[1\text{-}CB_{11}H_{12}]^- \xrightleftharpoons{CH_2Cl_2} Ag^+{}_2[Ag_2(1\text{-}CB_{11}H_{12})_4]^{2-} \xrightleftharpoons[CH_2Cl_2]{2\ Ag^+[1\text{-}CB_{11}H_{12}]^-} 2Ag^+{}_2[Ag(1\text{-}CB_{11}H_{12})_3]^{2-}$$

Scheme 3. Synthesis of $[Ar^1SnPh_2]^+[3\text{-}Co\text{-}(1,2\text{-}C_2B_9H_{11})_2]^-$ (3) and $[Ar^2SnPh_2]^+[3\text{-}Co\text{-}(1,2\text{-}C_2B_9H_{11})_2]^-$ (4)



and decomposes, giving a mixture of **1** with the starting compound $Ag^+[1\text{-}CB_{11}H_{12}]^-$ after standing for 48 h in CH_2Cl_2 solution, which suggests reversibility of all reactions of Scheme 2.

Successful were also preparations of the $[Ar^1SnPh_2]^+$ and $[Ar^2SnPh_2]^+$ cations with the cobaltadicarbaborane anion $[3\text{-}Co\text{-}(1,2\text{-}C_2B_9H_{11})_2]^-$.[16] Although reactions of Ar^1SnPh_2Cl and Ar^2SnPh_2Cl with $Cs^+[3\text{-}Co\text{-}(1,2\text{-}C_2B_9H_{11})_2]$ in CH_2Cl_2 did not lead to CsCl elimination and formation of the expected compounds $[Ar^1SnPh_2]^+[3\text{-}Co\text{-}(1,2\text{-}C_2B_9H_{11})_2]^-$ (**3**) and $[Ar^2SnPh_2]^+[1\text{-}Co\text{-}(2,3\text{-}C_2B_9H_{11})_2]^-$ (**4**), nevertheless, these compounds could be prepared smoothly in respective yields of 97 and 95% via metathesis of the corresponding triflates, as outlined in Scheme 3.

NMR, IR, and Mass Spectra. The values of ^{119}Sn NMR (−20.0 (**1**), −16.3 (**2**), and −22.3 (**3**) ppm, respectively) are typical for [3+2]-coordinated triorganotin cations.[25,31] As expected, the $^{11}B\{^1H\}$ NMR spectra of **1** and **2** are rather different, since **1** and **2** contain different carborane anions. While the $^{11}B\{^1H\}$ NMR spectrum of **1**, showing three distinct 1:5:5 resonances, is typical for the free $[1\text{-}CB_{11}H_{12}]^-$ anion,[1] only two signals of intensities 1:10 are observed in the spectrum of **2**. It should be noted that the same tendency for the coalescence of the two high-field ^{11}B resonances has also been observed for the related Ag^+ complexes, $Ag^+[1\text{-}CB_{11}H_{12}]^-$ and $[Ag_2(1\text{-}CB_{11}H_{12})_4]^{2-}$, when measured in noncoordinating solvents.[26] The ^{11}B NMR spectra of **3** and **4** well approximate those found for the free cobalt bisdicarbollide anion.[16] The ^1H NMR spectra of all compounds isolated contain resonances diagnostic for the corresponding organotin cations and counteranions. The IR spectrum of **1** shows an absorption at 2551 cm^{-1} corresponding to ν(B−H). Two bands at 2551 and 2347 cm^{-1}, which are diagnostic for ν(B−H) and ν(Ag−H), were found in the IR spectrum of **2**. The negative-ion ESI mass spectrum of **1** shows a peak at $m/z = 143$ assigned to the $[CB_{11}H_{12}]^-$ anion, while compound **2** exhibits peaks at $m/z = 143$ and 394, which is consistent with fragmentation to $[CB_{11}H_{12}]^-$ and $[Ag(CB_{11}H_{12})_2]^-$. Compounds **3** and **4** exhibit similar trends in the IR (ν(B−H) = 2551 cm^{-1}) and MS spectra ($m/z = 324$, $[Co(C_2B_9H_{11})_2]^-$).

