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Abstract: The synthesis of two bis(carboranyl) (**bc**) magnesium reagents is described. Treatment of 1,1′-bis(o-carborane) (**H₂-bc**) or 8,8′,9,9′,10,10′,12,12′-octamethyl-1,1′-bis(o-carborane) (**H₂-Mebc**) with Mg(*n*Bu)₂ in 1,2-dimethoxyethane (DME) affords (**bc**)Mg(DME)₂ (**1a,b**) as crystalline solids. The magnesium compounds, which have been characterized by NMR spectroscopy and single-crystal X-ray crystallography in the case of **1a**, serve as competent Grignard-type reagents to generate **bc**-containing species of tin from Me₂SnCl₂ (**2a,b**). The type of substitution of the bis(o-carboranyl) ligand framework is found to strongly affect the electronic character of the tin center, as judged by ¹¹⁹Sn NMR spectroscopy. The disclosed compounds, which are stable solids under an atmosphere of dry nitrogen gas at room temperature, provide a new class of **bc**-transfer reagents.

Introduction

Commonly considered three-dimensional surrogates of benzene,[1] the charge-neutral, icosahedral carboranes, have gained attention as potentially useful building blocks in areas of research ranging from catalysis to polymer chemistry.[2] The σ-aromatic delocalization of bonding electron density imparts high kinetic stability, distinguishing these polyhedral boranes from commonly encountered tricoordinate boron-centered species.[3] This feature, in conjunction with the non-uniform electron distribution of the carborane molecule,[4] renders carboranes attractive for a wide array of applications.

1,1′-Bis(o-carborane) (**H₂-bc**) – a carborane-based biphenyl analogue – has been used as a sterically encumbering and weakly donating ligand for transition metals and main group elements.[5] This progress has been highlighted by the foundational works of Hawthorne's group[6] and some recent work from Welch and co-workers.[7] In addition, Peryshkov and co-workers have recently observed unique cage-opening reactivity with dilithiated bis(o-carborane) in the presence of P-based electrophiles.[8] The bis(o-carboranyl) fragment is typically installed by lithiation of the carbon vertices followed by salt metathesis with transition metal or main group electrophiles. We

wondered, however, whether Grignard-like reagents could be synthesized and whether they would behave as effective **bc** transfer reagents (Scheme 1). In addition, the mitigated nucleophilicity of Grignard-type reagents with respect to alkyllithium compounds might circumvent complications known to arise from the deboronation of lithiocarboranes by other lithiated carboranes in solution.[2e,9] Here we report the successful synthesis of Mg-based bis(o-carboranyl) reagents and their utility in **bc**-transfer reactions.
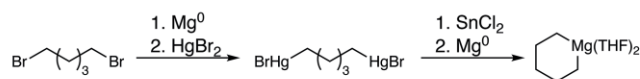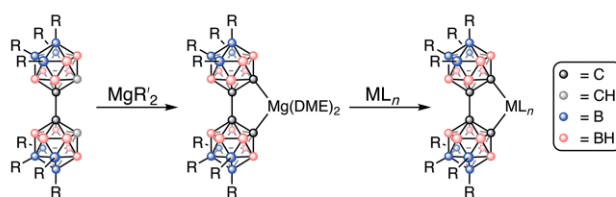
Scheme 1. Top: Previous work by Bickelhaupt detailing the multistep syntheses of cyclic dialkylmagnesiates. Bottom: The present work provides access to bis(o-carboranyl)magnesiates in a single step, which subsequently behave as **bc**-transfer agents.

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Results and Discussion

The acidity of the C–H vertices of icosahedral carboranes compared to their B–H congeners is known and often used as a means of functionalizing C-vertices of carboranes.[1] The acidity of these C–H bonds have been measured to range from pK_a values of about 20–30 for unsubstituted *ortho*-, *meta*-, and

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para-carborane isomers.[10] We therefore wondered whether this acidity could be leveraged to generate a Grignard-type reagent from simple dialkylmagnesium precursors via protonolysis of MgR$_2$ by **H$_2$-bc**. Several examples of tethered Grignard reagents, developed predominantly by Bickelhaupt and co-workers (Scheme 1), have been reported in the literature.[11] In addition, Ramsden reported the use of a cyclic internal butene dianion generated from the reduction of 1,3-butadiene with magnesium metal,[12] and Wreford and Whitney later reported the use of this reagent in synthesizing transition metal butadiene/cyclobutene complexes.[13] Furthermore, while the use of monodentate *o*-caboranylmagnesium halides has been reported,[14] to the best of our knowledge 1,1′-bis(*o*-carboranyl)magnesium or any such derivatives of this type have not been disclosed.

