

**Electronic Supplementary Information (ESI) for:**

**Overcoming NHCs Neutrality: Installing Tetracarbenes on Group 13 and 14 Metals**

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**Table of Contents**

*Experimental Section: S2-S4*

*Figure S1: S5*

*References for ESI: S5*

## Experimental Section

All reactions were performed under a dry nitrogen atmosphere with the use of either a drybox or standard Schlenk techniques. Solvents were dried on an Innovative Technologies (Newburgport, MA) Pure Solv MD-7 Solvent Purification System and degassed by three freeze-pump-thaw cycles on a Schlenk line to remove O<sub>2</sub> prior to use. Acetonitrile-*d*<sub>3</sub>, benzene-*d*<sub>6</sub>, and tetrahydrofuran-*d*<sub>8</sub> were degassed by three freeze-pump-thaw cycles prior to drying over activated molecular sieves. These NMR solvents were then stored under N<sub>2</sub> in a glovebox. (B(Me)<sub>2</sub>,EtTC<sup>H</sup>)(Br)<sub>2</sub> was prepared as described previously.<sup>1</sup> All reagents were purchased from commercial vendors and used without purification. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} were recorded at ambient temperature on a Varian VNMRS 500 MHz narrow-bore broadband system. <sup>119</sup>Sn NMR spectra was recorded at ambient temperature on a Bruker Avance 400 MHz NMR. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts were referenced to the residual solvent. <sup>119</sup>Sn NMR chemical shifts are reported relative to an external standard of Sn(Me)<sub>4</sub> in acetonitrile-*d*<sub>3</sub>. All mass spectrometry analyses were conducted at the Mass Spectrometry Center located in the Department of Chemistry at the University of Tennessee. The ESI/MS analyses were performed using a QSTAR Elite quadrupole time-of-flight (QTOF) mass spectrometer with an electrospray ionization source from AB Sciex (Concord, Ontario, Canada). Mass spectrometry sample solutions of metal complexes were prepared in acetonitrile. Infrared spectra were collected on a Thermo Scientific Nicolet iS10 with a Smart iTR accessory for attenuated total reflectance. Carbon, hydrogen, and nitrogen analyses were obtained from Atlantic Microlab, Norcross, GA.

**Synthesis of (B(Me)<sub>2</sub>,EtTC<sup>H</sup>)Sn(Br)<sub>2</sub> (3a).** (B(Me)<sub>2</sub>,EtTC<sup>H</sup>)(Br)<sub>2</sub> (300 mg, 0.530 mmol) was added to a 20 mL vial with tetrahydrofuran (10 mL) and stirred at room temperature (450 rpm) for 5 min. The resulting slurry was cooled to -30 °C. <sup>n</sup>BuLi (2.50 M, 0.849 mL, 2.12 mmol) was added to the slurry and allowed to stir until the white slurry became an orange-yellow solution (~15 min.). Tin(IV) bromide (232 mg, 0.530 mmol) was then added to the resulting solution and allowed to stir at room temperature overnight. The reaction mixture was then filtered over Celite and the resulting solution was concentrated to 3 mL under reduced pressure. The colorless product was crystallized by vapor diffusion of pentane into this solution (25.9 mg, 7.2% yield). <sup>1</sup>H NMR (CD<sub>3</sub>CN, 499.74 MHz): δ 7.29 (d, *J* = 1.8 Hz, 4H), 7.16 (d, *J* = 1.7 Hz, 4H), 4.78 (s, 8H), 0.25 (s, 12H). <sup>13</sup>C NMR (CD<sub>3</sub>CN, 125.66 MHz): δ 166.86, 124.86, 122.89, 51.24, 23.04, 14.32. <sup>119</sup>Sn NMR (CD<sub>3</sub>CN, SnMe<sub>4</sub> ext., 149.16 MHz): δ -1099.4. <sup>11</sup>B NMR (CD<sub>3</sub>CN, 128.42 MHz): δ 0.5. IR (neat): 3378, 3132, 3008, 2943, 2932, 1631, 1545, 1418, 1400, 1299, 1288, 1206, 1155, 1119, 1071, 1031, 942, 828, 798, 743, 708, 669 cm<sup>-1</sup>. ESI/MS (*m/z*): [M-Br]<sup>+</sup> 608.09. Anal. Calcd for C<sub>22.5</sub>H<sub>34</sub>N<sub>8</sub>B<sub>2</sub>Br<sub>2</sub>Sn (3a·½C<sub>5</sub>H<sub>12</sub>): C, 37.71; H, 4.78; N, 15.63. Found: C, 37.03; H, 4.51; N, 15.31.

