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Synthesis and Reactivity of Intramolecularly Stabilized Organotin Compounds Containing the C,N-Chelating *o*-Carboranylamino Ligand [o-$C_2B_{10}H_{10}(CH_2NMe_2)$-$C,N$]$^-$ (Cab^{C,N}). X-ray Structures of (Cab^{C,N})SnR_2X (R = Me, X = Cl; R = Ph, X = Cl), (Cab^{C,N})$_2$Hg, and [(Cab^{C,N})SnMe_2]$_2$[†]

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A variety of organotin complexes, containing the *o*-carboranylamino ligand (Cab^{C,N}), has been prepared by the reaction of LiCab^{C,N} (**1**) with organotin halides or tin tetrachloride. In this way, the tetraorganotin compound (Cab^{C,N})SnMe_3 (**2**), triorganotin halide (Cab^{C,N})SnR_2X (**3**: R = Me, X = Cl, **3a**; R = Ph, X = Cl, **3b**; R = Me, X = Br, **3c**), diorganotin dichloride (Cab^{C,N})SnPhCl_2 (**4**), and monoorganotin trichloride (Cab^{C,N})SnCl_3 (**5**) have been synthesized and characterized. ^{1}H and ^{119}Sn NMR spectroscopy indicates that the tin center in the tetraorganotin compound **2** is tetracoordinate, whereas this center in mono-, di-, and triorganotin compounds **3**−**5** is pentacoordinate as a result of intramolecular Sn−N coordination. Complexes **3a**,**c** were also formed by redistribution of (Cab^{C,N})SnMe_3 (**2**) with the corresponding Me_2SnX_2 (X = Cl, Br). The molecular structures of **3a**,**b** were determined by X-ray analysis. As a result of the Sn−N interaction, the tin atoms in **3a**,**b** exhibit distorted-trigonal-bipyramidal configurations with the electronegative atoms (N and Cl) in apical positions. The reaction of 2 equiv of **2** with $HgCl_2$ resulted in transmetalation of (Cab^{C,N})SnMe_3 (**2**), giving the diorganomercury compound (Cab^{C,N})$_2$Hg (**6**). The structure of **6** was determined by an X-ray structural study. The mercury atom is four-coordinate, both nitrogen atoms being involved in intramolecular coordination. The reaction of **3c** with Na in a 1:1 ratio afforded the bis(*o*-carboranylamino)distannane [(Cab^{C,N})SnMe_2]$_2$ (**7**). The crystal structure of **7** was determined by an X-ray structural study. The two four-coordinate tin moieties exhibit approximately pseudotetrahedral geometries showing only negligible, if any, interactions between the tin atoms and the amino nitrogen atoms.

Introduction

It has been well-established that by using the properties of C,N-chelating ligands,[1] organometallic compounds that have interesting properties and special reactivity can be prepared. These properties are attributable to an extension of their coordination number by intramolecular coordination of a C,N-chelating ligand. There is a variety of organotin halides with C,N-chelating ligands which are bonded to the tin atom by a Sn−C covalent bond and a Sn−N dative bond.[2] It was, therefore, of interest to investigate the possibility of synthesizing such intramolecularly coordinated complexes using the potentially bidentate C,N-chelating *o*-carboranylamino ligand system LiCab^{C,N} (**1**).[3] In this respect, we have started investigating the synthesis of intramolecularly coordinated organotin compounds bearing a bulky *o*-carborane unit[4] that might potentially stabilize the pentacoordinate tin center.

In this study, organotin complexes of the type (Cab^{C,N})-SnR^1R^2X (**3**−**5**), in which the tin center may be regarded as pentacoordinate as a result of intramolecular Sn−N coordination, have been prepared and characterized. Such a Sn−N interaction in these compounds is favored

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[†] This contribution is dedicated to Professor Dietmar Seyferth on the occasion of his 70th birthday.

[‡] Korea University.

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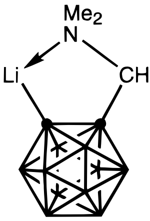
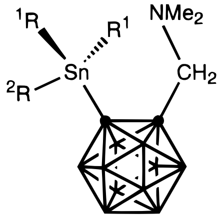
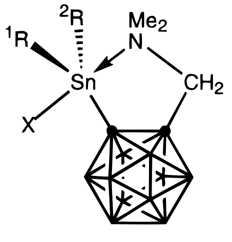


LiCab^{C,N} **1**



(Cab^{C,N})SnR$^1_2$R^2

R^1 = Me, R^2 = Me **2**;
R^1 = Me, R^2 = (Cab^{C,N})SnMe$_2$ **7**



(Cab^{C,N})SnR^{1}R^{2}X

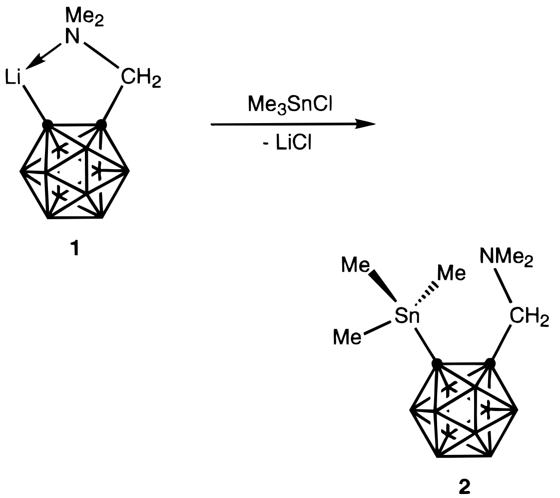
R^1 = R^2 = Me, X = Cl **3a**;
R^1 = R^2 = Ph, X = Cl **3b**;
R^1 = R^2 = Me, X = Br **3c**;
R^1 = Ph, R^2 = X = Cl **4**;
R^1 = R^2 = X = Cl **5**

by an electronegative substituent on tin, such as halogen, *trans* to the Lewis-basic group. In contrast, tetraorganotin compounds of the type (Cab^{C,N})SnR$^1_2$R^2 (**2** and **7**), bearing four Sn−C bonds, are reluctant to form pentacoordinate complexes. In fact, at best only weak interactions can be expected if electronegative substituents are absent.[1a] A similar pentacoordinate arrangement of the tin atom is in principle possible if the alkyl substituents are replaced by electronegative substituents. Thus, the redistribution reaction of **2** with Me$_2$SnX$_2$ (X = Cl, Br) gave the pentacoordinate triorganotin compound **3**, resulting in the formation of a stable Sn−N bond. In addition, the intramolecularly stabilized diorganomercury compound (Cab^{C,N})$_2$Hg (**6**) has been synthesized by the transmetalation reaction of **2** with HgCl$_2$.

To the best of our knowledge, this is the first example in which a C,N-chelating *o*-carboranylamino ligand is intramolecularly coordinated with a tin atom, thus improving the stability of the pentacoordinate tin center. We now report the detailed synthesis and complete characterization of a series of mono-, di-, tri-, and tetraorganotin compounds containing the potentially bidentate *o*-carboranylamino ligand.