Treatment of **H$_2$-bc** with Mg(*n*Bu)$_2$ in DME solvent resulted in the precipitation of a pale yellow solid within 20 minutes upon mixing at room temperature (Scheme 2). This solid product was isolated by vacuum filtration and subjected to spectroscopic characterization. ^{1}H NMR spectroscopic analysis of the isolated solid dissolved in [D$_8$]THF solvent revealed two sets of inequivalent singlets assigned as the methyl (CH$_3$) and methylene (CH$_2$) groups of bound DME. By proton-coupled ^{11}B NMR spectroscopy, no singlet resonances were observed, suggesting that the Mg center is bound through the carbon vertices of the **bc** framework. A single-crystal X-ray diffraction study on crystals of **1a** grown from THF/*n*-pentane revealed a structure consistent with the NMR spectroscopic data. Compound **1a** co-crystallizes with a *C,C*′-κ^2-bound **bc** ligand as an equimolar mixture of enantiomers with two THF molecules per molecule of **1a** in the unit cell (Figure 1).
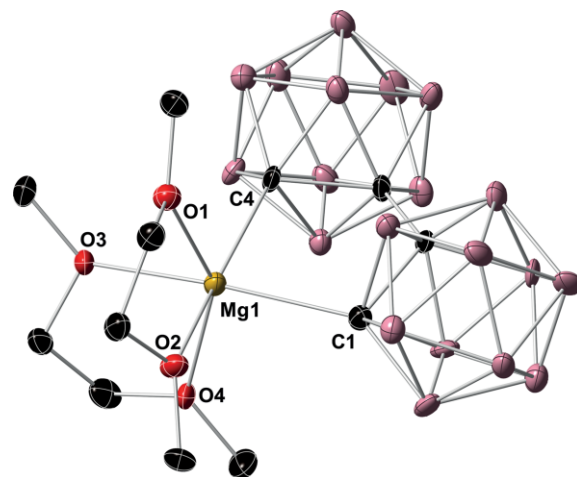

Figure 1. Single-crystal X-ray structure of **1a**. Two co-crystallized THF molecules and protons are omitted for clarity. Thermal ellipsoids are displayed at 50 % probability. Selected distances [Å] and angles [°]: Mg1–C1 2.308, Mg1–C4 2.278, Mg1–O1 2.185, Mg1–O2 2.152, Mg1–O3 2.166, Mg1–O4 2.131; C1–Mg1–C4 84.17, C1–C2–C3–C4 25.75.

Scheme 2. Synthetic scheme for (**bc**)Mg(DME)$_2$ (R = H, **1a**; Me, **1b**).

Beyond the generally straightforward substitution at the carbon vertices of carboranes, multiple avenues of substitution chemistry at *boron* vertices have been disclosed. These methods, which include transition-metal-catalyzed cross-coupling and electrophilic substitution,[15] enable site-selective substitution from simple precursors that provide derivatized carboranes with tailored steric and electronic profiles. Taking advantage of such functionalization avenues, we synthesized **H$_2$-Mebc** from **H$_2$-bc** using Hawthorne's method[16] with the intent of evaluating the potential role of such *B*-vertex substitution on the behavior of Mg-based bis(*o*-carboranyl) transfer reagents.

The reaction of **H$_2$-Mebc** with Mg(*n*Bu)$_2$ was conducted under conditions similar to those used to synthesize **1a** (Scheme 1). Treatment of **H$_2$-Mebc** with Mg(*n*Bu)$_2$ in THF af-

fords a yellow solution. After approximately six hours, conversion of **H$_2$-Mebc** to a new species was determined by ^{11}B NMR spectroscopic analysis of the crude reaction mixture. Consistent with **1a**, the ^{11}B NMR spectroscopic features of **1b** likewise suggest a κ^2-*C,C*′-chelating mode of the bis(*o*-carboranyl) fragment to the Mg center. As expected, **1b** displays several resonances from about 11.0–5.0 ppm, which appear as singlets in both the ^{11}B and ^{11}B{^{1}H} NMR spectra and correspond to the boron atoms bearing the methyl substituents. In the ^{1}H NMR spectrum, the methyl groups attached to the cluster cage are observed as three broad singlets from about 0.1 to –0.3 ppm in [D$_8$]THF. These chemical shifts are consistent with other *o*-caboranes containing *B*-bound alkyl substituents reported in the literature.[15j–15l,16,17] In contrast to **1a**, only one set of methyl and methylene peaks are observed in [D$_8$]THF solvent, and they correspond to the bound DME ligands. According to ^{13}C NMR spectroscopy, the carbon resonances corresponding to the cage-bound methyl groups in **1b** are severely broadened due to coupling with quadrupolar ^{11}B and ^{10}B nuclei ($S = 3/2$, 80 % natural abundance; $S = 3$, 20 % natural abundance, respectively) but can be observed between about 0.5 and –3.0 ppm. Importantly, we find that both **1a** and **1b** are stable solids at room temperature under a dry nitrogen atmosphere as well as in THF solution. The absence of observed intermolecular deboronation is potentially advantageous in view of previous reports stating that lithiated carboranes and 1,1′-bis(*o*-carborane) undergo intermolecularly induced deboronation.[2e,9]

The performance of **1a** and **1b** as **bc**-transfer reagents was evaluated through treatment with Me$_2$SnCl$_2$ in THF at room temperature, which resulted in the decoloration of the yellow solutions of **1a** and **1b**. Shifts of the resonances in the ^{11}B NMR spectra, as well as the presence of ^{119}Sn- and ^{117}Sn-coupled methyl protons (distinct from the Me$_2$SnCl$_2$ starting material) in the ^{1}H NMR spectra, suggest conversion to new products (see Figure 2). Upon removal of the magnesium salt byproducts, bis(*o*-carboranyl)tin compounds **2a** and **2b** were obtained in 80