X-ray Diffraction Studies. The structural investigations on compound **1** were, unfortunately, affected by extensive disorder of the carbon vertex in the anionic part of the molecule. The structural studies were, however, successful on compounds **2**, **3**, and **4** (see Figures 1−3 below). The crystallographic data and selected bond lengths and angles are given in Tables 1 and 2.

In the triaryltin cations of **2**, **3**, and **4**, the central Sn(IV) atom is surrounded by carbon and two oxygen atoms from Ar^1 or Ar^2 in a tridentate fashion and by two phenyl substituents. The resulting geometry is a distorted trigonal bipyramid formed by three carbon atoms in the equatorial plane and two oxygen atoms in apical positions. The C_3Sn girdles are essentially planar (range of $\sum C{-}Sn{-}C = 359.88(16){-}359.98(15)°$) and the Sn−O distances are nearly equivalent in the cationic parts of **2**, **3**, and **4** (see Table 2). The strongest Sn−O intramolecular interaction was found in **3**, the Sn−O bond length being 2.273(3) Å. These distances indicate strong Sn−O interactions in **2**, **3**, and **4**, and the values are comparable with those found in diorganotin compounds (range of Sn−O distances 2.203−2.278 Å)[32] and in the organotin cation containing a different type of O,C,O-chelating ligand (aryldiphosphonic ester $C_6H_2[P(O)(OEt)_2]_2$-1,3-*t*-Bu-5) (Sn−O distances 2.249(2) and 2.241(3) Å).[24c] Since both oxygen atoms are part of one tridentate O,C,O-chelating ligand, the main deviation from ideal trigonal-bipyramidal geometry derives from the O−Sn−O angles that range between 149.32(9)° and 149.90(6)° for compounds **2**, **3**, and **4**.

A spectroscopic view of the crystal packing in **2** shows sheets of ionic arrays, a feature encountered also with other known silver−carborane complexes. In the case of **2**, the main structural motif consists of the alteration of two organotin cations and one $[Ag(CB_{11}H_{12})_3]^{2-}$ anion to form a $(\text{cation−anion−cation})_n$ arrangement in one dimension of the lattice.

The anionic component of **2** consists of the central Ag^+ ion, which is surrounded by three $(CB_{11}H_{12})^-$ anionic cluster-carborane ligands. Each of them coordinates the silver via two unsupported Ag−H−B bridges, which results in a 6-fold coordination of Ag^+ by the B−H bonds. The coordination polyhedron around the Ag atom approximates a distorted octahedral shape. This mode of Ag−H−B interaction, however, does not significantly affect distances in the carborane cage in relation to the uncomplexed carborane anion.[1] The Ag−H distances (2.2388−2.2583 Å; see Table 3) are longer than those established for $Ag^+[1\text{-}CB_{11}H_{12}]^-\cdot 2C_6H_6$ (1.968−1.974 Å)[28] and $[Ag_2(1\text{-}CB_{11}H_{12})_4]^{2-}$ (1.96−2.23 Å).[26]

Similarly, the Ag−H−B angles (106.28−106.87°) are rather different from those found for $Ag^+[1\text{-}CB_{11}H_{12}]^-\cdot 2C_6H_6$.[28] These differences arise from changes in the Ag^+ coordination number (1 to 3) with respect to the $(CB_{11}H_{12})^-$ ligation in comparison with $Ag^+[1\text{-}CB_{11}H_{12}]^-\cdot 2C_6H_6$. Each of the $(CB_{11}H_{12})^-$ ligands in **2** is bonded to the Ag^+ center via bridging B12−H−Ag (opposite to the cage carbon) and B8−H−Ag (adjacent to B12) bonds. These two boron atoms are the most negative cluster sites, and therefore B12−H and B8−H bonds would be expected to be of hydridic character, which is a convenient setting for the formation of metal−hydrogen bridging bonds.[33]

