

Supporting Information

Selective Cage Boron/Carbon Extrusion Reaction of 13- Vertex Carborane μ -1,2-(CH₂)₃-1,2-C₂B₁₁H₁₁: Formation of *nido*-CB₁₀, *closo*-CB₁₀, and *closo*-C₂B₁₀ Species

Jian Zhang, Hoi-Shan Chan, and Zuowei Xie*

Department of Chemistry and State Key Laboratory on Synthetic Chemistry,
The Chinese University of Hong Kong,
Shatin, NT, Hong Kong, China

Table of Contents

Experimental Section	S2
Crystal Data and Summary of Data Collection and Refinement for [2][PSH], [2i][PSH], 3 and 4	S6
References	S7

Experimental Section

General Procedures. Unless otherwise noted, all experiments were performed under an atmosphere of dry dinitrogen or argon with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. CH_2Cl_2 were refluxed over CaH_2 for several days and distilled immediately prior to use. Other organic solvents were refluxed over sodium benzophenone ketyl for several days and freshly distilled prior to use. All chemicals were purchased from either Aldrich or Acros Chemical Co. and used as received unless otherwise noted. μ -1,2- $(\text{CH}_2)_3$ -1,2- $\text{C}_2\text{B}_{11}\text{H}_{11}$ (**1**) was prepared according to literature methods.¹ Infrared spectra were obtained from KBr pellets (prepared in the glovebox if the complex was hygroscopic or air sensitive) on a Perkin-Elmer 1600 Fourier transform spectrometer. The ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 spectrometer or a Bruker DPX 400Q spectrometer at 400 and 100 MHz, respectively. The ^{11}B NMR spectra were recorded on a Bruker DPX 300 spectrometer at 96 MHz, or a Bruker DPX 400 spectrometer or a Bruker DPX 400Q spectrometer at 128 MHz. All chemical shifts are reported in δ units with references to the residual protons of the deuterated solvents for proton chemical shifts, to the carbons of the deuterated solvents for carbon chemical shifts according to the literature, to external $\text{BF}_3\cdot\text{OEt}_2$ (0.0 ppm) for boron chemical shifts. Mass spectra were recorded on a Thermo Finnigan MAT 95 XL spectrometry. Elemental analyses were performed by MEDAC Ltd., U.K. or Shanghai Institute of Organic Chemistry, CAS, Shanghai, China.

Preparation of [nido- μ -7,8- $(\text{CH}_2)_3\text{CHB}(\text{OMe})_2$ -7- $\text{CB}_{10}\text{H}_{11}$][PSH] ([2][PSH]). A solution of Et_3N (1.0 mL, 726 mg, 7.2 mmol) in MeOH (10.0 mL) was added to **1** (98 mg, 0.50 mmol) at 0 °C, and the mixture was stirred at room temperature for 24 h. A

PS solution in MeOH (0.25 M, 10.0 mL, 2.5 mmol) was then added to give a white suspension in 5 min. After removal of the volatile materials, the residue was thoroughly washed with Et₂O to afford **[2][PSH]** as a white solid (214 mg, 90%). X-ray-quality crystals were obtained by recrystallization from THF. Found: C, 53.58; H, 9.14; N, 5.82. Calc. for C₂₁H₄₃B₁₁N₂O₂: C, 53.16; H, 9.13; N, 5.90%. ¹H NMR (400 MHz, CD₂Cl₂): δ = 8.03 (dd, *J*₁ = 8.3 Hz, *J*₂ = 0.9 Hz, 2H, C₁₀H₆), 7.79 (dd, *J*₁ = 7.6 Hz, *J*₂ = 1.0 Hz, 2H, C₁₀H₆), 7.72 (t, *J* = 7.9 Hz, 2H, C₁₀H₆), 3.49 (s, 6H, OCH₃), 3.19 (d, *J* = 2.7 Hz, 12H, NCH₃), 2.22 (m, 1H, δ-CH₂), 1.61 (m, 1H, δ-CH₂), 1.56 (m, 1H, γ-CH₂), 1.50 (m, 1H, β-CH₂), 1.33 (m, 1H, β-CH₂), 1.19 (m, 1H, γ-CH₂), 0.80 (br, 1H, α-CH), -3.20 (br, 2H, bridging H). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ = 143.9, 136.0, 130.2, 127.7, 121.6, 119.0 (C₁₀H₆), 52.0 (br, cage C), 51.4 (OCH₃), 47.0 (NCH₃), 39.0 (δ-CH₂), 28.3 (γ-CH₂), 25.6 (β-CH₂), 11.1 (br, α-CH). ¹¹B NMR (128 MHz, CD₂Cl₂): δ = 32.0 (s, 1B), -2.1 (s, 1B), -5.3 (d, *J*_{B,H} = 142 Hz, 1B), -10.1 (d, *J*_{B,H} = 119 Hz, 3B), -23.4 (d, *J*_{B,H} = 132 Hz, 1B), -24.5 (d, *J*_{B,H} = 162 Hz, 1B), -25.7 (d, *J*_{B,H} = 140 Hz, 1B), -30.4 (d, *J*_{B,H} = 142 Hz, 1B), -34.4 (d, *J*_{B,H} = 127 Hz, 1B). IR (KBr): ν_{max}/cm⁻¹ 2519 (vs, BH).

