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Note

Chiral organotin complexes stabilized by *C,N*-chelating oxazolinyl-*o*-carboranes

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ABSTRACT

A series of chiral organotin halides containing 2-(4-*R*)-oxazolinyl-*o*-carboranes (R = *i*-propyl **1**, *t*-butyl **2**; Cab^{Oxa}) was prepared from *o*-carborane with a chiral oxazoline auxiliary. X-ray structural analysis of the representative chiral organotin halide, [2-(4-*i*-propyl)-oxazolinyl-*o*-carboranyl]$SnMe_2Br$ (**4**), revealed the formation of a stable penta-coordinated tin center due to a N → Sn interaction. Similar O → Sn assisted intramolecular penta-coordinated tin complexes (**9** and **10**) were prepared from methoxy-*o*-carborane ligands, MeOCH(Z)-*o*-carborane (Z = H **7**, Ph **8**; Cab^{OMe}), respectively, and a rigid *o*-carboranyl backbone provided the basic skeleton for the facile formation of organotin complexes.

1. Introduction

Chiral organotin complexes have been developed as efficient reagents for a wide variety of organic transformations in stereospecific reactions [1–3]. The most important work involves the chiral induction of organotin complexes, one of the notable accomplishments being free-radical enantioselective reductions [4–6]. In such cases, a penta-coordinated tin center was completed with intramolecularly coordinated nitrogen atoms [7–12]. It has been reported that chiral oxazoline rings induce stereospecific reactions [13–16] due to the closer proximity of the stereogenic motif to the metal center. Such a superior chiral auxiliary can be more efficient when a suitable ligand backbone is provided. In this study, a rigid and sterically demanding *o*-carborane backbone was used to assist the proceeding stereospecific reactions [17].

Chiral oxazolinyl-*o*-carborane (Cab^{Oxa}) ligands have a nitrogen donor atom adjacent to the stereogenic carbon center at the oxazoline ring. When these ligands coordinate to the metal center, the stereogenic carbon atom will induce chiral recognition most effectively. This paper reports the synthesis and characterization of chiral organotin complexes (**3**–**6**) with bidentate chiral oxazoline ligands containing *o*-carbaborane as the rigid backbone. In addition, comparative studies using *C,O*-chelating ligands, Cab^{OMe}, have assisted in determining the relationship between the tin complexes (**9** and **10**) with respect to the structures and electronic effects of each ligand series.

2. Results and discussion

The ligand systems, chiral [2-(4-R)-oxazolinyl]-*o*-carborane (R = *i*-propyl **1**, *t*-butyl **2**), consisted of two dissimilar coordination modes of carbon in carborane. The imine functionalities of the oxazoline unit were produced using a standard procedure [17] by reacting lithio-*o*-carborane with 2-bromo-(4-R)-oxazoline in a THF solution. Treatment of compounds **1** and **2** with a 1.1 equiv of *n*-BuLi and 1 equiv of Me_2SnX_2 (X = Cl, Br) in diethyl ether at −10 °C for 10 min gave the chiral oxazoline substituted *o*-carboranylorganotin halides with the general formula [2-(4-R)-oxazolinyl-*o*-carboranyl]$SnMe_2X$ (R = *i*-propyl, X = Cl **3**, Br **4**; R = *t*-butyl, X = Cl **5**, Br **6**) in good yield (**3**: 77%, **4**: 84%, **5**: 75%, **6**: 81%, Scheme 1).

All new compounds were characterized by Fourier transform infrared (IR), ^1H, ^{11}B, ^{13}C and ^{119}Sn nuclear magnetic resonance (NMR) spectroscopy, elemental analysis, high-resolution mass spectroscopy, and single-crystal X-ray crystallography. Compounds **3**–**6** were moderately stable in air and decomposed only slowly when in contact with moisture. The kinetic stability of compounds **3**–**6** is due to the formation of a five-membered chelate ring, which protects the Sn atom from external nucleophilic attack. The ^1H NMR signals for both NC*H* and OCH_2 of the oxazoline ring in compounds **3**–**6** were observed downfield from those found in the free ligands. This can be explained by the trigonal-bipyramidal geometry with the nitrogen atom of the oxazoline unit and the halogen atom in the axial positions as well as by evidence of Sn–N coordination in solution. Information on the ligand geometry in solution at tin in compounds **3**–**6** was obtained from the ^{119}Sn chemical shifts and $^2J(^{119}Sn-C^1H_3)$ values. These depend on the coordination number

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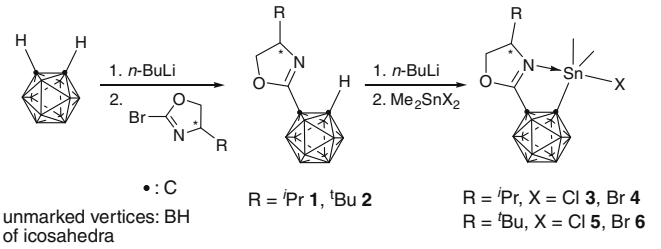
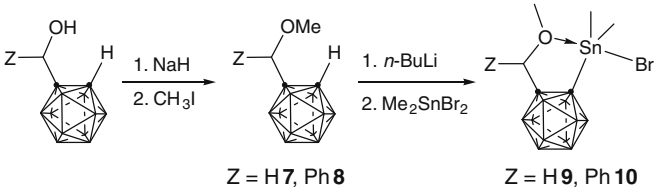