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and 75 % yield, respectively. While some tin compounds containing o-carborane substituents[18] and several main group species containing chelating 1,1′-bis(o-carborane) ligands are known,[7,19] to the best of our knowledge these are the first examples of 1,1′-bis(o-carboranyl)stannyl species.
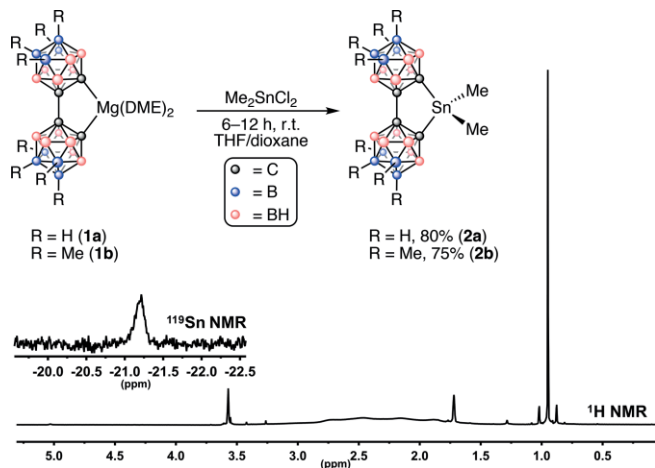

Figure 2. Synthesis of bis(o-carboranyl)tin species **2a** and **2b**. ^{1}H NMR and ^{119}Sn NMR spectra for **2a** (**2b** not shown) in [D8]THF reveal diagnostic product peaks corresponding to a [119]Sn- and [117]Sn-coupled methyl resonance and a broad, shielded [119]Sn resonance.

The electronic influence of the substituents (H vs. Me) appended to the **bc** scaffold[20] in **2a** and **2b** is most clearly denoted by the chemical shift differences of the tin atoms as well as the methyl groups bound to tin by ^{119}Sn NMR spectroscopy (see the Supporting Information): a decrease in shielding of the [119]Sn nucleus is observed in **2b** relative to **2a** as judged by the respective [119]Sn chemical shifts in [D8]THF [–9.20 ppm (**2b**) vs. –21.22 ppm (**2a**)] (vide infra) at room temperature. This observation suggests that the methyl substituents on the **Mebc** cage in **2b** exert an apparent inductively electron-withdrawing ("–I") effect on the tin nucleus.

In an effort to further evaluate the role of the eight methyl substituents of **2b** on the overall molecular orbital description relative to unfunctionalized **2a**, density functional theory (DFT) calculations were carried out. The geometries of **2a,b** based on the crystal structure of **1a** were optimized at the PBE-D3(BJ):TZP level, and single-point calculations were carried out at the B3LYP-D3(BJ):TZ2P level of theory (Figure 3A, see the Supporting Information for details). The highest occupied molecular orbital (HOMO) for **2a** was found to be largely localized along the C–Sn bond paths. In addition, the B–H fragments of the **bc** cage, which are antipodal ("trans") to the tin-bound carbon atoms, significantly contribute to the HOMO. The mutual electronic influence of antipodal atoms in polyhedral boranes has been discussed in the literature.[21] The lowest unoccupied molecular orbital (LUMO) is concentrated largely on the Sn center. Interestingly, the presence of methyl groups in the **Mebc** ligand in **2b** adjusts the molecular orbital picture relative to **2a** to involve more of the **Mebc** scaffold in the HOMO level, while the LUMO remains localized on the "SnMe2" fragment. We attribute the nature of the difference in localization of the HOMO between **2a** and **2b** to reside in the stabilization of the C–Sn bonds by the antipodal methyl substituents in **2b**. Indeed, the molecular orbital corresponding to the C–Sn bonds in **2b** was calculated to be the HOMO-1, approximately 12 kcal/mol lower in energy than the corresponding orbital (HOMO) in **2a** (see the Supporting Information). Ultimately, this suggests that simple substitution patterns may greatly affect the electronic landscape of atoms within the **bc** framework.[2e]

Given the well-recognized analogy of the carborane molecule as a three-dimensional analogue of benzene (vide supra),