Results and Discussion

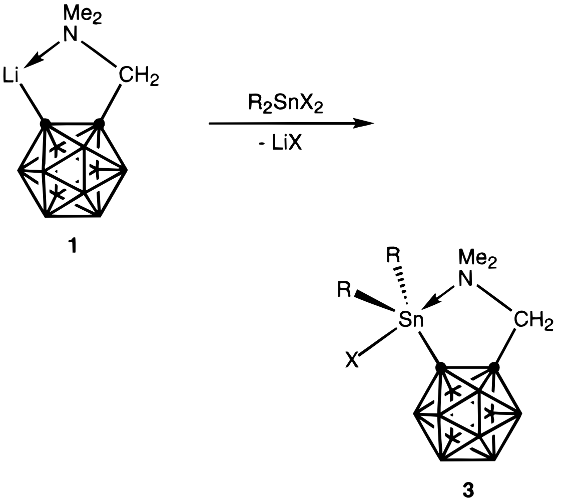
Synthesis of the Tetraorganotin Complex (Cab^{C,N})SnMe$_3$ (2). (Cab^{C,N})SnMe$_3$ (**2**) was prepared as a colorless solid by the reaction of LiCab^{C,N} (**1**) with a stoichiometric amount of Me$_3$SnCl according to eq 1. The complex decomposes slowly in the presence of air, both in the solid state and in solution; in both cases neutral *o*-carboranylamine is set free. It is moderately soluble in pentane, benzene, and toluene.



(1)

The composition of **2** was confirmed by elemental analysis and high-resolution mass spectral analysis. The ^{119}Sn, ^{13}C, ^{11}B, and relevant ^{1}H NMR spectroscopic data for **2** are given in Table 1. The signals for both N(CH$_3$)$_2$ and NCH$_2$ in the ^{1}H NMR spectrum are at a higher field than for the free ligand. The ^{1}H NMR data suggest that compound **2** is tetracoordinated in solution. This is demonstrated most clearly by both the downfield shift of the ^{119}Sn NMR resonance at 35.38 ppm and the decrease in the $^2J(^{119}\mathrm{SnC}^1\mathrm{H}_3)$ coupling constant to 56.0 Hz compared with those of Me$_3$PhSn ($\delta(^{119}\mathrm{Sn})$ −28.6 ppm; $^2J(^{119}\mathrm{SnC}^1\mathrm{H}_3) = 54.5$ Hz)[5a] and Me$_2$PhSnCl ($\delta(^{119}\mathrm{Sn})$ 48.3 ppm; $^2J(^{119}\mathrm{SnC}^1\mathrm{H}_3) = 58.5$ Hz).[6] Such a correlation between $\delta(^{119}\mathrm{Sn})$ and $^2J(^{119}\mathrm{SnC}^1\mathrm{H}_3)$ and the tin coordination number is well-documented.[5] Thus, the main feature of the structure of **2** in solution is the tetrahedral ligand arrangement around the tin atom.

Synthesis of the Triorganotin Halides (Cab^{C,N})SnR$_2$X (3). One procedure for the synthesis of **3** used the reaction of **1** with the respective dialkyltin dihalide (eq 2). Compounds **3** were purified by low-temperature



(2)

R = Me, X = Cl **3a**;
R = Ph, X = Cl **3b**;
R = Me, X = Br **3c**

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Table 1. NMR Spectroscopic Data for Compounds 2−7

compd	NMR (δ)[a] ^{1}H	^{13}C	^{11}B	^{119}Sn
HCab^N	2.33 (s, 6H, $N-CH_3$) 3.00 (s, 2H, $N-CH_2$) 3.99 (s, 1H, $H-C_{cab}$)	46.73 (s, 2C, $N-CH_3$) 58.77 (s, 1C, $CHCB_{10}H_{10}$) 63.23 (s, 1C, $N-CH_2$) 75.75 (s, 1C, $CHCB_{10}H_{10}$)	−13.43 (d, 4B, J_{BH} = 120 Hz) −11.87 (d, 2B, J_{BH} = 110 Hz) −9.27 (d, 2B, J_{BH} = 160 Hz) −5.48 (d, 1B, J_{BH} = 150 Hz) −3.33 (d, 1B, J_{BH} = 140 Hz)	
2	0.39 (s, 6H, $Sn-CH_3$) (56.0 Hz)[b] 2.26 (s, 6H, $N-CH_3$) 2.90 (s, 2H, $N-CH_2$)	1.20 (s, $Sn-CH_3$) 61.73 (s, $N-CH_3$) 62.77 (s, NCH_2)	−13.04 (d, 6B, J_{BH} = 145 Hz) −9.40 (d, 2B, J_{BH} = 155 Hz) −3.96 (d, 1B, J_{BH} = 155 Hz) −2.52 (d, 1B, J_{BH} = 150 Hz)	35.38
3a	1.00 (s, 6H, $Sn-CH_3$) (69.6 Hz)[b] 2.39 (s, 6H, $N-CH_3$) 3.19 (s, 2H, $N-CH_2$)	3.26 (s, $Sn-CH_3$) 51.20 (s, $N-CH_3$) 65.58 (s, $N-CH_2$)	−13.69 (d, 1B, J_{BH} = 150 Hz) −11.19 (d, 2B, J_{BH} = 180 Hz) −10.67 (d, 4B, J_{BH} = 155 Hz) −7.19 (d, 2B, J_{BH} = 140 Hz) −4.13 (d, 1B, J_{BH} = 130 Hz)	−121.44
3b	2.01 (s, 6H, $N-CH_3$) 3.09 (s, 2H, $N-CH_2$) 7.49 (m, 6H, $N-C_6H_5$) 7.75 (m, 4H, $N-C_6H_5$)	51.29 (s, $N-CH_3$) 65.88 (s, $N-CH_2$) 129.69 ($Sn-C_6H_5$) (89.3 Hz)[c] 130.76 ($Sn-C_6H_5$) (16.60 Hz)[c] 136.03 ($Sn-C_6H_5$) (45.5 Hz)[c] 73.55 (C_2B_{10} unit)	−13.14 (d, 1B, J_{BH} = 135 Hz) −11.63 (d, 2B, J_{BH} = 170 Hz) −9.44 (d, 3B, J_{BH} = 140 Hz) −7.22 (d, 1B, J_{BH} = 155 Hz) −3.59 (d, 2B, J_{BH} = 165 Hz) −0.68 (d, 1B, J_{BH} = 155 Hz)	−118.63
3c	1.11 (s, 6H, $Sn-CH_3$) (68.8 Hz)[b] 2.39 (s, 6H, $N-CH_3$) 3.18 (s, 2H, $N-CH_2$)	4.85 (s, $Sn\text{-}CH_3$) 51.09 (s, $N-CH_3$) 65.88 (s, $N-CH_2$)	−10.47 (d, 5B, J_{BH} = 150 Hz) −7.32 (d, 2B, J_{BH} = 135 Hz) −3.98 (d, 2B, J_{BH} = 150 Hz) −1.93 (d, 1B, J_{BH} = 160 Hz)	−109.82
4	2.38 (s, 6H, $N-CH_3$) 3.21 (s, 2H, $N-CH_2$) 7.53 (m, 3H, $N-C_6H_5$) 7.61 (m, 2H, $N-C_6H_5$)	53.63 (s, $N-CH_3$) 66.67 ($N-CH_2$) 126.83 ($Sn-C_6H_5$) 131.32 ($Sn-C_6H_5$) 137.86 ($Sn-C_6H_5$)	−8.32 (d, 4B, J_{BH} = 140 Hz) −7.24 (d, 4B, J_{BH} = 145 Hz) −4.88 (d, 1B, J_{BH} = 160 Hz) −1.69 (d, 1B, J_{BH} = 150 Hz)	−130.49
5	2.74 (s, 6H, $N-CH_3$) 3.36 (s, 2H, $N-CH_2$)	51.29 (s, $N-CH_3$) 63.26 ($N-CH_2$) 77.06 (C_2B_{10} unit)	−7.48 (d, 4B, J_{BH} = 160 Hz) −6.68 (d, 4B, J_{BH} = 135 Hz) −5.01 (d, 1B, J_{BH} = 145 Hz) −1.84 (d, 1B, J_{BH} = 140 Hz)	−149.15
6	2.42 (s, 6H, $N-CH_3$) 3.14 (s, 2H, $N-CH_2$)	49.40 (s, $N-CH_3$) 63.06 ($N-CH_2$)	−14.84 (d, 2B, J_{BH} = 160 Hz) −10.72 (d, 5B, J_{BH} = 145 Hz) −8.21 (d, 2B, J_{BH} = 160 Hz) −4.64 (d, 1B, J_{BH} = 180 Hz)	
7	0.69 (s, 6H, $Sn-CH_3$) (50.23 Hz)[b] (13.6 Hz)[d] 2.28 (s, 6H, $N-CH_3$) 2.89 (s, 2H, $N-CH_2$)	−2.88 (s, $Sn-CH_3$) 47.08 (s, $N-CH_3$) 65.67 (s, $N-CH_2$)	−13.19 (d, 2B, J_{BH} = 145 Hz) −11.66 (d, 1B, J_{BH} = 140 Hz) −9.15 (d, 3B, J_{BH} = 145 Hz) −5.41 (d, 1B, J_{BH} = 140 Hz) −3.21 (d, 2B, J_{BH} = 160 Hz) 0.13 (d, 1B, J_{BH} = 160 Hz)	8.11 (2610 Hz)[e]