Scheme 1. Synthesis of [2-(4-R)-oxazolinyl-*o*-carboranyl]$SnMe_2X$ (R = ^{i}Pr, X = Cl **3**, Br **4**; ^{t}Bu, X = Cl **5**, Br **6**).

of tin [18–20] and were compared with those of the penta-coordinated methyl-substituted organotin halides. The observed $\delta(^{119}Sn)$ and $^{2}J(^{119}Sn{-}C^{1}H_3)$ values suggested penta-coordinate geometry at tin for compounds **3**–**6**. Indeed, there was close agreement of the NMR spectroscopic data between compounds **3**–**6** and (Ar^{Oxa})-Me_2SnBr [21], particularly the $^{2}J(^{119}Sn{-}C^{1}H_3)$ coupling constants (77.2 Hz in $(Cab^{Oxa})Me_2SnBr$ (**4**) and 75 Hz in $(Ar^{Oxa})Me_2SnBr$). The spectroscopic data suggests that complexes **3**–**6** have a related structure. A trigonal-bipyramidal structure for compounds **3**–**6** in solution was proposed based on the ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopy. This was expected because the tin atom in organotin halides containing a *C*,*N*-chelating ligand normally has trigonal-bipyramidal coordination geometry due to intramolecular coordination. It is believed that the *o*-carboranyl carbon atom and two alkyl ligands are at the equatorial sites, while the more electronegative nitrogen atom of oxazolinyl-*o*-carborane and halide atom reside at the axial positions.

New types of *C*,*O*-chelated organotin bromides with Sn–O intramolecular interactions were attempted as a variation of the generation of organotin compounds stabilized by *o*-carboranyl ligands. Accordingly, the synthesis and single-crystal X-ray crystallographic studies of organotin bromides containing new types of methoxy-*o*-carborane ligands, MeOCH(Z)-*o*-carborane (Z = H **7**, Ph **8**), were carried out. *C*,*O*-chelating ligands, **7** and **8**, were prepared by reacting *o*-carboranyl- or *o*-carboranyl(phenyl)methanol [22] with CH_3I in the presence of 3 equiv of NaH in THF at 0 °C (Scheme 2). After ligand deprotonation of compounds **7** and **8** by *n*-BuLi at −10 °C in diethyl ether for 10 min, methathesis reactions with Me_2SnBr_2 were carried out to produce the desired intramolecularly stabilized *C*,*O*-chelated organotin complexes, **9** and **10**, in good yield (**9**: 84%; **10**: 83%, Scheme 2).

The *C*,*O*-chelating organotin complexes were stabilized by the formation of a five-membered chelate ring. Compounds **9** and **10** were purified by low-temperature recrystallization in toluene. Satisfactory elemental analyses were obtained for compounds **9** and **10**, and the ^{1}H, ^{13}C, and ^{119}Sn NMR spectral data was consistent with the presence of methoxymethyl-*o*-carboranyl ligands. Downfield shifts of the signals for both OCH_3 and OCH_2 were observed in the ^{1}H NMR spectra in compounds **9** and **10**, which is in accord with the presence of Sn–O bonds. ^{1}H NMR suggested that compounds **9** and **10** are penta-coordinated in solution. Additional evidence for penta-coordinate tin centers in these compounds was



Scheme 2. Synthesis of $[CH_3OCH(Z)$-*o*-carboranyl$]SnMe_2Br$ (Z = H **9**, Ph **10**).

provided by the observed absolute ^{119}Sn NMR chemical shifts values. As reported in the literature [23], $\delta(^{119}Sn)$ values in the range −210 to −400, −90 to −190, and 200 to −60 ppm are associated with six-, five-, and four-coordinate tin centers, respectively. Compounds **9** and **10** exhibited chemical shifts of ($\delta(^{119}Sn)$ −108.2 (**9**) and −110.3 (**10**) ppm) with respect to $Ph_2BrSn(CH_2$-16-crown-5) [24] ($\delta(^{119}Sn)$ −96 ppm). Overall, these results favor the existence of an intramolecular Sn–O interaction in compounds **9** and **10**, which leads to the trigonal-bipyramidal coordination of the Sn atom. The spectroscopic data indicates that complexes **9** and **10** have a related structure. It is believed that the *o*-carboranyl carbon atom and two alkyl ligands are at the equatorial sites, while the more electronegative oxygen atom of methoxymethyl-*o*-carborane and the bromide atom reside at the axial positions.

2.1. Structural study

The structures of compounds **4**, **7**, **8**, and **9** were determined by X-ray structural analysis. Selected interatomic distances and angles are presented in the appropriate figure caption (Figs. 1–4). Detailed information on the structural determinations and structural features of all four compounds are provided in the Supporting Information. Figs. 1 and 4 show the penta-coordinated organotin bromide structures tethered by chiral oxazolinyl- (**4**) and methoxymethyl- (**9**) *o*-carborane, respectively. Figs. 2 and 3 show the conformations of the ligands, consisting of methoxymethyl- (**7**) and methoxy(phenyl)methyl-*o*-carborane (**8**), respectively. In compounds **4** and **9**, each central tin atom has a distorted trigonal-bipyramid structure with the electronegative atoms (N, Br (**4**) or O, Br (**9**)) in the axial positions and all carbon atoms in equatorial positions, which is in accordance with previously published