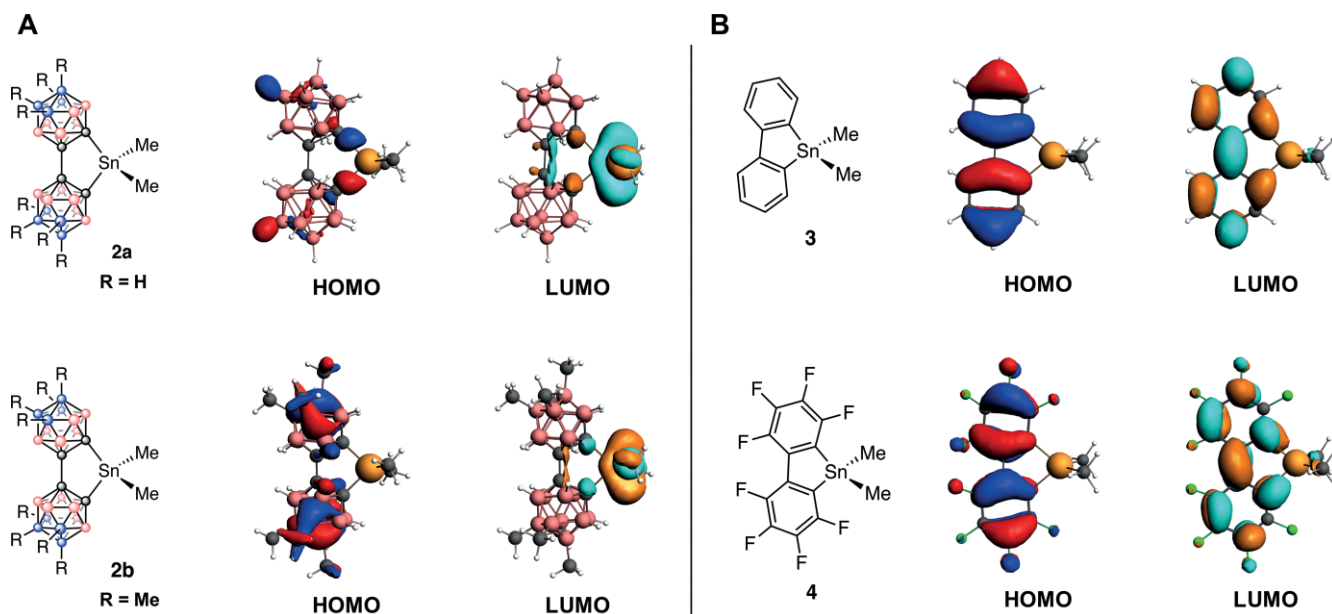Figure 3. (A) Frontier molecular orbitals for **2a** (R = H), **2b** (R = Me), **3**, and **4** [B3LYP-D3(BJ):TZ2P]. The HOMOs and LUMOs for **2a** and **2b** show major contributions from the "SnMe2" fragment as well as from the **Mebc** substituent in the case of **2b**. (B) The HOMO and LUMO levels for both **3** and **4** are localized primarily on the biphenyl framework with minimal contribution from the "SnMe2" fragment.

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we chose to further evaluate the frontier molecular orbital picture of the bis(o-carboranyl) ligands in **2a** and **2b** in the context of analogous *biphenyl*-containing tin compounds previously reported by Piers and co-workers[22] (**3** and **4**, Figure 3B) by using DFT. We therefore performed geometry optimizations and single-point calculations on **3** and **4** at the B3LYP-D3(BJ):TZ2P level of theory. In contrast to the frontier orbitals of both **2a** and **2b**, which heavily involve the tin center and to a lesser degree the bis(o-carboranyl) ligands, the "SnMe$_2$" fragment is found to remain largely absent from the HOMO and LUMO for **3** and **4**; rather, the most significant contribution to these molecular orbitals originate from the biphenyl and perfluorobiphenyl ligands, respectively. The strongly electron-withdrawing nature of the perfluorinated ligand in **4** prompted the question of what the electronic influence of the **bc** and **Mebc** ligands in **2a** and **2b**, respectively, was, as compared to that of the biphenyl analogues. We considered that the chemical shift of the tin nucleus, as judged by a solution ^{119}Sn NMR spectroscopic experiment, might be an appropriate reporter of the relative deshielding effect of the chelating ligand [bis(o-carboranyl) vs. biphenyl]. Indeed, Piers and co-workers reported the ^{119}Sn NMR chemical shifts of **3** and **4** to be –34.1[22b] and 30.3 ppm[22a] respectively, in C$_6$D$_6$ solvent, which suggests that the fluorinated biphenyl ligand strongly deshields the ^{119}Sn nucleus relative to the nonfluorinated analogue. Though compound **2a** could not be compared because it was insoluble in C$_6$D$_6$, we find that **2b** exhibits a ^{119}Sn NMR chemical shift of 53.10 ppm in C$_6$D$_6$, which implies that the octamethylated **Mebc** ligand of **2b** exerts an even stronger electron-withdrawing influence than a perfluorinated biphenyl ligand for this set of tin compounds.

Conclusions

We have introduced magnesium-based bis(o-carboranyl) transfer reagents **1a,b**, which are stable solids under an inert atmosphere that cleanly participate in salt metathesis with Me$_2$SnCl$_2$ to afford species of the type (**bc**)SnMe$_2$ (**2a,b**). Complications arising from the use of alkali metal bases to generate the bis(carboranyl)metal compound, such as intermolecular cage deboronation, are avoided with this approach, as evidenced by the solution stability of **1a** and **1b**. The DFT studies presented here show that the frontier orbitals are generally localized on the Sn–C$_{carborane}$ and antipodal B–H bonds **2a,b**, while in the "all-organic" derivatives **3** and **4** the frontier orbitals are localized across the biphenyl framework, suggesting potentially divergent reactivity between these otherwise analogous sets of compounds. Importantly, the electronic influence of methyl substituents in **2b** relative to **2a** highlights the possibility of employing functionalized bis(carboranyl) ligands to modulate the ligand fields of chelated main group or transition metals while holding the steric environment in the immediate vicinity of the chelated atom constant. Given recent advances in the development of methods toward selectively functionalizing specific boron vertices of *ortho*- and *meta*-carborane,[15–17] other functionalized derivatives of this bis(carboranyl) ligand class may prove useful for clearly identifying and strategically leveraging electronic effects when employed as supporting ligands.