[a] All NMR spectra were recorded in $CDCl_3$ at room temperature. [b] $^2J(^{119}Sn-^1H)$. [cn] $J(^{119}Sn-^{13}C)$, $n = 2, 3$. [d] $^3J(^{119}Sn-^1H)$. [e] $^1J(^{119}Sn-^{117}Sn)$.

recrystallization from toluene as colorless crystals. Satisfactory elemental analyses were obtained for **3**, and the ^{1}H, ^{11}B, and ^{13}C NMR spectral data are consistent with the presence of the bidentate *o*-carboranylamino ligand (see Experimental Section).

Compounds **3** are moderately stable in air and decompose only slowly when in contact with moisture. The kinetic stabilization of compounds **3** is due to the formation of a five-membered chelate ring, thus blocking the Sn atom from external nucleophilic attack. The ^{1}H NMR signals for both $N(CH_3)_2$ and NCH_2 in **3a**,**c** are at lower field than for the free ligand. This can be explained on the basis of a trigonal-bipyramidal geometry with amino and halide ligands in the axial positions and evidence of Sn−N coordination in solution. This observation is consistent with similar findings for the general intramolecularly coordinated triorganotin halides of the $Ar^{C,N}$ ligand system ($Ar^{C,N} = C_6H_4(CH_2NMe_2)\text{-}C,N)^-$.[2n,o,7] The data for **3b** also reveal that the replacement of Me (**3a**,**c**) by Ph (**3b**) groups on the central tin atom has little effect on the $\delta(N(CH_3)_2)$ and $\delta(NCH_2)$ values in both the ^{1}H and ^{13}C NMR spectra. Information about the ligand geometry in solution at tin in **3** was obtained from the ^{119}Sn chemical shifts and $^2J(^{119}SnC^1H_3)$ values for **3a**,**c**. These depend on the coordination number of the tin[5] and are compared with those of pentacoordinate methyl-substituted triorganotin halides. The observed $\delta(^{119}Sn)$ and $^2J(^{119}SnC^1H_3)$ values suggest a pentacoordinate geometry at tin for **3a**,**c**. In fact, there is a close agreement of the NMR spectroscopic data between **3a** and $(Ar^{C,N})SnMe_2Cl$,[8] particularly the $^2J(^{119}SnC^1H_3)$ coupling constants (69.6 Hz in $(Cab^{C,N})SnMe_2Cl$ (**3a**) and 63.9 Hz in $(Ar^{C,N})SnMe_2Cl$). The spectroscopic data indicate that complexes **3** have a related structure. On the basis of ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopic studies, a trigonal-bipyramidal structure for **3** in solution is proposed. This is as expected, since in the triorganotin halides containing a C,N-chelating ligand, normally the tin atom has a trigonal-bipyramidal coordination geometry, as a result of intramolecular coordination.[1] It is anticipated that the *o*-carboranyl carbon atom and two alkyl ligands are at the equatorial sites, while the more electronegative

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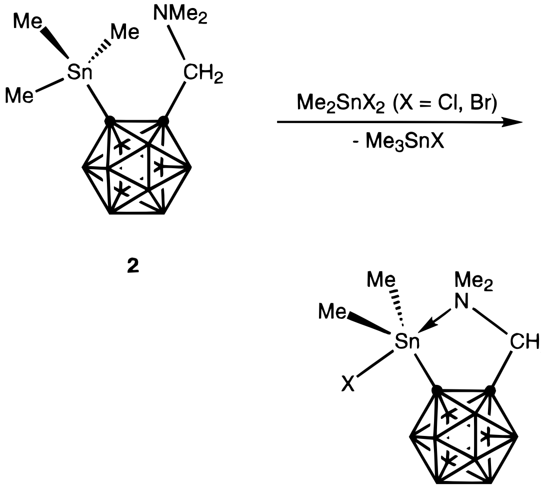
nitrogen atom of *o*-carboranylamine and the halide atom reside at axial positions.

A second route to **3** involved the redistribution reaction[9] of the tetraorganotin compound $(\mathrm{Cab}^{C,N})\mathrm{SnMe}_3$ (**2**) with 1 equiv of the corresponding dimethyltin dihalide $\mathrm{Me_2SnX_2}$ (X = Cl, Br) (eq 3).



2

(3)

3a,**c**

The NMR spectra of these products were identical with those of **3a**,**c** prepared by the method of eq 2. Although this reaction requires overnight reflux in benzene, its simple reaction path and facile product isolation make this route attractive.

Molecular Geometry and Crystal Structure of 3a,b. The molecular structure of **3a** as determined by X-ray crystallography is shown in Figure 1. The crystallographic data are collected in Table 2, and the interatomic distances and angles are listed in Table 3. In compound **3a**, a donor−acceptor interaction stronger than that in **7** between the nitrogen atom of the amino group and the tin center is found. This interaction leads to a trigonal-bipyramidal coordination of the Sn atom and places the three organic substituents in the equatorial plane. The Sn atom resides 0.133(6) Å below the equatorial plane (C(1), C(6), C(7)), and the N(1)−Sn(1)−Cl(1) configuration deviates from linearity (168.9(1)°). Such a distortion originates mainly from the formation of five-membered C,N-chelate bonding of the bulky *o*-carboranylamino group with a bite angle (N(1)−Sn(1)−C(1)) of 75.5(2)°. The value of 2.648(6) Å for the Sn(1)−N(1) distance is in the range observed for other pentacoordinated triorganotin halides with Sn−N coordination.[2c,g,n,p] As a consequence of the Sn−N interaction, the Sn(1)−Cl(1) distance (2.458(2) Å) is longer than that found in tetracoordinate $\mathrm{Me_3SnCl}$ (2.430 Å).[10] The lengthening is of the same order of magnitude as observed for other hypervalent triorganotin chlorides.[11]

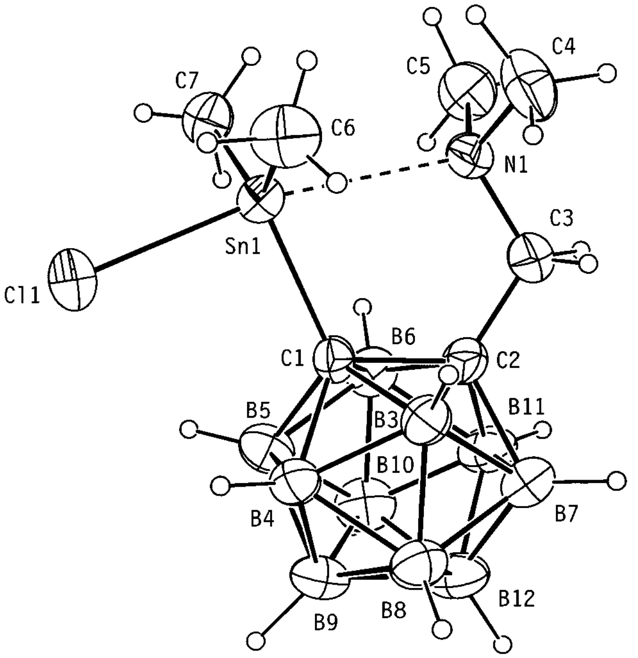


Figure 1. Molecular structure of $(\mathrm{Cab}^{C,N})\mathrm{SnMe_2Cl}$ (**3a**). The thermal ellipsoids are drawn at the 30% probability level.