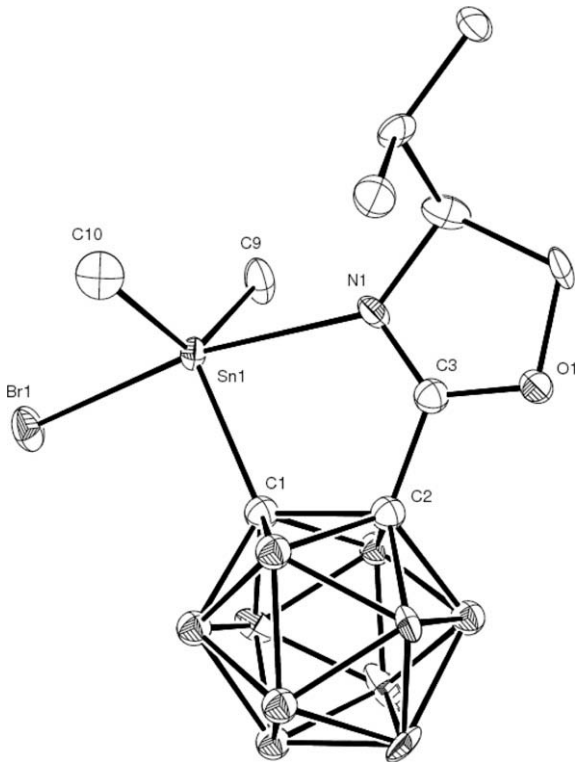


Fig. 1. ORTEP presentation at the 30% probability level of the molecular structure of compound **4**. The hydrogen atoms are omitted for clarity. Selected interaction distances (Å) and angles (°): Sn(1)–N(1) = 2.500(1), Sn(1)–Br(1) = 2.614(2), Sn(1)–C(1) = 2.197(2), C(2)–C(3) = 1.492(2), C(3)–N(1) = 1.241(2); Br(1)–Sn(1)–N(1) = 169.6(3), Br(1)–Sn(1)–C(1) = 95.3(4), C(1)–Sn(1)–N(1) = 74.7(5), Sn(1)–N(1)–C(3) = 114.5(1).

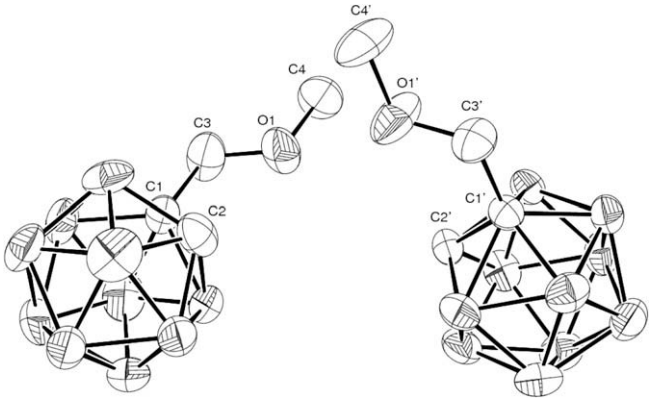


Fig. 2. ORTEP presentation at the 30% probability level of the molecular structure of compound **7**. The hydrogen atoms are omitted for clarity. Selected interaction distances (Å) and angles (°): O(1)–C(3) = 1.327(4), O(1)–C(4) = 1.425(4), O(1′)–C(3′) = 1.336(4), O(1′)–C(4′) = 1.420(3); C(3)–O(1)–C(4) = 113.7(3), O(1)–C(3)–C(1) = 111.6(3), C(3')–O(1′)–C(4′) = 112.2(3), O(1')–C(3′)–C(1′) = 110.9(3).

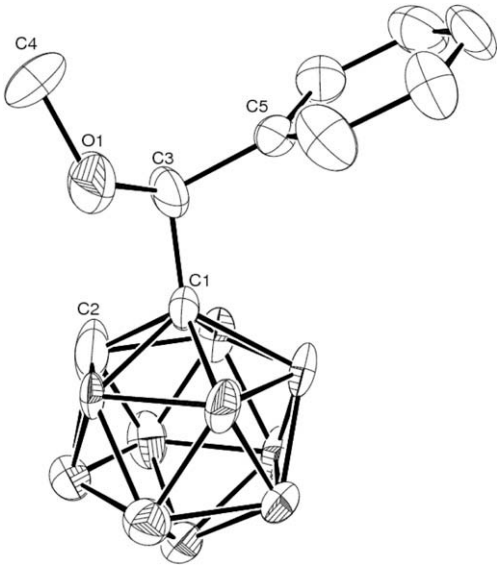


Fig. 3. ORTEP presentation at the 30% probability level of the molecular structure of compound **8**. The hydrogen atoms are omitted for clarity. Selected interaction distances (Å) and angles (°): O(1)–C(3) = 1.297(1), O(1)–C(4) = 1.413(1); C(3)–O(1)–C(4) = 116.8(9), O(1)–C(3)–C(1) = 109.4(7), C(1)–C(3)–C(5) = 112.4(7), O(1)–C(3)–C(5) = 117.3(9).