Preparation of [nido-μ-η:η:η-7,8,10-(CH₂)₃CHB(OMe)-7-CB₁₀H₁₀][PSH] ([2i][PSH]). A MeOH solution (5 mL) of PS (118 mg, 0.55 mmol) was added to **1** (98 mg, 0.50 mmol) with stirring for 5 min to give a white suspension. After removal of the solvent, the residue was thoroughly washed with Et₂O to afford **[2i][PSH]** as a white solid (199 mg, 90%). X-ray-quality crystals were obtained by recrystallization from THF. Found: C, 54.40; H, 8.60; N, 6.53. Calc. for C₂₀H₃₉B₁₁N₂O: C, 54.29; H, 8.88; N, 6.33%. ¹H NMR (400 MHz, CD₂Cl₂): δ = 8.04 (d, *J* = 8.2 Hz, 2H, C₁₀H₆), 7.85 (d, *J* = 7.6 Hz, 2H, C₁₀H₆), 7.74 (dd, av. *J* = 7.9 Hz, 2H, C₁₀H₆), 3.70 (s, 3H, OCH₃), 3.20 (d, *J* = 2.4 Hz, 12H, NCH₃), 2.45 (m, 1H, δ-CH₂), 2.30 (m, 1H, β-CH₂),

1.74 (m, 1H, δ -CH₂), 1.66 (m, 1H, γ -CH₂), 1.59 (br, 1H, α -CH), 1.32 (m, 1H, γ -CH₂), 1.16 (m, 1H, β -CH₂). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ = 143.8, 135.8, 130.1, 127.5, 121.7, 118.8 (C₁₀H₆), 104.0 (cage C), 55.4 (OCH₃), 46.8 (NCH₃), 37.4 (δ -CH₂), 29.8 (β -CH₂), 27.1 (γ -CH₂), 15.7 (α -CH). ¹¹B NMR (96 MHz, CD₂Cl₂): δ = 42.5 (s, 1B), 20.4 (d, $J_{B,H}$ = 144 Hz, 1B), 0.2 (d, $J_{B,H}$ = 166 Hz, 1B), -2.5 (d, $J_{B,H}$ = 132 Hz, 1B), -9.9 (d, $J_{B,H}$ = 128 Hz, 1B), -12.0 (d, $J_{B,H}$ = 139 Hz, 1B), -14.0 (d, $J_{B,H}$ \approx 106 Hz, 1B), -14.6 (d, $J_{B,H}$ = 115 Hz, 2B), -18.3 (d, $J_{B,H}$ = 115 Hz, 1B), -21.3 (d, $J_{B,H}$ = 117 Hz, 1B). IR (KBr): $\nu_{\max}/\text{cm}^{-1}$ 2514 (vs, BH).

Preparation of μ -2,4-(CH₂)₃CHBH(Py)₂-2-CB₁₀H₉ (3). Compound **1** (98 mg, 0.50 mmol) was slowly added to Py (5 mL) at -30 °C. The resulting dark blue solution was stirred at room temperature overnight. After removal of the solvent, the residue was washed with THF to give **3** as a white powder (200 mg, 56%). X-ray-quality crystals were obtained by recrystallization from DMSO/MeOH. Found: C, 50.59; H, 7.85; N, 7.57. Calc. for C₁₅H₂₇B₁₁N₂: C, 50.85; H, 7.68; N, 7.91%. ¹H NMR (400 MHz, DMSO-*d*₆): δ = 9.07 (d, J = 5.4 Hz, 2H, C₅H₅N), 9.00 (d, J = 5.4 Hz, 2H, C₅H₅N), 8.35 (t, J = 7.6 Hz, 1H, C₅H₅N), 8.32 (t, J = 7.7 Hz, 1H, C₅H₅N), 7.90 (t, J = 7.0 Hz, 2H, C₅H₅N), 7.84 (t, J = 7.0 Hz, 2H, C₅H₅N), 2.53 (m, 1H, δ -CH₂), 2.28 (m, 1H, δ -CH₂), 1.69 (m, 1H, γ -CH₂), 1.28 (m, 1H, γ -CH₂), 0.94 (m, 2H, β -CH₂), 0.52 (m, 1H, α -CH). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ = 147.7, 146.3, 143.9, 143.7, 127.3, 126.4 (C₅H₅N), 72.8 (cage C), 34.8 (δ -CH₂), 27.1 (β -CH₂), 26.5 (γ -CH₂), 14.9 (α -CH). ¹¹B NMR (128 MHz, DMSO-*d*₆): δ = 1.9 (br, unresolved, 1B), -10.2 (br, 9B), -15.5 (br, 1B). IR (KBr): $\nu_{\max}/\text{cm}^{-1}$ 2492 (vs, BH).

