Crystal Structure of *n*-Bu_3Sn^+ $CB_{11}Me_{12}^-$

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The only structurally characterized species among the extremely electrophilic R_3E^+ ions[1−7] (R = alkyl, E = Si, Ge, Sn, Pb) are the adducts of R_3Si^+ to toluene[2] or to halogenated carboranyl anions,[3] and a related delocalized cyclotrigermenium cation.[4] Crystallization is difficult, as adducts form even with weakly nucleophilic solvents, and solubility is often too low in sufficiently inert ones. Reaction of the strong neutral oxidant,[8] $CB_{11}Me_{12}^{\bullet}$, with a neutral R_3E-containing precursor in an inert solvent to produce the R_3E^+ salt of the solubilizing[9] and only weakly nucleophilic[8] $CB_{11}Me_{12}^-$ anion[10] suggests a general solution to this problem.[11] We report the single-crystal X-ray structure of *n*-Bu_3Sn^+ $CB_{11}Me_{12}^-$ (**1**) prepared in this manner (Scheme 1).

Two equivalents of $CB_{11}Me_{12}^{\bullet}$ reacted rapidly with *n*-Bu_6Sn_2 in dry pentane to form a white solid, identified as **1** by spectroscopy,[12,13] by trapping with PhMgBr, which afforded *n*-Bu_3SnPh[14] in 91% isolated yield, and by trapping with Et_2O, which yielded the known[7] *n*-$Bu_3SnOEt_2^+$ cation.[13]

X-ray diffraction analysis[13] of a single crystal of **1** grown from hexane revealed a tributylstannyl cation[13] weakly coordinated to methyl groups of two $CB_{11}Me_{12}^-$ anions in a trigonal bipyramid (Figure 1A). Each anion is coordinated to two cations through two antipodal methyl groups in infinite columns of alternating *n*-Bu_3Sn^+ and $CB_{11}Me_{12}^-$ ions,[13] similar to those of numerous covalent R_3SnX compounds (R = alkyl, X = O, N, S, Cl, etc.)[15] in which Sn and X atoms alternate. In all previously known compounds of this type X was a strong ligand and the Sn-X distance was short (2.1−2.4 Å for X = O, N and 2.3−2.6 Å for X = S, Cl). Perpendicular to the columns, **1** packs in hexagonal sheets, where every other vertex of a hexagon contains an Sn atom (Figure 1B). The edges are formed by *n*-Bu chains, and the central holes are filled with $CB_{11}Me_{12}^-$.

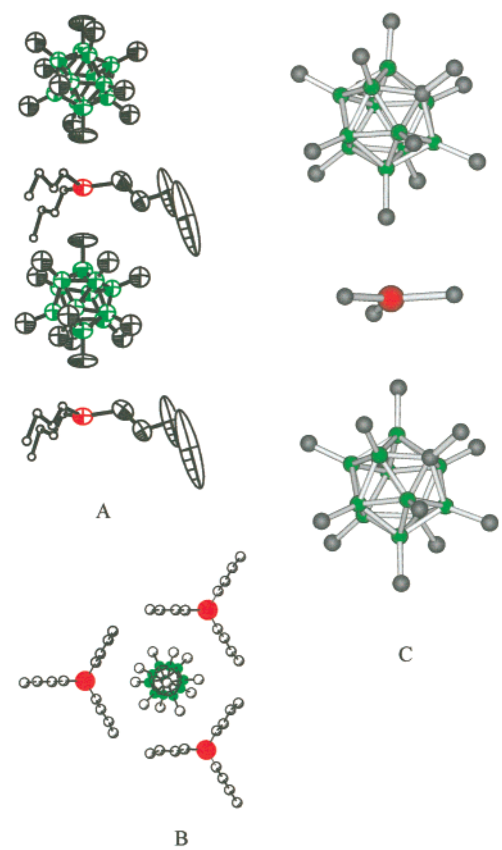
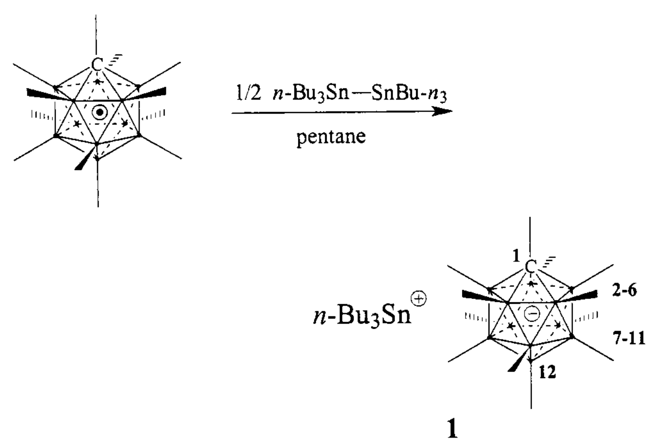


Figure 1. Structure of *n*-Bu_3Sn^+ $CB_{11}Me_{12}^-$ (**1**). Thermal ellipsoids are at 50%. Hydrogen atoms and one component of the disordered butyl groups are omitted for clarity, Sn atoms are red, C atoms are black, B atoms are green. (A) Part of an infinite column of alternating cations and anions. (B) View of the crystal packing of **1** along a direction slightly off the column axis. (C) Optimized (B3LYP/SDD) geometry of the [$CB_{11}Me_{12}^-$ Me_3Sn^+ $CB_{11}Me_{12}^-$] ion triple.