results [25]. As expected, compound **4** is chiral, crystallizing in the orthorhombic $P2_12_12_1$ space group with the Flack parameter [26] refining to 0.00, which confirms the presence of an enantiomerically pure compound. Unfortunately, the nine non-hydrogen atoms of compound **4**, C(1), C(2), C(3), B(3), B(4), B(6), B(7), B(9), and B(10), were refined isotropically because of their non-positive temperature factors that might occur due to systematic errors in the observed amplitudes originating in possible merohedral twinning. A strong Sn–N interaction was found in compound **4** with a distance of 2.500(1) Å, which lies in the normal range of $N_{sp^2} \rightarrow Sn$ dative bonding. A shorter Sn–N distance is expected because the coordinating nitrogen atom is sp^2-hybridized. Indeed, the Sn–N distance in compound **4** is approximately 0.15 Å shorter than the $Sn–N_{sp^3}$ distances (2.648(6) Å) [25]. Recently, a similar strong $N_{sp^2} \rightarrow Sn$ interaction was reported in tin complexes by Zhang and co-workers [27] and Wade and co-workers [28]. As a consequence of the Sn–N interaction, the Sn(1)–Br(1) distance (2.614(2) Å) is longer than that observed in other hypervalent triorganotin bromides (2.599(4) Å) [29]. The structure shows that the nitrogen atom of the oxazoline ring coordinates preferentially to tin, even though Sn–O coordination would lead to a sterically less crowded molecule. Furthermore, considerable distortions from an idealized trigonal-bipyramid are evident in the solid state due to the sp^2 C(3) and N(1) of the oxazoline ring. Therefore, the angle associated with axial ligand N(1)–Sn(1)–Br(1) deviates from linearity (169.6(3)°) due to its proximity to the sterically incumbent oxazolinyl unit.

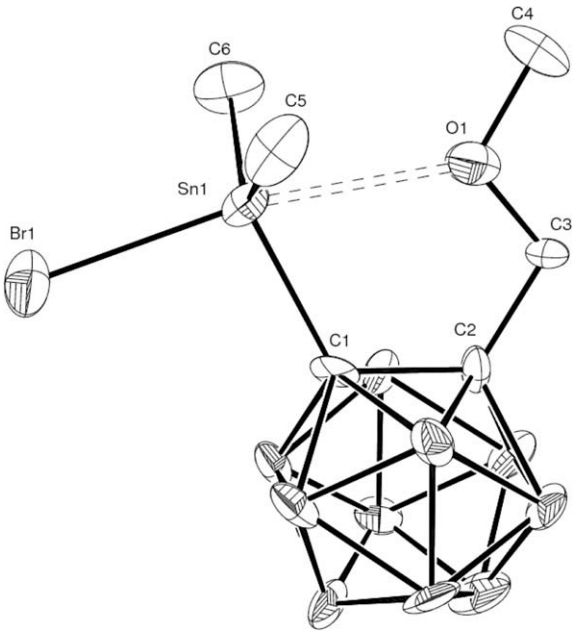


Fig. 4. ORTEP presentation at the 30% probability level of the molecular structure of compound **9**. The hydrogen atoms are omitted for clarity. Selected interaction distances (Å) and angles (°): Sn(1)–O(1) = 2.579(4), Sn(1)–Br(1) = 2.537(3), Sn(1)–C(1) = 2.193(2); Br(1)–Sn(1)–O(1) = 169.8(3), Br(1)–Sn(1)–C(1) = 98.4(5), C(1)–Sn(1)–O(1) = 71.4(6), Sn(1)–O(1)–C(3) = 121.1(1).

X-ray structural determinations of compound **9** authenticated the expected trigonal-bipyramid geometries illustrated in Fig. 4. The overall geometry was similar to that observed in compound **4**. Therefore, the Sn atom has a distorted trigonal-bipyramid geometry with the O(1) and Br(1) atoms in the axial positions and *o*-carboranyl carbon atom and two alkyl ligands in the equatorial plane. The angular distortions of the trigonal-bipyramid arise from the geometric constraints associated with the bite angle of the bidentate ligands [O(1)–Sn(1)–C(1)) angle of 71.4(6)°] in the presence of the O(1)–Sn(1)–Br(1) bond angle (169.8(3)°). Sn(1)–O(1) and Sn(1)–Br(1) bond distances of 2.579(1) and 2.537(3) Å are similar to the corresponding normal values for Sn–O (2.564(2) Å) dative and Sn–Br (2.6088(4) Å) single bonds [24].

3. Conclusion

In conclusion, chiral organotin compounds were synthesized from chiral oxazolinyl auxillary containing *o*-carborane as a rigid backbone and their structure was determined. NMR and single-crystal X-ray crystallographic studies of compound **4** showed that the chiral oxazolinyl-*o*-carborane ligands at the tin metal center significantly affect both the stability of the starting compounds and the electronic properties of the metal center due to the strength of the Sn–N bond.