It should be added that bond distances and angles in the anionic parts of compounds **3** and **4** are essentially the same as those established for the free $[3\text{-}Co\text{-}(1,2\text{-}C_2B_9H_{11})_2]^-$ anion.[34]

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(31) These ^{119}Sn values are typical for pentacoordinate phenyl cations C_3Sn^+ of *trans*-trigonal bipyramidal geometry (carbon atoms form the equatorial plane and two donor atoms are in axial positions) found in triorganotin compounds containing N,C,N-chelating ligands.

(32) (a) Mehring, M.; Schürmann, M.; Jurkschat, K. *Organometallics* **1998**, *17*, 1227. (b) Mehring, M.; Vrasidas, I.; Horn, D.; Schûrmann, M.; Jurkschat, K. *Organometallics* **2001**, *20*, 4647. (c) Mehring, M.; Löw, Ch.; Uhlig, F.; Schürmann, M.; Jurkschat, K.; Mahieu, B. *Organometallics* **2000**, *19*, 4613.

(33) See, for example: Grimes, R. N. In *Metal Interactions with Boron Clusters*; Grimes, R. N., Ed.; Plenum Press: New York, 1982; Chapter 7.

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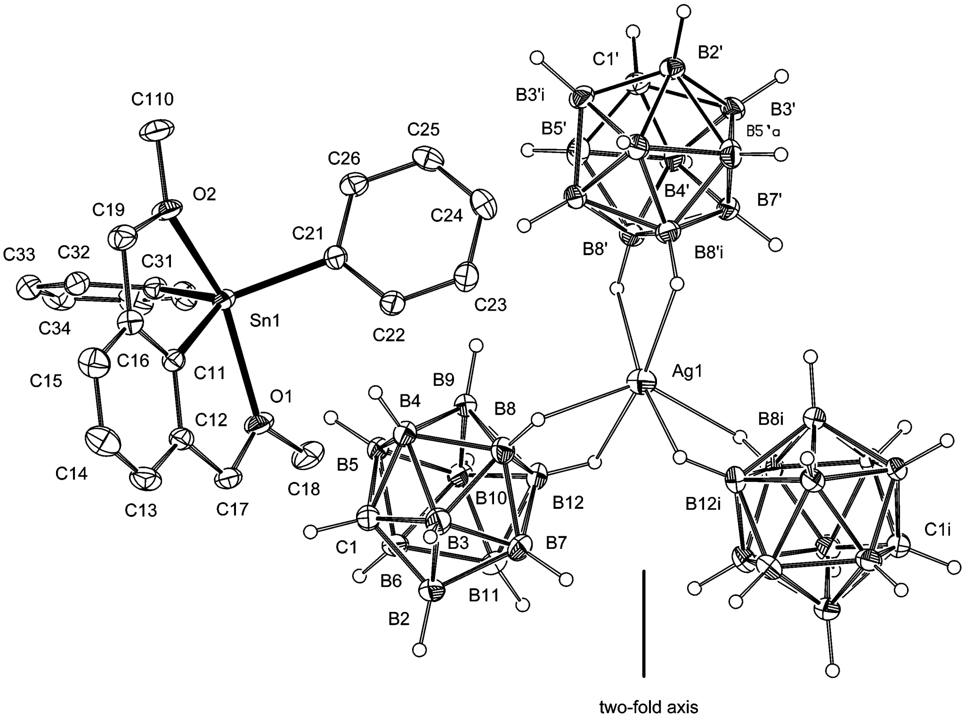

Figure 1. ORTEP representation of the molecular structure of $[Ar^1SnPh_2]^+{}_2[Ag(1\text{-}CB_{11}H_{12})_3]^{2-}$ (**2**) showing 30% probability displacement ellipsoids and the atom-numbering scheme. The $[Ag(1\text{-}CB_{11}H_{12})_3]^{2-}$ anion is placed on a 2-fold axis going through the Ag atom and one of the borane cages (half of C1′ and B2′ distance, symmetry code: (i) 1/*x*, *y*, 1/2−*z*). Disordered atoms, hydrogen atoms of the cation, and one molecule of the cation are omitted for clarity.