Complex **3b** crystallizes with two pairs of independent molecules (molecules 1 and 2) in an orthorhombic unit cell. The main feature of the structure is the intramolecular coordination between tin and nitrogen with a distorted-trigonal-bipyramidal arrangement as shown in Figure 2, with selected bond lengths and bond angles listed in Table 3. Thus, a similar C,N-chelate structure is seen in **3b**, where the amine N again coordinates to an axial position opposite to the chlorine atom with the three Sn−C bonds in equatorial positions. The two molecules are identical and show slight differences in bond distances and angles compared to each other. The bite angle of C(1)−Sn(1)−N(1)/C(1′)−Sn(1′)−N(1′) is only 74.5(3)/75.4(3)°, the N(1)−Sn(1)−Cl(1)/N(1′)−Sn(1′)−Cl(1′) configuration is bent to 167.3(2)/167.5(2)°, and the Sn atom is displaced 0.248(6)/0.212(5) Å from the (C(1), C(6), C(12))/(C(1′), C(6′), C(12′)) plane toward the Cl ligand. The values of 2.701(8) Å in molecule 1 and 2.666(8) Å in molecule 2 for the Sn−N distance are in the range observed for other pentacoordinate triorganotin halides with Sn−N coordination.[2c,g,n,p] As a consequence of the weak Sn−N interaction, the expected shortening of the Sn−Cl bonds to 2.408(3) Å in molecule 1 and 2.421(3) Å in molecule 2 is observed.

The structures of **3a**,**b** agree with conclusions[12] from the solution NMR data on the general placement of atoms in a trigonal-bipyramidal framework. However, considerable distortions from an idealized trigonal bipyramid are evident in the solid state. According to the X-ray structure analysis of **3a**,**b**, it is most likely that the structure as found in the solid state is retained in solution. The sum of the Sn−N and Sn−Cl bonds appears to be remarkably constant, revealing an inverse correlation between the Sn−N and Sn−Cl distances.

Synthesis of Mono- and Diorganotin Compounds $(\mathrm{Cab}^{C,N})\mathrm{SnRCl_2}$ (R = Ph, 4; R = Cl, 5). $(\mathrm{Cab}^{C,N})\mathrm{SnRCl_2}$

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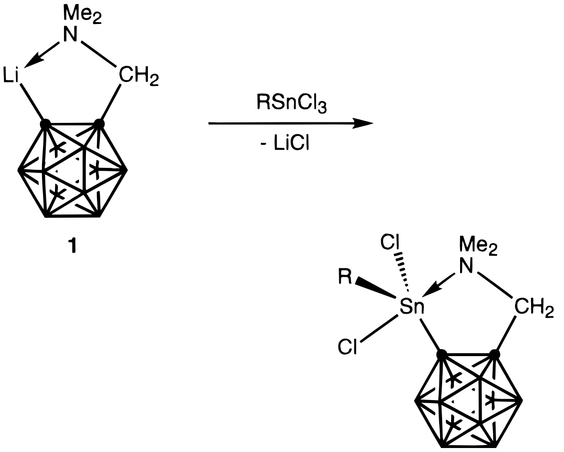
Table 2. X-ray Crystallographic Data and Processing Parameters for Compounds 3a,b, 6, and 7

	3a	**3b**	**6**	**7**
formula	$B_{10}C_7H_{24}ClNSn$	$B_{10}C_{17}H_{28}ClNSn$	$B_{20}C_{10}H_{36}N_2Hg$	$B_{20}C_{14}H_{48}N_2Sn_2$
fw	384.51	508.64	601.22	698.12
cryst class	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$Pna2_1$ (No. 33)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
Z	4	8	4	4
cell constants				
a, Å	12.8470(3)	20.4020(4)	10.2530(7)	16.8285(1)
b, Å	10.2730(4)	8.3610(1)	9.5172(8)	9.8086(1)
c, Å	13.4510(4)	27.3250(6)	13.374(1)	20.1975(4)
V, Å^3	1739.34(9)	4661.1(1)	1267.8(2)	3329.85(8)
β, deg	101.540(2)	103.715(7)	92.8180(1)	
μ, cm^{-1}	1.603	1.216	12.120	1.511
cryst size, mm	0.20 × 0.25 × 0.30	0.10 × 0.10 × 0.15	0.20 × 0.30 × 0.30	0.20 × 0.30 × 0.20
D_{calcd}, g/cm^3	1.468	1.450	1.575	1.393
F(000)	760	2032	850	1384
radiation	Mo Kα ($\lambda = 0.7170$ Å)			
θ range, deg	2.51−24.80	2.00−24.74	2.04−24.97	1.54−23.25
h, k, l collected	+15, ±11, ±15	+24, ±9, ±32	±12, +11, +15	±17, ±7, +21
no. of rflns measd	2936	4063	2405	14 454
no. of unique rflns	2936	4063	2225	4752
no. of rflns used in refinement ($I > 2\sigma(I)$)	2936	4063	2225	4752
no. of params	277	765	163	367
data/param ratio	10.60	5.31	13.65	12.95
R1[a]	0.0556	0.0420	0.0507	0.0468
wR2[b]	0.1228	0.1119	0.1338	0.1122
GOF	1.134	0.954	1.170	0.792

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ (based on reflections with $F_o^2 > 2\sigma(F_o^2)$). [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.095P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$ (also with $F_o^2 > 2\sigma(F_o^2)$).

(R = Ph, **4**; R = Cl, **5**) were prepared as colorless solids by the reaction of **1** with a stoichiometric amount of $RSnCl_3$ (R = Ph, Cl) according to eq 4. Complexes **4** and **5** are stable in air and show slow decomposition when in contact with moisture.