4. Experimental

4.1. General procedures

All manipulations were carried out under a dry, oxygen-free nitrogen or argon atmosphere using standard Schlenk techniques or in a Vacuum Atmosphere HE-493 drybox. Solvents were dried by standard methods and distilled prior to use. The ^{1}H, ^{11}B, ^{13}C and ^{119}Sn NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.1, 96.3, 75.4 and 111.9 MHz, respectively. The chemical shifts are reported (δ, ppm) in reference to tetramethylsilane for ^{1}H and ^{13}C, boron trifluoride etherate for ^{11}B, or tetramethyltin for ^{119}Sn spectroscopy. The IR spectra were recorded on a Biorad FTS-165 spectrophotometer. *o*-Carborane was purchased from KatChem, and tetrabutylammonium fluoride, paraformaldehyde, benzaldehyde, *n*-BuLi, dimethyltin dichloride and dimethyltin dibromide were purchased from Aldrich chemicals. The compounds were used without purification. 2-(4-R)-oxazolinyl-*o*-carboranes (R = *i*-propyl, *t*-butyl)[4] and methoxymethyl- and methoxy(phenyl)methyl-*o*-carborane[7] were prepared using literature methods. Elemental analyses were performed using a Carlo Erba Instruments CHNS-O EA1108 analyzer. The high-resolution mass spectra were measured at the Korea Basic Science Institute. All melting points were uncorrected.

4.2. Preparation of 2-(4-i-propyl)-oxazolinyl-o-carborane (**1**)

n-BuLi (2.0 mL, 5.0 mmol, 2.5 M solution in hexane) was added dropwise to a solution of *o*-carborane (0.72 g, 5.0 mmol) in 50 mL of dry THF at −78 °C with constant stirring. The mixture was allowed to stir for 30 min at −78 °C at which time 2-bromo-4-*i*-propyl-oxazoline (1.06 g, 5.5 mmol) was added dropwise. The solution was stirred for 1 h and then warmed to ambient temperature. The reaction was quenched with water, extracted with ether, and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by silica gel column chromatography using hexane as the eluent (R_f 0.4) to afford compound **1** as a pale yellow oil in 74% yield (0.94 g, 3.7 mmol). Anal. Calc for $C_8H_{21}B_{10}NO$: C, 37.63; H, 8.29; N, 5.48. Found: C, 37.60; H, 8.32; N, 5.44%. IR (KBr pellet, cm^{-1}) ν(C–H) 3014, 2990, 2982, ν(B–H) 2604, ν(C=N) 1700. ^{1}H NMR ($CDCl_3$) δ 0.92 (d, 3H, CH(CH_3)$_2$, $^{3}J_{CH-CH_3}$ = 6.6 Hz), 0.99 (d, 3H, CH(CH_3)$_2$, $^{3}J_{CH-CH_3}$ = 6.9 Hz), 1.92 (m, 1H, C*H*(CH$_3$)$_2$), 3.85 (brs, 1H, Cab-*H*), 4.16 (m, 1H, C*H*N), 4.19 (dd, 1H, CH_2O, $^{2}J_{C-H}$ = 8.4 Hz), 4.45 (dd, 1H, CH_2O, $^{2}J_{C-H}$ = 8.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 14.2, 18.6 (CH(*C*H$_3$)$_2$); 30.5 (*C*H(CH$_3$)$_2$); 68.4 (*Cab*), 70.5, 71.2 (OCH$_2$*C*HN); 73.8 (*Cab*); 168.5 (*C*=N). ^{11}B NMR (96.3 MHz, $CDCl_3$) δ–14.05 (2H), –12.51 (3H), –8.93 (2H), –5.74 (3H).

4.3. Preparation of 2-(4-t-butyl-)oxazolinyl-o-carborane (**2**)

A procedure analogous to the preparation of compound **1** was used but instead starting from *o*-carborane (0.72 g, 5.0 mmol) with 2-brome-4-*t*-butyl-oxazoline (1.33 g, 5.5 mmol). Compound **2** was obtained as a pale yellow oil by silica gel column chromatography using hexane as the eluent (R_f 0.36) (0.93 g, 3.5 mmol, 69%). Anal. Calc. for $C_9H_{23}B_{10}NO$: C, 40.13; H, 8.61; N, 5.20. Found: C, 40.10; H, 8.29; N, 5.17%. IR (KBr pellet, cm^{-1}) ν(C–H) 3007, 2989, 2984, ν(B–H) 2599, ν(C=N) 1692. ^{1}H NMR ($CDCl_3$) δ 0.96 (s, 9H, C(CH_3)$_3$), 3.84 (brs, 1H, Cab-*H*), 4.18 (t, 1H, C*H*N), 4.21 (dd, 1H, CH_2O, $^{2}J_{C-H}$ = 8.1 Hz), 4.40 (dd, 1H, CH_2O, $^{2}J_{C-H}$ = 8.2 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 22.4 (C(*C*H$_3$)$_3$); 33.8 (*C*(CH$_3$)$_3$); 68.1 (*Cab*), 70.9, 72.1 (OCH$_2$*C*HN); 72.6 (*Cab*); 168.7 (*C*=N). ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –19.62 (4H), –16.33 (2H), –12.72 (2H), –4.68 (2H).