Experimental Section

General Considerations: All manipulations were carried out under a glovebox atmosphere of dry N$_2$ gas at room temperature (ca. 20–23 °C) unless otherwise noted. Tetrahydrofuran (THF) and diethyl ether (Et$_2$O) were sparged with argon and passed through a double column of alumina before use. 1,2-Dimethoxyethane was dried with Na/benzophenone and vacuum-transferred to a receiving flask, brought in the glovebox, and stored over 3Å molecular sieves. 1,4-Dioxane was stored over molecular sieves.

Materials: Deuterated solvents were purchased from Cambridge Isotope Laboratories and were stored over 3Å molecular sieves prior to use. *o*-Carborane was purchased from Boron Specialties and was purified prior to use in the following procedure: a round-bottomed flask was charged with *o*-carborane (15 g, 10.4 mmol) and MeOH (150 mL). Concentrated HCl (50 mL) was added slowly to the reaction vessel, and the resulting mixture was heated to 50 °C and stirred overnight. The solution was then cooled, H$_2$O (200 mL) was added, and the resulting white solid was isolated by vacuum filtration, washed with water, and air-dried. The solid was then dissolved in CH$_2$Cl$_2$, dried with MgSO$_4$, and filtered through Celite. The solution was dried in vacuo to afford a white powder. The powder was then sublimed at 60 °C under dynamic vacuum. After sublimation away from the yellow residue, the white sublimate was dissolved in C$_2$H$_4$Cl$_2$. Activated carbon/charcoal (ca. 3–5 g) was added, and the mixture was stirred for 6 h at about 75 °C. The suspension was then filtered, and the filtrate was concentrated under vacuum. The resulting white solid was again sublimed at 60 °C to afford purified *o*-carborane. Di-*n*-butylmagnesium [Mg(*n*Bu)$_2$], dimethyltin dichloride (Me$_2$SnCl$_2$), 1,2-dimethoxyethane (DME), anhydrous 1,4-dioxane, Et$_2$O, and THF were purchased from Sigma Aldrich. Celite was purchased from Fisher Scientific. All other reagents were used as received unless otherwise indicated. 1,1′-bis(o-carborane)[5f] and 9,9′,10,10′,11,11′,12,12′-octamethyl-bis(o-carborane)[16] were synthesized according to published procedures.

Synthetic Procedures

(bc)Mg(DME)$_2$ (1a): A 20 mL vial was charged with 1,1′-bis(o-carborane) (485 mg, 1.69 mmol) and DME (5 mL). Mg(*n*Bu)$_2$ (1.0 M in heptane, 1.69 mL, 1.69 mmol) was added dropwise. A precipitate gradually formed with a concomitant change in color to pale yellow. The reaction was stirred for 6 h, after which the precipitate was isolated on a frit and washed twice with DME and twice with Et$_2$O. Yield: 700 mg, 85 %. ^{1}H NMR (500 MHz, [D$_8$]THF): δ = 3.43–3.42 (overlapping singlets, 8 H, CH$_2$), 3.26–3.25 (overlapping singlets, 12 H, CH$_3$) ppm. ^{13}C NMR (125 MHz): δ = 91.48, 80.23, 72.58, 72.56, 59.20, 59.16 ppm. ^{11}B NMR (160 MHz): δ = –1.69 (d, 2 B), –3.44 (d, 2 B), –5.0 to –15.0 (m, 16B) ppm.

(Mebc)Mg(DME)$_2$ (1b): A 20 mL vial was charged with 1,1′-bis(o-carborane) (100 mg, 0.251 mmol) and DME (3 mL). Mg(*n*Bu)$_2$ (1.0 M in heptane, 0.251 mL, 0.251 mmol) was added dropwise, and the solution gradually turned yellow. After 18 h, the solution was dried in vacuo, and Et$_2$O (ca. 5 mL) was added to produce a white precipitate. The solid was isolated on a frit and dried under vacuum to afford 114 mg (76 %) of the product. ^{1}H NMR (500 MHz, [D$_8$]THF): δ = 3.44 (s, 8 H, CH$_2$), 3.28 (s, 12 H, CH$_3$), 0.07 (br. s, 12 H, Me), –0.17 (s, 3 H, Me), –0.22 (s, 3 H, Me) ppm. ^{13}C NMR (125 MHz): δ = 78.26, 72.68, 72.51, 59.00, 0.24 (br), –2.11 (br) ppm. ^{11}B NMR (160 MHz): δ = 10.20 (s, 2 B), 8.59 (2 B), 5.16 (4 B), 5.27 (m, 8 B), 8.61 (m, 4 B) ppm.

(bc)SnMe$_2$ (2a): Me$_2$SnCl$_2$ (45 mg, 0.204 mmol) was dissolved in THF (1 mL) and dioxane (1 mL) in a 20 mL vial. To this solution was added a slightly yellow solution of **1a** (100 mg, 0.204 mmol) dis-

solved in THF (ca. 2 mL). The resulting solution, which gradually developed a precipitate after about 15 min, was stirred for 24 h. The mixture was then filtered through Celite, and the pad was washed with THF. The filtrate was dried in vacuo, and Et_2O was added to afford a white solid, which was isolated on a frit by filtration. Yield (71 mg, 80 %). ^1H NMR (500 MHz, $[D_8]THF$): δ = 3.2–1.5 (br. m, 20 H, BH), 0.86 (s, 6 H, CH_3) ppm. ^{13}C NMR (125 MHz): δ = 80.16, 79.07, 0.87 ppm. ^{11}B NMR (160 MHz): δ = –0.26 (d, 2 B), –2.78 (2 B), –5.5 to –10.0 (m, 16B) ppm. ^{119}Sn NMR (186 MHz): δ = –21.22 ppm.