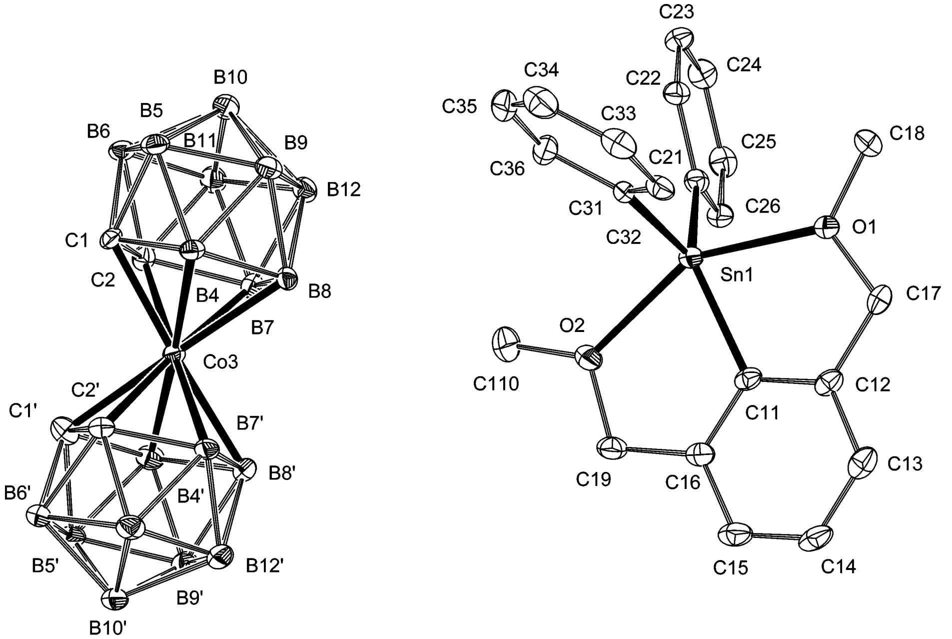

Figure 2. General view (ORTEP) of a molecule showing 30% probability displacement ellipsoids and the atom-numbering scheme for **3**. The hydrogen atoms are omitted for clarity.

Experimental Section

General Methods. The starting compounds Ar^1SnPh_2Cl,[27] Ar^1SnPh_2OTf, Ar^2SnPh_2OTf,[25] $Ag^+[1\text{-}CB_{11}H_{12}]^-\cdot 1.5C_6H_6$,[28] and $Cs^+[1\text{-}Co\text{-}(2,3\text{-}C_2B_9H_{11})_2]^-$ [16b] were prepared according to literature. All reactions were carried out under argon, using standard Schlenk techniques.[35] Solvents were dried by standard methods, distilled prior to use, and operations with silver salts were light protected. The ^1H,^{11}B, and ^{119}Sn NMR spectra were recorded on a Bruker AMX360 spectrometer at 300 K in $CDCl_3$. Appropriate chemical shifts were calibrated on the residual peak of $CHCl_3$ ($\delta = 7.27$ ppm) for ^1H, external $BF_3\cdot OEt_2$ ($\delta = 0.00$ ppm) for ^{11}B, and external tetramethylstannane ($\delta = 0.00$ ppm) for ^{119}Sn. Chemical shift data are given in ppm and coupling constants in Hz. Electrospray mass spectra (ESI/MS) were recorded in the positive mode on an Esquire3000 ion trap analyzer (Bruker Daltonics) (range 100−600 *m*/*z*) and in the negative mode on the Platform quadrupole analyzer (range 100−800 *m*/*z*). The samples were dissolved in acetonitrile and analyzed by direct infusion (flow rate 1−10 μL/min). For the detection of negative ions of *m*/*z*