4.4. General synthesis of the chiral organotin halides [2-(4-i-propyl)-oxazolinyl-o-carboranyl]SnMe$_2$Cl (**3**)

A 2.5 M *n*-BuLi solution (1.3 mL, 3.3 mmol) was added to a stirred solution of compound **1** (0.77 g, 3.0 mmol) in diethyl ether (30 mL) at −10 °C through a syringe. The resulting solution was stirred at −10 °C for 30 min. A solution of Me_2SnCl_2 (0.66 g, 3.0 mmol) in diethyl ether (10 mL) was added slowly to the 30 mL diethyl ether solution of compound **1**·Li at –10 °C. The reaction temperature was maintained at –10 °C for 10 min. The reaction mixture was filtered and the organic solvent was evaporated. The crude product was dissolved in fresh distilled toluene. The volume of the toluene solution was reduced and the resulting concentrated solution allowed to stand at −10 °C for 2 days to allow crystallization. Compound **3** was obtained as colorless crystals in 77% yield (1.01 g, 2.3 mmol). Mp: 168–170 °C (dec). HRMS: Calcd for $[^{12}C_{10}{}^{1}H_{26}{}^{11}B_{10}{}^{35}Cl{}^{14}N{}^{16}O{}^{119}Sn]^+$ 441.1655. Found: 441.1631. Anal. Calc. for $C_{10}H_{26}B_{10}ClNOSn$: C, 27.38; H, 5.98; N, 3.19. Found: C, 27.40; H, 5.95; N, 3.21%. IR (KBr pellet, cm^{-1}) ν(C–H) 3205, 3085, 2980, ν(B–H) 2588, ν(C=N) 1690. ^{1}H NMR ($CDCl_3$) δ 0.33 (s, 6H, Sn–CH_3, $^{2}J_{^{119}Sn-CH_3}$ = 75.3 Hz), 0.94 (d, 3H, CH(CH_3)$_2$, $^{3}J_{CH-CH_3}$ = 6.6 Hz), 1.11 (d, 3H, CH(CH_3)$_2$, $^{3}J_{CH-CH_3}$ = 6.9 Hz), 1.94 (m, 1H, C*H*(CH$_3$)$_2$), 4.23 (m, 1H, C*H*N), 4.22 (m, 1H, CH_2O), 4.47 (m, 1H, CH_2O). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 4.21 (Sn–*C*H$_3$); 13.6, 16.0 (CH(*C*H$_3$)$_2$); 28.8 (*C*H(CH$_3$)$_2$); 68.6 (*Cab*); 68.9, 70.5 (OCH$_2$*C*HN); 70.3 (*Cab*); 166.3 (*C*=N). ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –14.27 (2H), –11.59 (1H), –10.37 (1H), –9.16 (1H), –5.86 (3H), –3.37 (1H). ^{119}Sn NMR (149.2 MHz, $CDCl_3$) δ –124.4 (*Sn*–CH$_3$).

4.5. Synthesis of organotin halide (**4**)

A procedure analogous to the preparation of compound **3** was used but instead starting from compound **1** (0.77 g, 3.0 mmol) with Me_2SnBr_2 (0.93 g, 3.0 mmol). Compound **4** was obtained as colorless crystals (1.22 g, 2.5 mmol, 84%). Mp: 183–185 °C (dec). HRMS: Calcd for $[^{12}C_{10}{}^{1}H_{26}{}^{11}B_{10}{}^{80}Br{}^{14}N{}^{16}O{}^{119}Sn]^+$ 485.1150. Found: 485.1160. Anal. Calc. for $C_{10}H_{26}B_{10}BrNOSn$: C, 24.86; H, 5.43; N, 2.90. Found: C, 24.84; H, 5.41; N, 2.93%. IR (KBr pellet, cm^{-1}) ν(C–H) 3207, 3085, 2982, ν(B–H) 2586, ν(C=N) 1688. ^{1}H NMR ($CDCl_3$) δ 0.31 (s, 6H, Sn–CH_3, $^{2}J_{^{119}Sn-CH_3}$ = 77.2 Hz), 0.94 (d, 3H, CH(CH_3)$_2$, $^{3}J_{CH-CH_3}$ = 6.6 Hz), 1.11 (d, 3H, CH(CH_3)$_2$, $^{3}J_{CH-CH_3}$ = 6.9 Hz), 1.94 (m, 1H, C*H*(CH$_3$)$_2$), 4.25 (m, 1H, C*H*N), 4.28 (m, 1H, CH_2O), 4.48 (m, 1H, CH_2O). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 4.18 (Sn–*C*H$_3$); 13.7, 16.4 (CH(*C*H$_3$)$_2$); 28.5 (*C*H(CH$_3$)$_2$); 68.6 (*Cab*); 68.7, 70.3 (OCH$_2$*C*HN); 70.1 (*Cab*); 166.2 (*C*=N). ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –15.88 (2H), –12.39 (3H), –9.88 (2H), –6.67 (3H). ^{119}Sn NMR (149.2 MHz, $CDCl_3$) δ –120.1 (*Sn*–CH$_3$).