(Mebc)SnMe₂ (2b): Me_2SnCl_2 (46 mg, 2.08 mmol) was dissolved in THF (1 mL) and dioxane (1 mL) in a 20 mL vial. To this solution was added a slightly yellow solution of **1b** (125 mg, 2.08 mmol) dissolved in THF (ca. 2 mL). The resulting solution, which gradually developed a precipitate after about 15 min, was stirred for 45 min. The mixture was then filtered through Celite, and the pad was washed with THF. The filtrate was dried in vacuo. Pentane (2 mL) was added to the resulting residue, and the mixture was again dried under vacuum. This process was repeated two times. Upon the last drying cycle, a white solid was obtained (85 mg, 75 %). ^1H NMR (500 MHz, C_6D_6): δ = 3.5–1.0 (m, 20 H, BH), 0.52 (br. s, 12 H, Me), 0.34 (br. s, 6 H, Me), 0.29 (br. s, 6 H, Me), 0.07 (s, 6 H, SnMe_2) ppm. ^{13}C NMR (125 MHz): δ = 72.51, 63.60, –0.24, –2.17, –6.11 ppm. ^{11}B NMR (160 MHz): δ = 9.98 (s, 4 B), 6.47 (s, 4 B), 3.08 (s, 8 B), –3.5 to –17.0 (m, 12B) ppm. ^{119}Sn NMR (186 MHz, C_6D_6): δ = 55.10 ppm. ^{119}Sn NMR (186 MHz, $[D_8]THF$): δ = –9.20 ppm.

CCDC 1551220 (for **1a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Acknowledgments

Keywords: Carboranes · Boron · Cluster compounds · Tin · Electronic structure

[1] R. N. Grimes in *Carboranes*, 3rd ed., Academic Press, New York, **2016**.

[2] a) Z. J. Leśnikowski, *J. Med. Chem.* **2016**, *59*, 7738–7758; b) M. Hailmann, S. Z. Konieczka, A. Himmelspach, J. Löblein, F. J. Reiss, M. Finze, *Inorg. Chem.* **2014**, *53*, 9385–9399; c) J. Plesek, *Chem. Rev.* **1992**, *92*, 269–278; d) S. Mukherjee, P. Thilagar, *Chem. Commun.* **2016**, *52*, 1070–1093; e) K. O. Kirlikovali, J. C. Axtell, A. Gonzalez, A. C. Phung, S. I. Khan, A. M. Spokoyny, *Chem. Sci.* **2016**, *7*, 5132–5138; f) J. C. Axtell, K. O. Kirlikovali, P. I. Djurovich, D. Jung, V. T. Nguyen, B. Munekiyo, A. T. Royappa, A. L. Rheingold, A. M. Spokoyny, *J. Am. Chem. Soc.* **2016**, *138*, 15758–15765; g) C. Selg, W. Neumann, P. Lönnecke, E. Hey-Hawkins, K. Zeitler, *Chem. Eur. J.* **2017**, *23*, 7932–7937; h) R. N. Grimes, *Dalton Trans.* **2015**, *44*, 5939–5956; i) Z. Yinghuai, N. S. Hosmane, *J. Organomet. Chem.* **2013**, *747*, 25–29; j) X. Li, H. Yan, Q. Zhao, *Chem. Eur. J.* **2016**, *22*, 1888–1898; k) A. L. Chan, J. Estrada, C. E. Kefalidis, V. Lavallo, *Organometallics* **2016**, *35*, 3257–3260; l) S. G. McArthur, L. Geng, J. Guo, V. Lavallo, *Inorg. Chem. Front.* **2015**, *2*, 1101–1104; m) D. Tu, D. Shao, H. Yan, C. Lu, *Chem. Commun.* **2016**, *52*, 14326–14329; n) L. Zhu, W. Lv, S. Liu, H. Yan, Q. Zhao, W. Huang, *Chem. Commun.* **2013**, *49*, 10638–10640.

[3] a) W. N. Lipscomb, *Boron Hydrides*, Benjamin, New York, **1963**; b) P. v. R. Schleyer, K. Najafian, *Inorg. Chem.* **1998**, *37*, 3454–3470; c) Z. Chen, R. B. King, *Chem. Rev.* **2005**, *105*, 3613–3642; d) R. B. King, *Chem. Rev.* **2001**, *101*, 1119–1152.

[4] a) A. M. Spokoyny, C. W. Machan, D. J. Clingerman, M. S. Rosen, M. J. Wiester, R. D. Kennedy, C. L. Stern, A. A. Sarjeant, C. A. Mirkin, *Nat. Chem.* **2011**, *3*, 590–596; b) A. M. Spokoyny, C. D. Lewis, G. Teverovskiy, S. L. Buchwald, *Organometallics* **2012**, *31*, 8478–8481; J. Estrada, C. A. Lugo, S. G. McArthur, V. Lavallo, *Chem. Commun.* **2016**, *52*, 1824–1826.