Scheme 1



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The interaction of the *n*-Bu_3Sn^+ cation with two axially disposed $CB_{11}Me_{12}^-$ methyl groups in **1** is weak but clearly present: (i) The average Sn−C distance is 2.81 Å, much longer than a covalent Sn−C bond (2.14 Å[15]), but much shorter than the sum (4.17 Å) of the van der Waals radii of a methyl (2.0 Å[16]) and tin (2.17 Å[15]). (ii) The sum of the C_α−Sn−C_α angles is 353.1° and the Sn atom is 0.32 Å out of the plane of the C_α atoms. The Sn−C_α bond length is 2.07 Å, shorter than a normal Sn(sp^3)−C bond length (2.14 Å[15]) and even the usual Sn−C bond

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(12) ^{119}Sn NMR (cyclohexane-d_{12}): δ 454.3. ^{1}H NMR (cyclohexane-d_{12}): δ 1.83 (6H, bs, α-CH_2), 1.43 (6H, m, β-CH_2), 0.98 (6H, m, γ-CH_2), 0.88 (9H, t, δ-CH_3), 0.84 (3H, s, CH_3−C_1), −0.25 (15H, s, CH_3−B_{7-11}), −0.38 (15H, s, CH_3−B_{2-6}), −0.46 (3H, CH_3−B_{12}). ^{11}B NMR (cyclohexane-d_{12}): δ −0.99 ppm (B_{12}), −8.09 (B_{7-11}), −8.49 (B_{2-6}). ESI/MS (acetonitrile): *n*-Bu_3Sn^+ (base peak at *m/e* 290), $CB_{11}Me_{12}^-$ (base peak at *m/e* 311), both with the expected isotopic distribution. IR (solid, reflection mode, gold surface): 578, 689, 769, 862, 959, 1069, 1142, 1249, 1291, 1377, 1463, 2846, 2866, 2925, 2963 cm^{-1}. UV (hexane): end absorption starting at ∼245 nm.
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Table 1. B3LYP/SDD Results for [Me_3Sn^+ $CB_{11}Me_{12}^-$] Ion Pairs and the [$CB_{11}Me_{12}^-$ Me_3Sn^+ $CB_{11}Me_{12}^-$] Ion Triple

		position[a]					
		none	12 (B)	7 (B)	2 (B)	1 (C)	9,2 (B,B)[b]
ΔE,[c] kcal/mol		–	0	2.8	9.0	22.4	–
d(Sn–C), Å		–	2.44	2.45	2.48	2.79	2.74, 2.98
d(C–B), Å		1.61	1.70	1.70	1.68	1.53 (C-C)	1.61, 1.63
∠SnCB, deg		–	176.4	178.2	173.4	144.0 (SnCC)	174.5 (SnCC)
$\sum\angle C_\alpha SnC_\alpha$, deg		–	346.9	348.1	349.5	347.4	359.5
∠BCH,[d] deg		109.5	97.3	98.0	99.0	109.0	106.9
$\delta(Me_3Sn^+)$,[e] e		–	+0.75	+0.76	+0.78	+0.86	–
vertex (CH_3) charge,[f] e	12	−0.09 (−0.31)	−0.07 (−0.29)	−0.09 (−0.29)	−0.07 (−0.29)	−0.06 (−0.29)	–
	7–11	−0.15 (−0.30)	−0.14 (−0.28)	−0.13 (−0.28)	−0.13 (−0.28)	−0.13 (−0.28)	–
	2–6	+0.11 (−0.31)	+0.14 (−0.29)	+0.13 (−0.29)	+0.13 (−0.30)	+0.11 (−0.31)	–
	1	−0.69 (+0.06)	−0.68 (+0.08)	−0.67 (+0.07)	−0.69 (+0.06)	−0.72 (+0.04)	–

[a] Position of the Me_3Sn^+ cation in the ion pair. [b] The ion triple. [c] Relative energy. [d] Average. [e] Ion charge from NBO analysis. [f] Average sum of charges on B, C, and H (C and H) atoms on a vertex.

length in R_3SnF (2.10 Å[15]), as anticipated for a near sp^2 hybridization. The distance between the C atom of the coordinating methyl and the adjacent cage atom is 1.61 Å, equal to the average B–C bond length in $C_6H_5NMe_2^+$ $CB_{11}Me_{12}^-$,[10] and the crystallographic diameter[13] of the icosahedral core of $CB_{11}Me_{12}^-$ has the standard[10] 3.27 Å value.