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[35] Shriver, D. F.; Drezdon, M. A. *Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

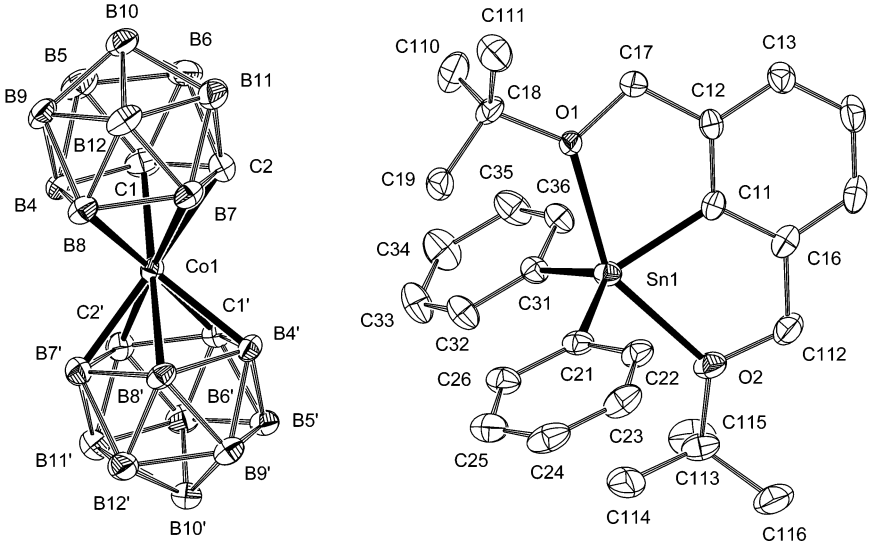

Figure 3. General view (ORTEP) of a molecule showing 30% probability displacement ellipsoids and the atom-numbering scheme for **4**. The hydrogen atoms are omitted for clarity.

Table 1. Crystal Data and Structure Refinement for 2, 3, and 4

	2	**3**	**4**
empirical formula	$C_3H_{36}AgB_{33}$, $2(C_{22}H_{23}O_2Sn)$	$C_{27}H_{46}B_{18}Cl_3CoO_2Sn$	$C_{32}H_{57}B_{18}CoO_2Sn$
color	colorless	yellow	red
cryst syst	monoclinic	triclinic	orthorhombic
space group	*C*2/*c* (No. 15)	$P\bar{1}$ (No. 2)	*Pbca* (No. 61)
a [Å]	14.6440(1)	12.5570(4)	22.4280(1)
b [Å]	20.5290(2)	13.4930(5)	14.0530(2)
c [Å]	22.6440(2)	14.5450(3)	26.9750(3)
α [deg]		64.6150(16)	
β [deg]	104.4030(4)	88.6190(16)	
γ [deg]		65.7080(12)	
Z	4	2	8
μ [mm^{-1}]	1.087	1.271	1.008
D_x [Mg m^{-3}]	1.424	1.467	1.322
cryst size [mm]	0.35 × 0.35 × 0.2	0.12 × 0.1 × 0.075	0.3 × 0.1 × 0.04
cryst shape	prism	plate	bar
θ range [deg]	1−27.5	1−27.5	1−27.5
$T_{\min,}$ $T_{\max}$	0.726, 0.807[a]		
no. of reflns measd	60r t566	32 526	123 685
no. of unique reflns; R_{int}	7540, 0.038	9113, 0.061	9723, 0.087
no. of obsd reflns [$I > 2\sigma(I)$]	6680	6319	6353
no. of params	395	471	493
S^b all data	1.055	1.018	1.022
final R^b [$I > 2\sigma(I)$]	0.029	0.044	0.047
$wR_2{}^b$ (all data)	0.076	0.094	0.127
w_1/w_2 [c]	0.0357, 10.0854	0.0351, 0.6184	0.0538, 15.4549
$\Delta\rho$, max., min., [e Å^{-3}]	0.674−1.584	0.845−0.607	2.509−1.281