[5] a) G. Thiripuranathar, W. Y. Man, C. Palmero, A. P. Y. Chan, B. T. Leube, D. Ellis, D. McKay, S. A. Macgregor, L. Jourdan, G. M. Rosair, A. J. Welch, *Dalton Trans.* **2015**, *44*, 5628–5637; b) Y. O. Wong, M. D. Smith, D. V. Peryshkov, *Chem. Commun.* **2016**, *52*, 12710–12713; c) I. Sivaev, *Commun. Inorg. Synth.* **2016**, *4*, 21–28; d) D. E. Harwell, J. McMillan, C. B. Knobler, M. F. Hawthorne, *Inorg. Chem.* **1997**, *36*, 5951–5955; e) R. A. Wiesboeck, M. F. Hawthorne, *J. Am. Chem. Soc.* **1964**, *86*, 1642–1643; f) S. Ren, Z. Xie, *Organometallics* **2008**, *27*, 5167–5168; g) G. Thiripuranathar, A. P. Y. Chan, D. Mandal, W. Y. Man, M. Argentari, G. M. Rosair, A. J. Welch, *Dalton Trans.* **2017**, *46*, 1811–1821.

[6] a) D. A. Owen, M. F. Hawthorne, *J. Am. Chem. Soc.* **1970**, *92*, 3194–3196; b) J. A. Dupont, M. F. Hawthorne, *J. Am. Chem. Soc.* **1964**, *86*, 1643; c) T. E. Paxson, K. P. Callahan, M. F. Hawthorne, *Inorg. Chem.* **1973**, *12*, 708–709; D. A. Owen, M. F. Hawthorne, *J. Am. Chem. Soc.* **1971**, *93*, 873–880.

[7] L. E. Riley, T. Krämer, C. L. McMullin, D. Ellis, G. M. Rosair, I. B. Sivaev, A. J. Welch, *Dalton Trans.* **2017**, *46*, 5218–5228.

[8] Y. O. Wong, M. D. Smith, D. V. Peryshkov, *Chem. Eur. J.* **2016**, *22*, 6764–6767.

[9] A.-R. Popescu, A. D. Musteti, A. Ferrer-Ugalde, C. Viñas, R. Núñez, F. Teixidor, *Chem. Eur. J.* **2012**, *18*, 3174–3184.

[10] a) M. A. Fox, A. K. Hughes, *Coord. Chem. Rev.* **2004**, *248*, 457–476; b) L. A. Leites, *Chem. Rev.* **1992**, *92*, 279–323; c) M. Scholz, E. Hey-Hawkins, *Chem. Rev.* **2011**, *111*, 7035–7062; d) K. Hermansson, M. Wójcik, S. Sjöberg, *Inorg. Chem.* **1999**, *38*, 6039–6048.

[11] a) H. C. Holtkamp, C. Blomberg, F. Bickelhaupt, *J. Organomet. Chem.* **1969**, *19*, 279–285; b) M. S. Goedheijt, T. Jijbacker, A. D. Horton, F. J. J. de Kanter, O. S. Akkerman, F. Bickelhaupt, *Eur. J. Inorg. Chem.* **2003**, 638–643; c) A. L. Spek, G. Schat, H. C. Holtkamp, C. Blomberg, F. Bickelhaupt, *J. Organomet. Chem.* **1977**, *131*, 331–340; d) F. J. M. Freijee, G. Schat, O. S. Akkerman, F. Bickelhaupt, *J. Organomet. Chem.* **1982**, *240*, 217–227; e) R. Fischer, H. Görls, J. Langer, M. Enke, M. Westerhausen, *Organometallics* **2016**, *35*, 587–594; f) F. Bickelhaupt, *J. Organomet. Chem.* **1994**, *475*, 1–14.

[12] H. E. Ramsden, U. S. Patent 3,388,179, **1968**.

[13] S. S. Wreford, J. F. Whitney, *Inorg. Chem.* **1981**, *20*, 3918–3924.

[14] a) W. Clegg, *J. Organomet. Chem.* **1987**, *325*, 39–46; b) A. V. Kazantsev, E. A. Otrashchenkov, M. M. Aksartov, K. M. Turdybekov, V. I. Yamovoi, S. M. Adekenov, *Russ. J. Org. Chem.* **2002**, *38*, 1635–1640; c) S. Bresadola, B. Longato, F. Morandini, *Inorg. Chim. Acta* **1977**, *25*, L135–L136.