**Synthesis of (B(Me)<sub>2</sub>,EtTC<sup>H</sup>)InBr (3b).** (B(Me)<sub>2</sub>,EtTC<sup>H</sup>)(Br)<sub>2</sub> (214 mg, 0.377 mmol) was added to a 20 mL vial with tetrahydrofuran (10 mL) and stirred at room temperature (450 rpm) for 5 min. The resulting slurry was cooled to -30 °C. <sup>n</sup>BuLi (2.50 M, 0.604 mL, 1.5 mmol) was added to the slurry and allowed to stir until the white slurry became an orange-yellow solution (~15 min.).

Indium(III) bromide (134 mg, 0.377 mmol) was then added to the resulting solution and allowed to stir at room temperature overnight. The reaction mixture was then filtered over Celite and the resulting solution was concentrated to 3 mL under reduced pressure. The colorless product was isolated by vapor diffusion of pentane into this solution (21.5 mg, 10% yield). Due to decomposition of the product in most solvents, full characterization was not possible within the time constraints of **3b** degrading. A single crystal suitable for X-ray diffraction can be obtained by vapor diffusion of pentane into a benzene solution containing the product. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 499.74 MHz): δ 7.14 (d, *J* = 1.6 Hz, 4H), 5.96 (d, *J* = 1.6 Hz, 4H), 4.66-4.59 (m, 4H), 3.13-3.07 (m, 4H), 0.82 (s, 6H), 0.59 (s, 6H). IR (neat): 3390, 3115, 2929, 1630, 1546, 1455, 1415, 1394, 1371, 1291, 1260, 1217, 1150, 1109, 1078, 1038, 1019, 966, 946, 839, 797, 750, 736, 727, 697, 670, 635 cm<sup>-1</sup>. ESI/MS (*m/z*): [M-Br]<sup>+</sup> 517.11.

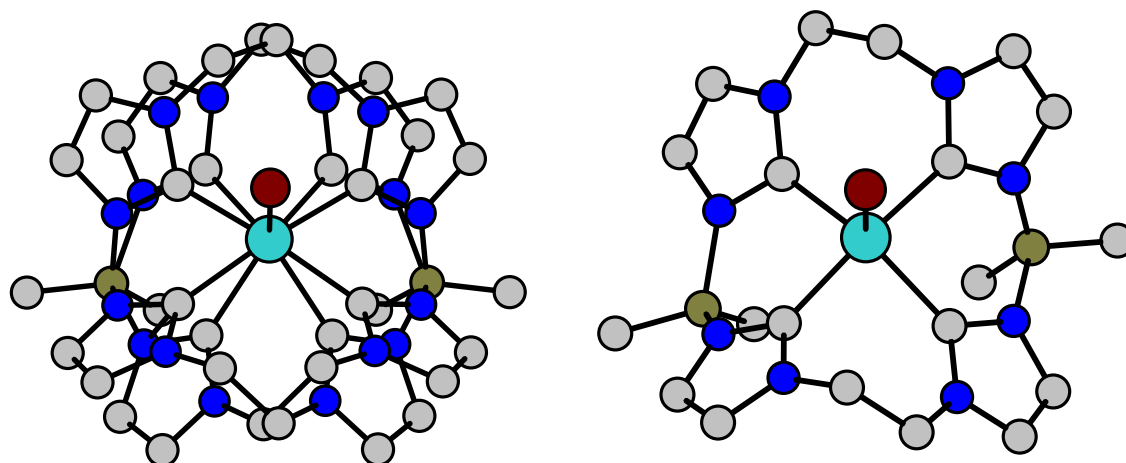
**Synthesis of (B<sup>(Me)<sub>2</sub>,Et</sup>TC<sup>H</sup>)AlBr (3c).** (B<sup>(Me)<sub>2</sub>,Et</sup>TC<sup>H</sup>)(Br)<sub>2</sub> (146 mg, 0.259 mmol) was added to a 20 mL vial with tetrahydrofuran (10 mL) and stirred at room temperature (450 rpm) for 5 min. The resulting slurry was cooled to -30 °C. <sup>n</sup>BuLi (2.50 M, 0.413 mL, 1.03 mmol) was added to the slurry and allowed to stir until the white slurry became an orange-yellow solution (~15 min.). Aluminum(III) bromide (68.9 mg, 0.259 mmol) was then added to the resulting solution and allowed to stir at room temperature overnight. The reaction mixture was then filtered over Celite and the volatiles were removed under reduced pressure resulting in a white powder. The powder was extracted with benzene (10 mL), filtered over Celite and the volatiles were again removed under reduced pressure yielding the pure white powder product (22.1 mg, 17% yield). Crystals suitable for single crystal X-ray diffraction were grown by vapor diffusion of pentane into a concentrated solution of **3c** in tetrahydrofuran. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 499.74 MHz): δ 7.13 (d, *J* = 1.6 Hz, 4H), 7.03 (d, *J* = 1.6 Hz, 4H), 5.53-5.43 (m, 4H), 4.37-4.31 (m, 4H), 0.25 (s, 6H), -0.20 (s, 6H). <sup>13</sup>C NMR (CD<sub>3</sub>CN, 125.66 MHz): δ 123.04, 121.78, 48.79, 15.63, 14.32. <sup>11</sup>B NMR (CD<sub>3</sub>CN, 128.42 MHz): δ -1.5. IR (neat): 3379, 3132, 2932, 1631, 1545, 1467, 1418, 1399, 1375, 1288, 1244, 1206, 1155, 1119, 1032, 971, 958, 942, 848, 797, 742, 730, 708, 669 cm<sup>-1</sup>. ESI/MS (*m/z*): [M-Br]<sup>+</sup> 429.20. Anal. Calcd for C<sub>20</sub>H<sub>28</sub>N<sub>8</sub>AlB<sub>2</sub>Br: C, 47.19; H, 5.54; N, 22.01. Found: C, 46.45; H, 6.18; N, 21.05.