[a] Correction by SORTAV program. [b] Definitions: $R(F) = \sum||F_o| - ||F_c||/\sum|F_o|$, $wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2]^{1/2}$, $S = [\sum(w(F_o^2 - F_c^2)^2)/(N_{reflns} - N_{params})]^{1/2}$. [c] Weighting scheme $w = [\sigma^2(F_o^2) + (w_1P) + w_2P]^{-1}$. $P = [\max(F_o^2, 0) + 2F_c^2]/3$. $R_{int} = \sum|F_o^2 - F_o^2\text{ (mean)}|/\sum F_o^2$ (summation is carried out only where more than one symmetry equivalent is averaged).

Table 2. Selected Geometric Parameters (Å, deg) of 2, 3, and 4

	2	**3**	**4**
Sn1−C11	2.086(2)	2.090(3)	2.088(4)
Sn1−C21	2.114(2)	2.107(3)	2.111(4)
Sn1−C31	2.110(2)	2.112(4)	2.114(4)
Sn1−O1	2.3040(15)	2.270(2)	2.366(2)
Sn1−O2	2.2912(14)	2.307(2)	2.394(3)
C11−Sn1−C21	123.57(8)	128.43(14)	121.67(16)
C11−Sn1−C31	114.10(8)	119.80(13)	115.19(15)
C21−Sn1−C31	122.26(8)	111.65(13)	123.12(16)
O1−Sn1−O2	149.90(6)	149.81(9)	149.32(9)

< 60, a quadropole analyzer had to be used in place of the ion trap. The IR spectra were recorded on a Perkin-Elmer 684 apparatus.

Synthesis of $[1\text{-}\{2,6\text{-}(MeOCH_2)_2C_6H_3\}SnPh_2]^+[1\text{-}CB_{11}H_{12}]^-$ (1). A solution of Ar^1Ph_2SnCl (27 mg, 0,060 mmol) in THF (40 mL) was stirred with $AgCB_{11}H_{12}\cdot 1.5C_6H_6$ (22 mg, 0.060 mmol) for 1 day. The AgCl was removed by filtration, the filtrate evaporated, and the solid residue washed with pentane (2 × 5 mL) to give **1** (yield 30.1 mg, 86%). For **1**: mp 160−163 °C. Anal. Calcd for $C_{23}H_{35}B_{11}O_2Sn$ (581.23): C, 47.48; H, 6.02. Found: C, 47.55; H, 5.95. Monoisotopic MW = 584. Positive-ion ESI-MS: *m/z* 439, $[M - CB_{11}H_{12}]^+$, 100%. Negative-ion ESI-MS: *m/z* 143, $[CB_{11}H_{12}]^-$, 100%. ^1H NMR ($CDCl_3$, 360 MHz): δ 2.38 (bs, 1H, CH-cage), 3.70 (s, 6H, CH_3), 5.09 (s, 4H, CH_2), 7.35−7.70 (complex pattern, 13H, $SnPh_2$, SnC_6H_3). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −4.9, −11.4, −14.5. ^{119}Sn NMR ($CDCl_3$): δ −20.0. IR: suspension in Nujol: ν(B−H) 2546 cm^{-1}.