[15] a) Y. Sevryugina, R. L. Julius, M. F. Hawthorne, *Inorg. Chem.* **2010**, *49*, 10627–10634; b) L. I. Zakharkin, A. I. Kovredov, V. A. Ol'Shevskaya, Zh. S. Shaugumbekova, *J. Organomet. Chem.* **1982**, *226*, 217–222; c) J. Li, C. F. Logan, M. Jones, *Inorg. Chem.* **1991**, *30*, 4866–4868; d) S. N. Mukhin, K. Z. Kabytaev, G. G. Zhigareva, I. V. Glukhov, Z. A. Starikova, V. I. Bregadze, I. P. Beletskaya, *Organometallics* **2008**, *27*, 5937–5942; e) R. M. Dziedzic, L. M. A. Saleh, J. C. Axtell, J. L. Martin, S. L. Stevens, A. T. Royappa, A. L. Rheingold, A. M. Spokoyny, *J. Am. Chem. Soc.* **2016**, *138*, 9081–9084; f) Y. Quan, Z. Xie, *Angew. Chem. Int. Ed.* **2016**, *55*, 1295–1298; *Angew. Chem.* **2016**, *128*, 1317–1320; g) Y. Quan, Z. Xie, *J. Am. Chem. Soc.* **2015**, *137*, 3502–3505; h) R. Cheng, Z. Qiu, Z. Xie, *Nat. Commun.* **2017**, *8*, https://doi.org/10.1038/ncomms14827; i) S. Erhardt, V. V. Grushin, A. H. Kilpatrick, S. A. Macgregor, W. J. Marshall, D. C. Roe, *J. Am. Chem. Soc.* **2008**, *130*, 4828–4835; j) L. I. Zakharkin, V. A. Ol'shevskaya, E. V. Vorontsov, P. V. Petrovsky, *Russ. Chem. Bull.* **1996**, *45*, 2614–2622; k) W. Jiang, C. B. Knobler, M. D. Mortimer, M. F. Hawthorne, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1332–1334; *Angew. Chem.* **1995**, *107*, 1470; l) V. I. Bregadze, *Chem. Rev.* **1992**, *92*, 209–223; m) T.-T. Xu, C.-Y. Zhang, K. Cao, J. Wu, L. Jiang, J. Li, B. Li, J. Yang, *ChemistrySelect* **2017**, *2*, 3396–3399.

[16] A. Herzog, A. Maderna, G. N. Harakas, C. B. Knobler, M. F. Hawthorne, *Chem. Eur. J.* **1999**, *5*, 1212–1217.

[17] Z. Zheng, W. Jiang, A. A. Zinn, C. B. Knobler, M. F. Hawthorne, *Inorg. Chem.* **1995**, *34*, 2095–2100.

[18] a) N. Harmgarth, D. Gräsing, P. Dröse, C. G. Hrib, P. G. Jones, V. Lorenz, L. Hilfert, S. Busse, F. T. Edelmann, *Dalton Trans.* **2014**, *43*, 5001–5013; b) L. Dostál, A. Růžička, R. Jambor, *Inorg. Chim. Acta* **2010**, *363*, 2051–2054; c)

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J.-D. Lee, H.-S. Kim, W.-S. Han, S. O. Kang, *J. Organomet. Chem.* **2010**, *695*, 463–468; d) A. S. Batsanov, M. A. Fox, T. G. Hibbert, J. A. K. Howard, R. Kivekäs, A. Laromaine, R. Sillanpää, C. Viñas, K. Wade, *Dalton Trans.* **2004**, 3822–3828; e) C. Lee, J. Lee, S. W. Lee, S. O. Kang, J. Ko, *Inorg. Chem.* **2002**, *41*, 3084–3090; f) V. I. Bregadze, G. Z. Suleimanov, V. Ts. Kampel, M. V. Petraishvili, S. G. Mamedova, P. V. Petrovskii, N. N. Godovikov, *J. Organomet. Chem.* **1984**, *263*, 131–138.

[19] a) J. R. Reiner, R. P. Alexander, H. Schroeder, *Inorg. Chem.* **1966**, *5*, 1460–1462; b) M. Yu. Antipin, N. G. Furmanova, A. I. Yanovskii, Yu. T. Struchkov, *Russ. Chem. Bull.* **1978**, *27*, 1264–1267; c) L. I. Zakharkin, N. F. Shemyakin, *Russ. Chem. Bull.* **1978**, *27*, 1267–1268; d) L. I. Zakharkin, N. F. Shemyakin, *Russ. Chem. Bull.* **1977**, *26*, 2184–2186; e) L. I. Zakharkin, N. F. Shemyakin, *Russ. Chem. Bull.* **1981**, *30*, 1525–1527; f) L. I. Zakharkin, N. F. Shemyakin, *Russ. Chem. Bull.* **1984**, *33*, 2572–2573; g) N. G. Bokii, A. I. Yanovskii, Yu. T.

Struchkov, N. F. Shemyakin, L. I. Zakharkin, *Russ. Chem. Bull.* **1978**, *27*, 328–334.

[20] A. V. Puga, F. Teixidor, R. Sillanpää, R. Kivekäs, M. Arca, G. Barberà, C. Viñas, *Chem. Eur. J.* **2009**, *15*, 9755–9763.

[21] a) S. Hermánek, *Inorg. Chim. Acta* **1999**, *289*, 20–44; b) S. Hermánek, *Chem. Rev.* **1992**, *92*, 325–362; c) F. Teixidor, C. Viñas, R. W. Rudolph, *Inorg. Chem.* **1986**, *25*, 3339–3345; d) F. Teixidor, G. Barberà, A. Vaca, R. Kivekäs, R. Sillanpää, J. Oliva, C. Viñas, *J. Am. Chem. Soc.* **2005**, *127*, 10158–10159; e) A. R. Siedle, G. M. Bodner, A. R. Garber, D. C. Beer, L. J. Todd, *Inorg. Chem.* **1974**, *13*, 2321–2324.

[22] a) P. E. Romero, W. E. Piers, S. A. Decker, D. Chau, T. K. Woo, M. Parvez, *Organometallics* **2003**, *22*, 1266–1274; b) P. A. Chase, W. E. Piers, B. O. Patrick, *J. Am. Chem. Soc.* **2000**, *122*, 12911–12912.