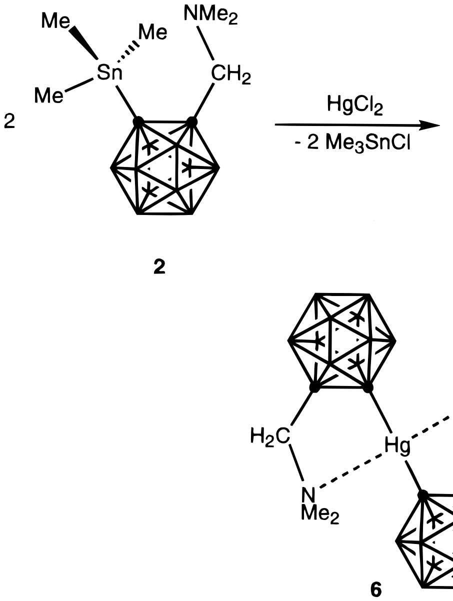
1

(4)

R = Ph **4**;
R = Cl **5**

The compositions of **4** and **5** were confirmed by elemental analysis and high-resolution mass spectral analysis. Because mono- and diorganotin halides are stronger Lewis acids than a triorganotin halide,[13] the intramolecular Sn−N coordination which was observed earlier in the corresponding triorganotin halide **3** should also occur in compounds **4** and **5**. To assess the strength of such intramolecular Sn−N interactions in **4** and **5**, solution NMR data for these compounds were compared with those of the triorganotin halides **3a**−**c**. Large downfield shifts of the signals for both $N(CH_3)_2$ and NCH_2 are observed in the ^1H NMR spectra of **4** and **5**, in accord with the presence of strong Sn−N bonds. Additional evidence for pentacoordinate tin centers in these compounds is the observed absolute ^{119}Sn NMR chemical shift values. The diorganotin halide **4** exhibits a considerable high-field shift ($\delta(^{119}Sn)$ −130.49 ppm) with respect to the tetracoordinate Me_2SnCl_2 ($\delta(^{119}Sn)$ 140 ppm).[14] This confirms the existence of the transannular donor−acceptor interaction in this molecule in solution. The same holds for monoorganotin halide **5** ($\delta(^{119}Sn)$ −149.15 ppm) when compared with $MeSnCl_3$ ($\delta(^{119}Sn)$ 21 ppm).[14] Taken together, these data favor the existence of an intramolecular Sn−N interaction in **4** and **5**, which leads to a trigonal-bipyramidal coordination of the Sn atom.

Transmetalation of the Tetraorganotin Complex (Cab^{C,N})SnMe$_3$ (2) with HgCl$_2$. The reaction of 2 equiv of **2** with $HgCl_2$ afforded $(Cab^{C,N})_2Hg$ **6** in 46% yield (eq 5).



2

6

(5)

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Table 3. Selected Interatomic Distances and Angles in 3a,b, 6, and 7

Bond Distances (Å)					
Compound **3a**					
Sn(1)−N(1)	2.648(6)	Sn(1)−Cl(1)	2.458(2)	Sn(1)−C(1)	2.194(6)
Sn(1)−C(6)	2.120(9)	Sn(1)−C(7)	2.121(9)	N(1)−C(3)	1.47(1)
N(1)−C(4)	1.49(1)	N(1)−C(5)	1.47(1)	C(2)−C(3)	1.52(1)
C(1)−C(2)	1.641(9)				
Compound **3b**					
Molecule 1					
Sn(1)−N(1)	2.701(8)	Sn(1)−Cl(1)	2.408(3)	Sn(1)−C(1)	2.20(1)
Sn(1)−C(6)	2.11(1)	Sn(1)−C(12)	2.15(1)	N(1)−C(3)	1.46(2)
N(1)−C(4)	1.49(2)	N(1)−C(5)	1.48(2)	C(2)−C(3)	1.55(2)
C(1)−C(2)	1.64(1)				
Molecule 2					
Sn(1′)−N(1′)	2.666(8)	Sn(1′)−Cl(1′)	2.421(3)	Sn(1′)−C(1′)	2.18(1)
Sn(1′)−C(6′)	2.14(1)	Sn(1′)−C(12′)	2.14(1)	N(1′)−C(3′)	1.48(2)
N(1′)−C(4′)	1.51(2)	N(1′)−C(5′)	1.45(2)	C(2′)−C(3′)	1.51(2)
C(1′)−C(2′)	1.64(1)				
Compound **6**					
Hg(1)−C(1)	2.092(8)	Hg(1)−N(1)	2.86(6)	N(1)−C(3)	1.46(1)
C(2)−C(3)	1.55(1)	C(1)−C(2)	1.66(1)		
Compound **7**					
Sn(1)−Sn(1′)	2.8058(8)	Sn(1)−C(6)	2.132(8)	Sn(1)−C(7)	2.147(8)
Sn(1)−C(1)	2.216(8)	Sn(1′)−C(6′)	2.136(8)	Sn(1′)−C(7′)	2.149(8)
Sn(1′)−C(1′)	2.221(8)	N(1)−C(3)	1.44(1)	N(1)−C(4)	1.48(1)
N(1)−C(5)	1.48(1)	C(2)−C(3)	1.51(1)	C(1)−C(2)	1.69(1)
N(1′)−C(3′)	1.45(1)	N(1′)−C(4′)	1.47(1)	N(1′)−C(5′)	1.48(1)
C(2′)−C(3′)	1.55(1)	C(1′)−C(2′)	1.66(1)		
Bond Angles (deg)					
Compound **3a**					
C(6)−Sn(1)−C(7)	131.2(4)	C(6)−Sn(1)−C(1)	115.9(4)	C(7)−Sn(1)−C(1)	111.7(3)
C(6)−Sn(1)−Cl(1)	93.1(3)	C(7)−Sn(1)−Cl(1)	94.0(3)	C(1)−Sn(1)−Cl(1)	93.6(2)
C(5)−N(1)−C(3)	110.1(7)	C(5)−N(1)−C(4)	106.5(8)	C(3)−N(1)−C(4)	109.8(7)
N(1)−Sn(1)−Cl(1)	168.9(1)				
Compound **3b**					
Molecule 1					
C(6)−Sn(1)−C(12)	122.6(4)	C(6)−Sn(1)−C(1)	120.0(4)	C(12)−Sn(1)−C(1)	113.5(4)
C(6)−Sn(1)−Cl(1)	98.4(3)	C(12)−Sn(1)−Cl(1)	97.4(3)	C(1)−Sn(1)−Cl(1)	93.9(3)
C(3)−N(1)−C(5)	109(1)	C(3)−N(1)−C(4)	110(1)	C(5)−N(1)−C(4)	107(1)
N(1)−Sn(1)−Cl(1)	167.3(2)				
Molecule 2					
C(12′)−Sn(1′)−C(6′)	121.9(4)	C(12′)−Sn(1′)−C(1′)	114.0(4)	C(6′)−Sn(1′)−C(1′)	121.2(4)
C(12′)−Sn(1′)−Cl(1′)	95.7(3)	C(6′)−Sn(1′)−Cl(1′)	97.6(3)	C(1′)−Sn(1′)−Cl(1′)	93.4(3)
C(5′)−N(1′)−C(3′)	110(1)	C(5′)−N(1′)−C(4′)	107(1)	C(3′)−N(1′)−C(4′)	108(1)
N(1′)−Sn(1′)−Cl(1′)	167.5(2)				
Compound **6**					
C(1)−Hg(1)−C(1)*	180.000(2)	N(1)−Hg(1)−C(1)	75.0(9)	Hg(1)−N(1)−C(3)	104.2(9)
N(1)−C(3)−C(2)	113.9(8)	C(3)−C(2)−C(1)	121.8(7)	C(2)−C(1)−Hg(1)	118.9(5)
Compound **7**					
C(6)−Sn(1)−C(7)	112.9(4)	C(6)−Sn(1)−C(1)	106.0(3)	C(7)−Sn(1)−C(1)	108.6(3)
C(6)−Sn(1)−Sn(1′)	118.8(3)	C(7)−Sn(1)−Sn(1′)	106.0(3)	C(1)−Sn(1)−Sn(1′)	103.9(2)
C(6′)−Sn(1′)−C(7′)	113.3(4)	C(6′)−Sn(1′)−C(1′)	109.8(3)	C(7′)−Sn(1′)−C(1′)	106.5(3)
C(6′)−Sn(1′)−Sn(1)	118.1(2)	C(7′)−Sn(1′)−Sn(1)	105.2(3)	C(1′)−Sn(1′)−Sn(1)	103.0(2)
C(3)−N(1)−C(4)	111.6(8)	C(3)−N(1)−C(5)	113.1(8)	C(4)−N(1)−C(5)	108.5(8)
C(3′)−N(1′)−C(4′)	110.9(7)	C(3′)−N(1′)−C(5′)	110.6(7)	C(4′)−N(1′)−C(5′)	108.5(7)