Synthesis of $[1\text{-}\{2,6\text{-}(MeOCH_2)_2C_6H_3\}SnPh_2]^+{}_2[Ag(1\text{-}CB_{11}H_{12})_3]^{2-}$ (2). A solution of Ar^1Ph_2SnCl (27 mg, 0,060 mmol) in CH_2Cl_2 (40 mL) was stirred with $AgCB_{11}H_{12}\cdot 1.5C_6H_6$ (33 mg, 0.090 mmol) for 2 h. The AgCl was removed by filtration, the filtrate evaporated, and the solid residue washed with pentane (2

Table 3. Selected Bond Distances (Å) and Angles (deg) for the $[Ag(CB_{11}H_{12})_3]^{2-}$ Anion[a]

Bond Distances	
Ag1−H8	2.239
Ag1−H8′	2.242
Ag1−H12	2.259
Bond Angles	
Ag1−H8−B8	106.87
Ag1−H8′−B8′	107.31
Ag1−H12−B12	106.57
H8−Ag1−H12	81.26
H8−Ag1−H8′	112.30
H12−Ag1−H8′	86.93
H8−Ag1−H8^i	136.73
H8−Ag1−H8′^{i}	100.25
H8−Ag1−H12^i	72.56
H8′−Ag1-H8′^{i}	81.80
H12−Ag1−H12^i	104.47
H12−Ag1−H8′^{i}	168.34

[a] Symmetry code (i): $1 - x, y, 1/2 - z$.

× 5 mL) to give **2** (yield 40 mg, 94%). For **2**: mp 200−205 °C (dec). Anal. Calcd for $C_{47}H_{82}B_{33}O_4Sn_2Ag$ (1413.19): C, 39.86; H, 5.84. Found: C, 39.55; H, 5.50. Monoisotopic MW = 1415. Positive-ion ESI-MS: *m/z* 439, $[M - Ag(CB_{11}H_{12})_3/2]^+$, 100%. Negative-ion ESI-MS: *m/z* 143, $[CB_{11}H_{12}]^-$, 100%, *m/z* 394, $[Ag(CB_{11}H_{12})_2]^-$, 67%. ^1H NMR ($CDCl_3$, 360 MHz): δ 2.46 (bs, 1H, CH-cage), 3.72 (s, 6H, CH_3), 5.12 (s, 4H, CH_2), 7.35−7.70 (complex pattern, 13H, $SnPh_2$, SnC_6H_3). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −14.49, −18.21. ^{119}Sn NMR ($CDCl_3$): δ −16.3. IR (Nujol): ν(B−H) 2553 cm^{-1}, ν(Ag−H) 2353 cm^{-1}.

Synthesis of $[1\text{-}\{2,6\text{-}(MeOCH_2)_2C_6H_3\}SnPh_2]^+[3\text{-}Co\text{-}(1,2\text{-}C_2B_9H_{11})_2]^-$ (3). A solution of Ar^1Ph_2SnOTf (29 mg, 0.05 mmol) in CH_2Cl_2 (20 mL) was stirred with $Cs[1\text{-}Co\text{-}(2,3\text{-}C_2B_9H_{11})_2]^-$ (23 mg, 0.05 mmol) for 2 days. The CsOTf was removed by filtration, the filtrate evaporated, and the solid residue washed with pentane (2 × 5 mL) to give **3** (yield 37 mg, 97%). For **3**: mp 205−209 °C. Anal. Calcd for $C_{32}H_{57}B_{18}O_2SnCo$ (761.87): C, 50.40; H, 7.48. Found: C, 50.05; H, 7.24. Monoisotopic MW = 763. Positive-ion ESI-MS: *m/z* 439, $[M - Co(C_2B_9H_{11})_2]^+$, 100%. Negative-ion ESI-MS: *m/z* 324, $[Co(C_2B_9H_{11})_2]^-$, 100%. ^1H NMR ($CDCl_3$, 360 MHz): δ 3.72 (s, 6H, CH_3), 3.91(s, 4H, CH), 5.13 (s, 4H, CH_2), 7.35−7.70 (complex pattern, 13H, $SnPh_2$, SnC_6H_3). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ 2.38, −1.79, −8.94, −10.09, −20.62, −26.13. ^{119}Sn NMR ($CDCl_3$): δ −22.3. IR (Nujol): ν(B−H) 2539 cm^{-1}.