4.6. Synthesis of organotin halide (**5**)

A procedure analogous to the preparation of compound **3** was used but instead starting from compound **2** (0.81 g, 3.0 mmol) with Me_2SnCl_2 (0.66 g, 3.0 mmol). Compound **5** was obtained as colorless crystals (1.02 g, 2.3 mmol, 75%). Mp: 176–178 °C (dec). HRMS: Calcd for $[^{12}C_{11}{}^{1}H_{28}{}^{11}B_{10}{}^{35}Cl{}^{14}N{}^{16}O{}^{119}Sn]^+$ 455.1812. Found: 455.1804. Anal. Calc. for $C_{11}H_{28}B_{10}ClNOSn$: C, 29.19; H, 6.24; N, 3.09. Found: C, 29.22; H, 6.26; N, 3.11%. IR (KBr pellet, cm^{-1}) ν(C–H) 3002, 2985, ν (B–H) 2582, ν(C=N) 1685. ^{1}H NMR ($CDCl_3$) δ 0.33 (s, 6H, Sn–CH_3, $^{2}J_{^{119}Sn-CH_3}$ = 75.7 Hz), 0.98 (s, 9H, C(CH_3)$_3$), 4.27 (m, 1H, C*H*N), 4.30 (dd, 1H, CH_2O, $^{2}J_{C-H}$ = 7.8 Hz), 4.44 (dd, 1H, CH_2O, $^{2}J_{C-H}$ = 7.9 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 4.06 (Sn–*C*H$_3$); 20.7 (C(*C*H$_3$)$_3$); 32.1 (*C*(CH$_3$)$_3$); 68.6 (*Cab*); 68.9, 71.2 (OCH$_2$*C*HN); 70.3 (*Cab*); 166.7 (*C*=N). ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –17.38 (3H), –14.59 (2H), –10.76 (2H), –7.64 (1H), –6.79 (1H), –3.18 (1H). ^{119}Sn NMR (149.2 MHz, $CDCl_3$) δ –119.6 (*Sn*–CH$_3$).

4.7. Synthesis of organotin halide (**6**)

A procedure analogous to the preparation of compound **3** was used but instead starting from compound **2** (0.81 g, 3.0 mmol) with Me_2SnBr_2 (0.93 g, 3.0 mmol). Compound **6** was obtained as colorless crystals (1.21 g, 2.4 mmol, 81%). Mp: 180–182 °C (dec). HRMS: Calcd for $[^{12}C_{11}{}^{1}H_{28}{}^{11}B_{10}{}^{80}Br^{14}N^{16}O^{119}Sn]^+$ 499.1307. Found: 499.1300. Anal. Calc. for $C_{10}H_{26}B_{10}BrNOSn$: C, 26.58; H, 5.68; N, 2.82. Found: C, 26.61; H, 5.65; N, 2.80%. IR (KBr pellet, cm^{-1}) ν(C–H) 2988, 2881, ν(B–H) 2586, ν(C=N) 1687. ^{1}H NMR ($CDCl_3$) δ 0.31 (s, 6H, Sn–CH_3, $^2J_{^{119}Sn-CH_3}$ = 76.1 Hz), 0.97 (s, 9H, C(CH_3)$_3$), 4.25 (m, 1H, C*H*N), 4.30 (dd, 1H, CH_2O, $^2J_{C-H}$ = 8.0 Hz), 4.44 (dd, 1H, CH_2O, $^2J_{C-H}$ = 8.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 4.01 (Sn–*C*H$_3$); 20.5 (C(*C*H$_3$)$_3$); 31.8 (*C*(CH$_3$)$_3$); 68.6 (*Cab*); 68.6, 71.0 (O*C*H$_2$*C*HN); 70.3 (*Cab*); 166.4 (*C*=N). ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –18.44 (3H), –10.24 (3H), –8.52 (2H), –6.44 (1H), –4.21 (1H). ^{119}Sn NMR (149.2 MHz, $CDCl_3$) δ –117.8 (*Sn*–CH$_3$).

4.8. Preparation of methoxymethyl-o-carborane (**7**)

NaH (0.36 g, 15.0 mmol) was added dropwise to a solution of *o*-carboranylmethanol (0.87 g, 5.0 mmol) in 50 mL of dry THF at 0 °C with stirring. The mixture was allowed to stir for 30 min at 0 °C at which time iodomethane (0.78 g, 5.5 mmol) was added dropwise. The solution was stirred for 1 h and then warmed to ambient temperature. The reaction was quenched with water, extracted with ether, and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was purified by recrystallization in hexane to afford compound **7** as colorless crystals in 92% yield (0.87 g, 4.6 mmol). Mp: 68–70 °C. Anal. Calc. for $C_4H_{16}B_{10}O$: C, 25.52; H, 8.57. Found: C, 25.57; H, 8.62%. IR (KBr pellet, cm^{-1}) ν(C–H) 3066, 2785, ν(B–H) 2581. ^{1}H NMR ($CDCl_3$) δ 3.41 (s, 3H, OCH_3), 3.94 (brs, 1H, Cab–*H*), 4.14 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$) δ 54.2 (OCH$_3$), 68.7 (*Cab*), 76.1 (*Cab*), 82.5 (CH$_2$). ^{11}B NMR ($CDCl_3$) δ –19.54 (4B), –16.82 (2B), –12.76 (2B), –8.33 (2B).

4.9. Preparation of methoxy(phenyl)methyl-o-carborane (**8**)

A procedure analogous to the preparation of compound **7** was used but instead starting from *o*-carboranyl(phenyl)methanol (1.25 g, 5.0 mmol). Compound **8** was obtained as colorless crystals (1.19 g, 4.5 mmol, 90%). Mp: 74–75 °C. Anal. Calc. for $C_{10}H_{20}B_{10}O$: C, 45.43; H, 7.63. Found: C, 45.33; H, 7.67%. IR (KBr pellet, cm^{-1}) ν(C–H) 3070, 2781, ν(B–H) 2593. ^{1}H NMR ($CDCl_3$) δ 3.44 (s, 3H, OCH_3), 3.93 (brs, 1H, Cab–*H*), 4.11 (s, 1H, PhC*H*), 7.14–7.30 (m, 5H, *Ph*). ^{13}C NMR ($CDCl_3$) δ 55.8 (OCH$_3$), 67.1 (*Cab*), 71.5 (*Cab*), 83.4 (PhCH), 125.4, 129.2, 129.8, 134.6 (*Ph*). ^{11}B NMR ($CDCl_3$) δ–19.85 (4B), –17.32 (2B), –11.76 (2B), –7.45 (2B).