The composition of **6** was established by elemental analysis. Furthermore, the spectroscopic data (^{1}H, ^{11}B, and ^{13}C NMR) for $(\mathrm{Cab}^{C,N})_2\mathrm{Hg}$ (**6**) also are consistent with its assigned structure. The ^{1}H NMR spectrum consists of a singlet due to the $\mathrm{NMe_2}$ at 2.42 ppm and a singlet due to the $\mathrm{NCH_2}$ protons at 3.14 ppm. Furthermore, the appearance of the $\mathrm{NMe_2}$ proton signals at lower field relative to the chemical shift of these protons in the free ligand HCab^{N} also provides evidence for Hg−N coordination. This observation is consistent with similar findings for the general intramolecularly coordinated metal complexes of the *o*-carboranylamino ligand system.[3]

Molecular Geometry and Crystal Structure of 6. Figure 3 and Table 3 show the ORTEP drawing and selected bond distances and bond angles for the structure of **6**, as determined by X-ray crystallography. The coordination geometry around Hg is best described as square planar, the preferred geometry in almost in all cases where such intramolecularly stabilized four-coordination has been observed.[15] The geometry about the Hg atom is planar, and this atom also lies close to coplanarity with both coordinating *o*-carboranylamino units. The C−Hg−C axis is constrained exactly to linearity by crystallographic symmetry with an Hg−C distance of 2.092(8) Å, in close agreement with values reported previously for $(\mathrm{Ar}^{C,N})_2\mathrm{Hg}$ (2.10(2) Å)[15b] and other diarylmercury compounds.[16] The Hg(1)−N(1) distance (2.86(6) Å) is only slightly shorter than that in $(\mathrm{Ar}^{C,N})_2\mathrm{Hg}$ (2.89(1) Å),[15b] and it is still in the range of bonding interaction.[17]

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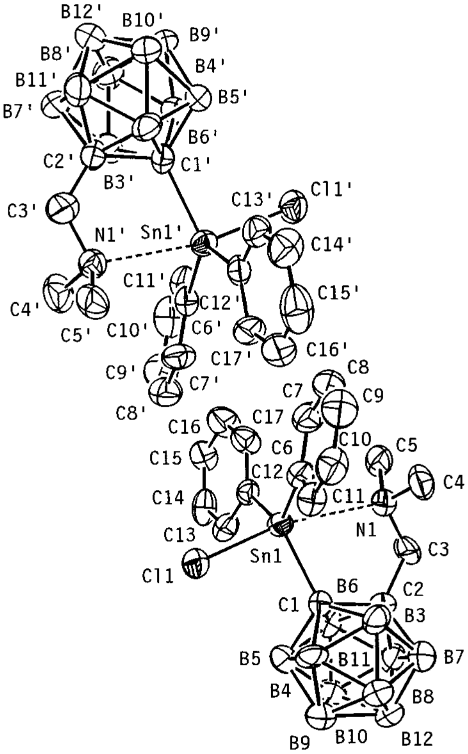


Figure 2. ORTEP plots of the molecule (Cab^{C,N})SnPh$_2$Cl (**3b**), showing the two independent molecules in the asymmetric unit. The atoms are drawn with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

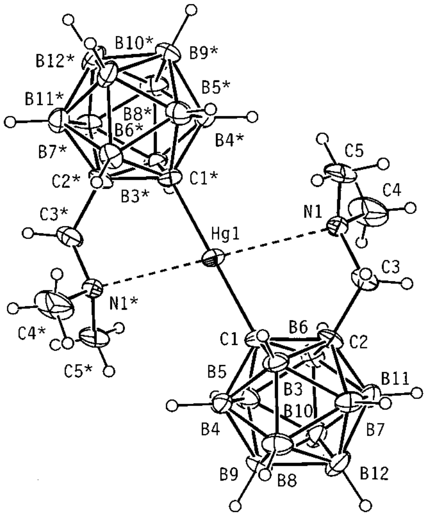
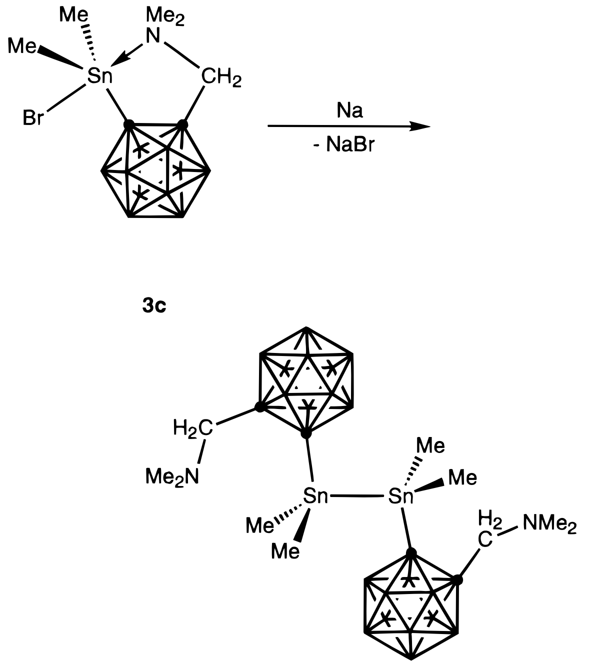


Figure 3. Molecular structure of (Cab^{C,N})$_2$Hg (**6**). The thermal ellipsoids are drawn at the 30% probability level.

Synthesis of the Bis(*o*-carboranylamino)distannane [(Cab^{C,N})SnMe$_2$]$_2$ (7). The Wurtz-type coupling reaction of **3c** using sodium metal afforded the corresponding distannane containing pseudo-tetracoordinate tin centers (eq 6). The reaction of **3c** with 10 equiv of



3c

7

(6)

sodium in toluene at mild reflux for 12 h gave the distannane [(Cab^{C,N})SnMe$_2$]$_2$ (**7**) in 18% isolated yield.

The composition of **7** was established by elemental analysis. The spectroscopic data (^{1}H, ^{11}B, and ^{13}C NMR) for **7** also are consistent with its assigned structure. In the ^{1}H and ^{13}C NMR spectra, the respective NCH$_2$ and NMe$_2$ resonances show only small upfield shifts. The solution ^{1}H NMR spectrum of the tetraorganotin compound **7** points to a structure in which there is tetrahedral geometry about Sn (see complex **2**) instead of the trigonal-bipyramidal geometry present in **3**−**5**. Furthermore, one signal was observed for the two methyl groups of the two magnetically equivalent dimethylamino groups in **7**, indicating that the rotation around the tin−tin bond is not hindered due to any interaction between Sn and N atoms. In addition, the Sn(CH$_3$)$_2$ protons in the ^{1}H NMR spectrum have a $^2J(^{119}\mathrm{Sn}-\mathrm{C}^1\mathrm{H}_3)$ value of about 50.2 Hz, which is the value expected for tetracoordinate organotin compounds. In the ^{119}Sn NMR spectrum, the value of 2610 Hz of the $^1J(^{119}\mathrm{Sn}-^{117}\mathrm{Sn})$ coupling constant also is characteristic of tetracoordinate tin atoms, because couplings in distannanes lie in the range 60−4500 Hz when the tin atoms are four-coordinate.[5a,18] On the basis of ^{1}H, ^{13}C, and ^{119}Sn solution NMR spectroscopic studies, a tetrahedral conformation at the tin atom for the bis(*o*-carboranylamino)distannane **7** may be assumed.