Synthesis of $[1\text{-}\{2,6\text{-}(t\text{-}BuOCH_2)_2C_6H_3\}SnPh_2]^+[3\text{-}Co\text{-}(1,2\text{-}C_2B_9H_{11})_2]^-$ (4). A solution of Ar^2Ph_2SnOTf (34 mg, 0.05 mmol) in CH_2Cl_2 (20 mL) was stirred with $Cs[1\text{-}Co\text{-}(2,3\text{-}C_2B_9H_{11})_2]^-$ (23 mg, 0.05 mmol) for 2 days. The CsOTf was removed by filtration, the filtrate evaporated, and the solid residue washed with pentane (2 × 5 mL) to give **4** (yield 40 mg, 95%). For **4**: mp 251−253 °C. Anal. Calcd for $C_{32}H_{57}B_{18}O_2SnCo$ (846.03): C, 45.39; H, 6.74. Found: C, 45.55; H, 6.35. Monoisotopic MW = 846. Positive-ion ESI-MS: *m/z* 523, $[M - Co(C_2B_9H_{11})_2)]^+$, 100%. Negative-ion ESI-MS: *m/z* 324, $[Co(C_2B_9H_{11})_2]^-$, 100%. ^1H NMR ($CDCl_3$, 360 MHz): δ 1.14 (s, 18H, CH_3), 4.00 (s, 4H, CH), 4.95 (s, 4H, CH_2), 7.35−7.70 (complex pattern, 13H, $SnPh_2$, SnC_6H_3). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ 2.46, −1.79, −8.64, −10.13, −20.53, −25.93. ^{119}Sn NMR ($CDCl_3$): δ −20.3. IR (Nujol): ν(B−H) 2545 cm^{-1}.

Crystallography Studies. Colorless crystals were obtained from layering of *n*-hexane onto a dichloromethane solution of the compounds. Crystals of compounds of **2**, **3**, and **4** were mounted on a glass fiber with epoxy cement and measured on a KappaCCD four-circle diffractometer with a CCD area detector by monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 150(2) K. The crystallographic details are summarized in Table 1, and empirical absorption corrections[36] were applied (multiscan from symmetry-related measurements). The structures were solved by the direct method (SIR97[37]) and refined by a full-matrix least-squares procedure based on F^2 (SHELXL97[38]). Hydrogen atoms were fixed into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2U_{eq}$ (pivot atom); for the methyl moiety a multiple of 1.5 was chosen. The final difference maps displayed no peaks of chemical significance. All three crystals suffered from disorder of the borane moieties. In **2** the $[Ag(1\text{-}CB_{11}H_{12})_3]^{2-}$ anion follows the symmetry of a 2-fold axis of space group *C*2/*c*. The symmetry element passes through the Ag atom and the centroid of one cage, so the other two cages are symmetrically identical. The cage placed on a 2-fold axis is disordered, as the positions of carbon atom C(1)′ and boron B(2)′ are overlapping each other. The electron density at this position was split in two, one occupied by 50% carbon and the second by 50% boron. The indication of disorder in crystals of **3** and **4** issues from analysis of C−C and C−B bond distances in the C_2B_3 open ring. In both crystals these distances are too close to each other, indicating their averaging due to rotation along the B(10)−Co−B(10′) axis. Crystallographic data for structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 610026, 610027, and 610028 for **2**, **3**, and **4**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk).

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Supporting Information Available: Spectroscopic view (along axis *y*) of the crystal packing in **2** and further details of the structure determination of compounds **2**, **3**, and **4**, including atomic coordinates, anisotropic displacement parameters, and geometric data are available free of charge via the Internet at http://pubs.acs.org.

OM060516C

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