**Synthesis of (B<sup>(Me)<sub>2</sub>,Et</sup>TC<sup>H</sup>)AlCl (3d).** (B<sup>(Me)<sub>2</sub>,Et</sup>TC<sup>H</sup>)(Br)<sub>2</sub> (294 mg, 0.520 mmol) was added to a 20 mL vial with tetrahydrofuran (10 mL) and stirred at room temperature (450 rpm) for 5 min. The resulting slurry was cooled to -30 °C. <sup>n</sup>BuLi (2.50 M, 0.832 mL, 2.08 mmol) was added to the slurry and allowed to stir until the white slurry became an orange-yellow solution (~15 min.). Aluminum(III) chloride (69.3 mg, 0.520 mmol) was then added to the resulting solution and allowed to stir at room temperature overnight. The reaction mixture was then filtered over Celite and the volatiles were removed under reduced pressure resulting in a white powder. The powder was extracted with benzene (10 mL) and filtered over Celite. By removing all solvents under reduced pressure a crude yield can be obtained (21.5 mg, 8.9% yield). Crystals suitable for single crystal X-ray diffraction were grown by vapor diffusion of pentane into a concentrated solution of

**3d** in benzene.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ , 499.74 MHz):  $\delta$  7.08 (d,  $J = 1.6$  Hz, 4H), 7.06 (d,  $J = 1.6$  Hz, 4H), 5.47-5.39 (m, 4H), 4.40-4.31 (m, 4H), 0.20 (s, 6H), -0.25 (s, 6H)

**X-ray Structure Determinations.** X-ray diffraction measurements were performed on single crystals coated with Paratone oil and mounted on glass fibers. Each crystal was frozen under a stream of  $\text{N}_2$  while data were collected on a Bruker APEX diffractometer. A matrix scan using at least 12 centered reflections was used to determine initial lattice parameters. Reflections were merged and corrected for Lorenz and polarization effects, scan speed, and background using SAINT 4.05. Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS, if necessary. Space group assignments were based upon systematic absences,  $E$  statistics, and successful refinement of the structure. The structures were solved by direct methods with the aid of successive difference Fourier maps, and were refined against all data using the SHELXTL 5.0 software package.

Structure **3c** exhibited positional disorder on the macrocyclic ligand. The macrocycle was refined using the PART instruction by splitting the macrocycle over two positions. Positional disorder prevented the anisotropic refinement of compound **3c**. Structure **3a** contains a half equivalent of pentane which was modeled at half occupancy.



**Figure S1.** Graphical representation of  $(^{B(\text{Me})_2, \text{Et}^r\text{TC}^H})\text{AlBr}$  (**3c**) as disordered (left) and with only one representative macrocycle shown (right) based on X-ray analysis. Teal, burgundy, olive, blue, and grey spheres represent Al, Br, B, N, and C. H atoms have been removed for clarity.

## References

1. H. M. Bass, S. A. Cramer, A. S. McCullough, K. J. Bernstein, C. R. Murdock and D. M. Jenkins, *Organometallics* **2013**, *32*, 2160-2167.