Molecular Geometry and Crystal Structure of 7. The structure of complex **7** was determined by X-ray diffraction. The crystallographic data are collected in Table 2, and selected bond distances and angles are summarized in Table 3. The ORTEP view of **7** is shown in Figure 4. The structure of **7** agrees with the conclusion based on the NMR data for the general placement

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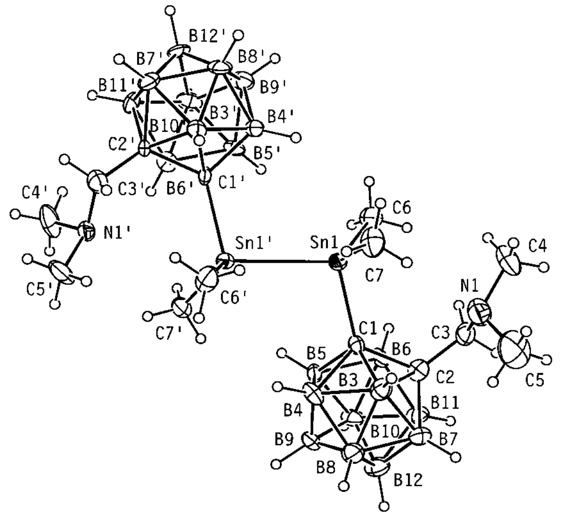

Figure 4. Molecular structure of [(Cab^{C,N})SnMe$_2$]$_2$ (**7**). The thermal ellipsoids are drawn at the 30% probability level.

of atoms in a tetrahedral framework. However, considerable distortions from an idealized tetrahedron are evident in the solid state. It must be noted that the Sn−N distances in **7** are extremely long (average 3.640(8) Å). These values, although longer than the sum of the covalent radii for nitrogen and tin (2.10 Å),[19] are shorter than the sum of the van der Waals radii (3.75 Å).[20] The tetrahedral angles range from 103 to 119°, but if the C(6)−Sn(1)−Sn(1′) and C(6′)−Sn(1′)−Sn(1) angles are excluded, the range is somewhat smaller: i.e., 103−113°. Because of steric hindrance by the two bulky *o*-carboranyl groups, the two four-coordinate moieties of the molecule are twisted by about 120° along the Sn−Sn vector: the dihedral angle between the planes Sn(1)−Sn(1)′−C(1)′ and Sn(1′)−Sn(1)−C(1) is 19.6(2)°. The Sn−C distances do not exhibit noteworthy differences with respect to those of other four-coordinate organotin compounds. It must be noted that the Sn−Sn bond length in **7** is extremely long (2.806(1) Å) for a Sn−Sn coordination bond,[21] while this value is almost the same as that found in [ClSn(CH$_2$CH$_2$CH$_2$)$_2$NMe]$_2$ (2.83 Å).[22] However, this Sn−Sn distance is in the range of lengths found in compounds containing tin atoms with bulky substituents.[23] It is reasonable to assume that in **7** the central Sn−Sn bond is elongated due to the steric repulsion between the two *o*-carboranylamino ligands.

Experimental Section

General Procedures. All manipulations were performed under a dry, oxygen-free nitrogen or argon atmosphere using standard Schlenk techniques or in a Vacuum Atmosphere HE−493 drybox. THF was freshly distilled from potassium benzophenone. Diethyl ether and toluene were dried over and distilled from sodium benzophenone. Hexane and pentane were dried and distilled from CaH$_2$. ^{1}H, ^{11}B, ^{13}C, and ^{119}Sn NMR spectra were recorded on a Varian Gemini 2000 spectrometer operating at 200.1, 64.2, 50.3, and 74.6 MHz, respectively. Chemical shifts are reported (δ, ppm) from internal tetramethylsilane for ^{1}H and ^{13}C, from boron trifluoride diethyl etherate for ^{11}B, or from tetramethyltin for ^{119}Sn spectroscopy. IR spectra were recorded on a Biorad FTS-165 spectrophotometer. High- and low-resolution mass spectra were obtained on a VG Micromass 7070H mass spectrometer. Elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA1108 analyzer. All melting points are uncorrected. Decaborane and (dimethylamino)-2-propyne were purchased from the Callery Chemical Co. and Aldrich, respectively, and used without purification. HCab^N (*o*-C$_2$B$_{10}$H$_{11}$(CH$_2$NMe$_2$)-*N*) was prepared by the literature methods.[24]

Synthesis of (Cab^{C,N})SnMe$_3$ (2). To a stirred solution of HCab^N (0.604 g, 3.0 mmol) in 30 mL of hexane, which was cooled to −20 °C, was added 1.6 M *n*-BuLi (2 mL, 3.2 mmol) via syringe. The resulting white suspension was stirred at −20 °C for 2 h and then transferred through a cannula to a suspension of Me$_3$SnCl (0.598 g, 3.0 mmol) in 30 mL of THF at −78 °C. The reaction temperature was maintained at −78 °C for 1 h, following which the reaction mixture was warmed slowly to room temperature. After being stirred for an additional 12 h, the reaction mixture was filtered. The solvent was removed under vacuum, and the resulting residue was taken up in a minimum of toluene and then recrystallized from this solution by cooling it to −20 °C. (Cab^{C,N})SnMe$_3$ (**2**) was isolated in 47% yield (0.513 g, 1.4 mmol). HRMS for ^{11}B$_{10}$^{12}C$_8$^{1}H$_{27}$^{14}N^{119}Sn (*m*/*e*): calcd, 367.2096; found, 367.2100. Anal. Calcd: C, 26.39; H, 7.47; N, 3.85. Found: C, 26.40; H, 7.55; N, 3.80. Mp: 187−188 °C. IR (KBr pellet, cm^{-1}): ν(CH) 3068, 2984; ν(BH) 2588.

General Synthesis of the Triorganotin Halides (Cab^{C,N})SnR$_2$X (3). A solution of R$_2$SnX$_2$ in diethyl ether (20 mL) was slowly added to a 50 mL diethyl ether solution of LiCab^{C,N} (**1**; 3.0 mmol, previously prepared by the reaction of HCab^N and LiBu^n) at −78 °C. LiCl precipitated upon warming the mixture to room temperature. The reaction mixture was stirred for 12 h at room temperature, after which all volatile components were distilled in vacuo at room temperature. The crude product was dissolved in toluene (40 mL) and the solution separated by filtration. The volume was then reduced to 20 mL, and crystallization at −20 °C gave pure **3**.

Preparative and Analytical Data for the Triorganotin Halides (Cab^{C,N})SnR$_2$X 3 (R = Me, X = Cl, 3a; R = Ph, X = Cl, 3b; R = Me, X = Br, 3c). (Cab^{C,N})SnMe$_2$Cl (3a) was prepared from 3.0 mmol (0.659 g) of Me$_2$SnCl$_2$. After recrystallization from toluene, **3a** (0.323 g, 0.84 mmol, 28% yield) was isolated as a white solid. Anal. Calcd: C, 21.87; H, 6.29; N, 3.64. Found: C, 21.92; H, 6.34; N, 3.70. Mp: 197−198 °C. IR spectrum (KBr pellet, cm^{-1}): ν(CH) 2925, 2886; ν(BH) 2588.