4.10. General synthesis of the organotin halides ($Cab^{C,O}$)Me_2SnBr (**9**)

A 2.5 M *n*-BuLi solution (1.3 mL, 3.3 mmol) was added to a stirred solution of compound **7** (0.56 g, 3.0 mmol) in diethyl ether (30 mL) at –10 °C through a syringe. The resulting solution was stirred at –10 °C for 30 min. A solution of Me_2SnBr_2 (0.93 g, 3.0 mmol) in diethyl ether (10 mL) was then added slowly to the 30 mL diethyl ether solution of compound **7**·Li at −10 °C. The reaction temperature was maintained at –10 °C for 10 min. The reaction mixture was then filtered and the organic solvent was evaporated. The crude product was dissolved in fresh distilled toluene. The volume of the toluene solution was reduced, and the resulting concentrated solution was allowed to stand at –10 °C for 2 days to allow crystallization. Compound **9** was obtained as colorless crystals in 84% yield (1.05 g, 2.5 mmol). Mp: 134–137 °C. HRMS: Calcd for $[^{12}C_6{}^{1}H_{21}{}^{11}B_{10}{}^{80}Br^{16}O^{119}Sn]^+$ 418.0728. Found: 418.0706. Anal. Calc. for $C_6H_{21}B_{10}BrOSn$: C, 17.33; H, 5.09. Found: C, 17.29; H, 5.11%. IR (KBr pellet, cm^{-1}) ν(C–H) 3178, 2888, ν(B–H) 2581. ^{1}H NMR ($CDCl_3$) δ 1.11 (s, 6H, Sn–CH_3, $^2J_{^{119}Sn-CH_3}$ = 69.8 Hz), 3.50 (s, 3H, OCH_3), 4.19 (d, 1H, CH_2, $^2J_{C-H}$ = 6.4 Hz), 4.25 (d, 1H, CH_2, $^2J_{C-H}$ = 6.5 Hz). ^{13}C NMR ($CDCl_3$) δ 4.97 (Sn–*C*H$_3$); 50.2 (O*C*H$_3$); 67.8, 76.0 (*Cab*); 79.6 (*C*H$_2$). ^{11}B NMR ($CDCl_3$) δ –18.47 (4B), –14.85 (1B), –10.57 (4B), –6.48 (1B). ^{119}Sn NMR (149.2 MHz, $CDCl_3$) δ –108.2 (*Sn*–CH$_3$).

4.11. Synthesis of organotin halide (**10**)

A procedure analogous to the preparation of **9** was used but instead starting from compound **8** (0.79 g, 3.0 mmol). Compound **10** was obtained as colorless crystals (1.23 g, 2.5 mmol, 83%). Mp: 140–141 °C. HRMS: Calcd for $[^{12}C_{12}{}^{1}H_{25}{}^{11}B_{10}{}^{80}Br^{16}O^{119}Sn]^+$ 494.1041. Found: 494.1078. Anal. Calc. for $C_{12}H_{25}B_{10}BrOSn$: C, 29.29; H, 5.12. Found: C, 29.41; H, 5.16%. IR (KBr pellet, cm^{-1}) ν(C–H) 3046, 2872, ν(B–H) 2580. ^{1}H NMR ($CDCl_3$) δ 1.00 (s, 6H, Sn–CH_3, $^2J_{^{119}Sn-CH_3}$ = 68.3 Hz), 3.50 (s, 3H, OCH_3), 4.27 (s, 1H, PhC*H*), 7.11–7.30 (m, 5H, *Ph*). ^{13}C NMR ($CDCl_3$) δ 3.26 (Sn–CH$_3$); 54.2 (OCH$_3$); 66.8, 70.4 (*Cab*); 81.2 (PhCH); 124.5, 127.1, 127.8, 130.4 (*Ph*). ^{11}B NMR ($CDCl_3$) δ –19.51 (3B), –16.48 (1B), –14.47 (4B), –6.81 (2B). ^{119}Sn NMR (149.2 MHz, $CDCl_3$) δ –110.3 (*Sn*–CH$_3$).

4.12. Crystal structure determination

Crystals of compounds **4**, **7**, **8**, and **9** were obtained from toluene at –10 °C, sealed in glass capillaries under argon, and mounted on the diffractometer. The preliminary examination and data collection were performed using a Bruker SMART CCD detector system in a single-crystal X-ray diffractometer equipped with a sealed-tube X-ray source (40 kV × 50 mA) using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The preliminary unit cell constants were determined using a set of 45 narrow-frame scans (0.3° inω). The double-pass method of scanning was employed to exclude noise. The collected frames were integrated using an orientation matrix determined from the narrow-frame scans. The SMART software package was used for data collection, and SAINT was employed for frame integration [30]. The final cell constants were determined using a global refinement of the *xyz* centroids of the reflections harvested from the entire data set. The structure solution and refinement were carried out using the SHELXTL-PLUS software package [31].

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Appendix A. Supplementary material

CCDC 742034, 742035, 742036, 742037 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.10.030.

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