Only the average Sn–C and B–C distances can be determined, owing to the *P*6$_3$*/mmc* symmetry of the disordered crystal, and the coordinating pair of anion vertices (1,12 or 2,9) is not identified.[13,17] The relative coordinating ability of the four nonequivalent vertices in CB_{11}^- is under debate, and coordination through positions 12[18] and 7[3] (symmetry equivalent to 9) is known. Purely electrostatic considerations (ref 19 and Table 1) do not differentiate the vertices clearly. Electrophilic interactions with the vertices are generally believed to decrease in the reactivity order, 12 > 7–11 > 2–6 ≫ 1, and the B3LYP/SDD[13] ion-pairing energies for four optimized isomers of an isolated Me_3Sn^+ $CB_{11}Me_{12}^-$ ion pair with Me_3Sn^+ next to position 1, 2, 7, or 12 follow this order (Table 1). The most stable 12-isomer is calculated to have the shortest Sn–CH_3 and the longest B–CH_3 distance, the flattest B–CH_3 group, the most pyramidalized Me_3Sn^+ cation, and the most inter-ion charge transfer. In 2-, 7-, and 12-methyl coordination the Sn atom lies near a 5-fold icosahedron axis, and the stabilizing interaction is both electrostatic and donor–acceptor. Me_3Sn^+ interacts much less with the 1-methyl group, with the Sn atom tilted 36° off the axis toward the 2-methyl group.

Assuming additivity, 2,9 dicoordination is 10.6 kcal/mol better than 1,12 dicoordination, and geometrical and energetic considerations both suggest that the infinite columns in Figure 1 are formed by random 2,9 and 9,2 dicoordination. The B3LYP/SDD optimized structure of the nearly coaxial[13] [$CB_{11}Me_{12}^-$ Me_3Sn^+ $CB_{11}Me_{12}^-$] ion triple with coordination through positions 2 and 9 of the anion (Figure 1C) supports this conclusion. The two nonequivalent Sn–C distances are 2.74 Å (9-Me) and 2.98 Å (2-Me). The average, 2.86 Å, exceeds slightly the average 2.81 Å Sn–C distance in the crystal of **1**, as expected.[20] The calculated B–CH_3 distances are 1.63 Å (9-Me) and 1.61 Å (2-Me), vs 1.61 Å in the crystal of **1**. The pyramidalization of the cation is underestimated (Sn atom 0.08 Å out of the C_α plane; in crystal, 0.32 Å).

Metal cation–alkane complexation is of current interest,[21] and crystal structures with a cationic transition metal coordinated to a methyl group are known.[22] The *n*-Bu_3Sn^+ cation seems to coordinate to the methyl carbon and act as if it were initiating a backside S_E2 displacement[23] (Table 1); the reaction of *t*-Bu_6Si_2 with $CB_{11}Me_{12}^{\bullet}$, expected to yield *t*-Bu_3Si^+ $CB_{11}Me_{12}^-$, yields *t*-Bu_3SiMe, presumably because the now more exothermic S_E2 substitution proceeds to completion, in analogy to the inverse of methide anion abstraction by R_3B from Cp_2ZrMe_2[24] and [*t*-BuN-*o*–$C_6H_4)_2O$]$ZrMe_2$.[25]

Ion aggregation via methyl coordination apparently also occurs in cyclohexane solution of **1**. Its ^{119}Sn NMR chemical shift, 454.3 ppm[26] [2D (^{119}Sn, ^{1}H) HSQC],[13] lies far upfield from the 806 ppm reported[5] for the trimesitylstannylium in benzene and the 1700 ppm estimated[6] for a gaseous trialkylstannylium ion. The signal of **1** is broad (~800 Hz), suggesting exchange processes in ion aggregates. The ^{1}H NMR shift of the α protons in *n*-Bu_3Sn^+ of **1** in cyclohexane (1.83 ppm), downfield from that of its analogue in *n*-Bu_3Sn^+ B[3,5-$(F_3C)_2C_6H_3]_4^-$ in CD_2Cl_2 (1.65 ppm),[7] suggests a reduced perturbation of stannylium character in the former. The ^{11}B NMR of **1**[12] is essentially identical with that of free $CB_{11}Me_{12}^-$.[10]

The scope of the present approach to crystalline salts of R_3E^+ and similar cations is limited by their low solubility in inert solvents and by the coordinating ability and chemical reactivity of the $CB_{11}Me_{12}^-$ anion. We are presently examining other highly alkylated radicals of the CB_{11} family.

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Supporting Information Available: Details of characterization of **1**, tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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