(Cab^{C,N})SnPh$_2$Cl (3b) was prepared from 3.0 mmol (1.03 g) of Ph$_2$SnCl$_2$. After recrystallization from toluene, **3b** (0.473 g, 0.93 mmol, 31% yield) was isolated as a white solid. Anal. Calcd: C, 40.14; H, 5.55; N, 2.75. Found: C, 40.18; H, 5.63; N, 2.70. Mp: 211−212 °C. IR spectrum (KBr pellet, cm^{-1}): ν(CH) 3071, 3051; ν(BH) 2607, 2584.

(Cab^{C,N})SnMe$_2$Br (3c) was prepared from 3.0 mmol (0.926 g) of Me$_2$SnBr$_2$. After recrystallization from toluene, **3c** (0.682 g, 1.59 mmol, 53% yield) was isolated as a white solid. Anal. Calcd: C, 19.60; H, 5.64; N, 3.27. Found: C, 19.64; H, 5.69; N, 3.19. Mp: 184−185 °C. IR spectrum (KBr pellet, cm^{-1}): ν(CH) 2979, 2924; ν(BH) 2597, 2570, 2551.

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Reaction of (Cab^{C,N})SnMe$_3$ (2) with Me$_2$SnCl$_2$. To a solution of 0.364 g (1.0 mmol) of **2** in benzene (15 mL) was added 0.220 g (1.0 mmol) of Me$_2$SnCl$_2$. The solution was heated at 80−90 °C until the reaction was complete (ca. 12 h). The progress of the reaction could easily be followed by NMR spectroscopy. The mixture was then evaporated, and the residue was extracted with toluene, filtered, and crystallized from toluene to afford 0.138 g (0.36 mmol, 36%) of **3a**.

Reaction of (Cab^{C,N})SnMe$_3$ (2) with Me$_2$SnBr$_2$. With Me$_2$SnBr$_2$ (0.309 g, 1.0 mmol) as the starting material, the synthesis of **3c** was analogous to the preparation of **3a**. **3c** was obtained in 42% yield (0.180 g, 0.42 mmol).

Synthesis of (Cab^{C,N})SnPhCl$_2$ (4). A solution of PhSnCl$_3$ (0.50 mL, 3.2 mmol) in diethyl ether (20 mL) was slowly added to a 50 mL diethyl ether solution of **1** (3.0 mmol) at −78 °C. The reaction temperature was maintained at −78 °C for 1 h, following which the reaction mixture was warmed slowly to room temperature. After it had been stirred for an additional 12 h, the reaction mixture was filtered. The solvent was removed under vacuum, and the resulting residue was taken up in a minimum of toluene and recrystallized from this solution by cooling to −20 °C. (Cab^{C,N})SnPhCl$_2$ (**4**) was isolated in 35% yield (0.490 g, 1.05 mmol). HRMS for $^{11}B_{10}{}^{12}C_{11}{}^{35}Cl_2{}^{1}H_{23}{}^{14}N^{119}Sn$ (*m*/*e*): calcd, 496.1160; found, 496.1165. Anal. Calcd.: C, 28.29; H, 4.96; N, 3.00. Found: C, 28.20; H, 4.89; N, 2.89. Mp: 215−216 °C. IR spectrum (KBr pellet, cm^{-1}): ν(CH) 3035, 2962; ν(BH) 2598.

Synthesis of (Cab^{C,N})SnCl$_3$ (5). A solution of SnCl$_4$ (0.35 mL, 3.0 mmol) in diethyl ether (20 mL) was slowly added to a 50 mL diethyl ether solution of **1** (3.0 mmol) at −78 °C. The reaction temperature was maintained at −78 °C for 1 h, following which the reaction mixture was warmed slowly to room temperature. After it had been stirred for an additional 12 h, the reaction mixture was filtered. The solvent was removed under vacuum, and the resulting residue was taken up in a minimum of toluene and recrystallized by cooling to −20 °C. (Cab^{C,N})SnCl$_3$ (**5**) was isolated in 86% yield (1.097 g, 2.58 mmol). HRMS for $^{11}B_{10}{}^{12}C_5{}^{35}Cl_3{}^{1}H_{18}{}^{14}N^{119}Sn$ (*m*/*e*): calcd, 427.0457; found, 427.0451. Anal. Calcd: C, 14.12; H, 4.27; N, 3.29. Found: C, 14.20; H, 4.35; N, 3.20. Mp: 196−198 °C. IR spectrum (KBr pellet, cm^{-1}): ν(CH) 3037, 2961; ν(BH) 2582.

Reaction of (Cab^{C,N})SnMe$_3$ (2) with HgCl$_2$. To a solution of 0.728 g (2.0 mmol) of **2** in toluene (15 mL) was added 0.326 g (1.2 mmol) of HgCl$_2$. The solution was stirred at room temperature until the reaction was complete (ca. 24 h). The progress of the reaction could easily be followed by NMR spectroscopy. The mixture was then evaporated, and the residue was extracted with toluene, filtered, and crystallized from toluene to afford 0.277 g (0.46 mmol, 46%) of (Cab^{C,N})$_2$-Hg (**6**). Anal. Calcd: C, 19.98; H, 6.04; N, 4.66. Found: C, 20.06; H, 6.08; N, 4.59. Mp: 158 °C. IR spectrum (KBr pellet, cm^{-1}): ν(CH) 2993, 2891; ν(BH) 2583, 2557, 2529.

Synthesis of the Bis(*o*-carboranylamino)distannane [(Cab^{C,N})SnMe$_2$]$_2$ (7). A solution of 0.429 g (1.0 mmol) of **3c** in 15 mL of toluene was added to Na (0.230 g, 10.0 mmol), stirred in 15 mL of toluene. The heterogeneous mixture was gently refluxed and monitored periodically by ^{1}H NMR spectroscopy. After ca. 90% conversion (ca. 12 h), the gray solution was evaporated to dryness. Hexane (10 mL) was added and again stripped off under vacuum to remove traces of **3c**, leaving a yellow to brown solid. The residue was washed with toluene (15 mL). Recrystallization from a toluene/hexane mixture gave white microcrystals of [(Cab^{C,N})SnMe$_2$]$_2$ (**7**), which was isolated by filtration, washed with cold pentane (3 × 5 mL), and dried under vacuum (0.126 g, 0.18 mmol, 18% yield). Anal. Calcd: C, 24.09; H, 6.93; N, 4.01. Found: C, 24.11; H, 7.00; N, 3.97. Mp: 164−165 °C. IR spectrum (KBr pellet, cm^{-1}): ν(CH) 2831; ν(BH) 2574.

X-ray Crystallography. Details of the crystal data and a summary of intensity data collection parameters for **3a**,**b**, **6**, and **7** are given in Table 2. Crystals of **3a**,**b**, **6**, and **7** were grown from toluene solutions stored at −20 °C and were mounted in thin-walled glass capillaries that were sealed under argon. The data sets for **3a**,**b** were collected on a Rigaku diffractometer with an area detector at a temperature of 195 K, and an Enraf CAD4 automated diffractometer was used for the collection of data for compounds **6**. A standard Siemens SMART CCD area detector was used for the collection of data for compound **7** at 223 K. Mo Kα radiation (λ = 0.7107 Å) was used for all structures. Each structure was solved by the application of direct methods using the SHELXS-96 program[25a] and least-squares refinement using SHELXL-97.[25b] All non-hydrogen atoms in compounds **3a**,**b**, **6**, and **7** were refined anisotropically. All other hydrogen atoms were located from the difference Fourier and were refined.

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Supporting Information Available: Tables describing the X-ray analysis (data collection and analysis), crystal data, atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and least-squares planes for **3a**,**b**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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