Preparation of 4-B(bipy)- μ -1,2-(CH₂)₃-1,2-C₂B₁₀H₉ (4). To a toluene (10 mL) solution of **1** (98 mg, 0.50 mmol) was added bipyridine (78 mg, 0.50 mmol) and the mixture was heated at 60 °C for 72 h in a sealed tube to give a red solution. After

filtration, toluene was removed and 1 mL of CH₂Cl₂ was added to dissolve the red solid, to which was added a 50 mL of *n*-hexane. After filtration and removal of the volatile materials, the residue was washed with a minimum amount of Et₂O to give **4** as a red solid (104 mg, 59%). X-ray-quality crystals were obtained by recrystallization from Et₂O. ¹H NMR (400 MHz, CD₂Cl₂): δ = 8.33 (d, *J* = 7.3 Hz, 2H, C₁₀H₈N₂B), 7.49 (dt, *J* = 9.1 Hz, 2H, C₁₀H₈N₂B), 6.43 (m, 2H, C₁₀H₈N₂B), 6.30 (m, 2H, C₁₀H₈N₂B), 2.53 (m, 2H, CH₂), 2.38 (m, 3H, CH₂), 2.20 (m, 1H, CH₂). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ = 129.0, 120.4, 118.4, 115.1, 111.2 (aromatic C), 86.6 (cage C), 35.3, 35.1 (CCH₂), 32.6 (CCH₂CH₂). ¹¹B NMR (128 MHz, CD₂Cl₂): δ = 19.7 (brs, 1B), -6.2 (br, 2B), -7.0 (br, 1B), -7.4 (br, 1B), -8.3 (br, 1B), -8.9 (br, 1B), -11.1 (br, 4B). IR (KBr): ν_{max}/cm⁻¹ 2569 (vs, BH). HRMS (EI): *m/z* calcd for C₁₅H₂₃¹¹B₉¹⁰B₂N₂ [M]⁺: 350.2952; Found: 350.2960.

X-ray Structure Determination. All single crystals were immersed in Paraton-N oil and sealed under N₂ in thin-walled glass capillaries. Data were collected on a Bruker SMART 1000 CCD diffractometer or a Bruker AXS kappa Apex II Duo diffractometer using Mo-Kα radiation at 173K for [2][PSH], 123K for [2i][PSH] and **4**, and 296K for **3**, respectively. An empirical absorption correction was applied using the SADABS program.² All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares calculations on *F*² using the SHELXTL program package.³ Most of the cage hydrogen atoms were located from different Fourier syntheses. All other hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinements were given in Table S1.

Table S1. Crystal Data and Summary of Data Collection and Refinement for [2][PSH], [2i][PSH], 3 and 4.

compd. No.	[2][PSH]	[2i][PSH]	3	4
formula	C ₂₁ H ₄₃ B ₁₁ N ₂ O ₂	C ₂₀ H ₃₉ B ₁₁ N ₂ O	C ₁₅ H ₂₇ B ₁₁ N ₂	C ₁₅ H ₂₃ B ₁₁ N ₂
crystal size (mm)	0.50 x 0.30 x 0.20	0.40 x 0.30 x 0.20	0.40 x 0.30 x 0.20	0.40 x 0.30 x 0.20
fw	474.5	442.4	354.3	350.3
crystal system	triclinic	monoclinic	orthorhombic	orthorhombic
space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>Pna</i> 2 ₁
<i>a</i> , Å	8.425(1)	15.573(1)	9.242(2)	24.306(2)
<i>b</i> , Å	10.907(1)	9.830(1)	12.376(2)	16.579(1)
<i>c</i> , Å	15.173(1)	18.031(1)	18.093(3)	14.290 (1)
α , deg	85.36(1)	90	90	90
β , deg	86.94(1)	104.10(1)	90	90
γ , deg	83.34(1)	90	90	90
<i>V</i> , Å ³	1378.9(1)	2677.2(2)	2069.5(6)	5758.3(7)
<i>Z</i>	2	4	4	12
<i>D</i> _{calcd} , Mg/m ³	1.143	1.098	1.137	1.212
radiation (λ), Å	Mo K α	Mo K α	Mo K α	Mo K α
	(0.71073)	(0.71073)	(0.71073)	(0.71073)
2 θ max, deg	50.5	50.0	50.5	50.5
μ , mm ⁻¹	0.065	0.060	0.058	0.062
<i>F</i> (000)	508	944	744	2184
no. of obsd	4967	4716	3724	10305
no. of params	337	307	262	757
goodness of fit	1.092	1.040	0.971	1.038
R1	0.052	0.099	0.058	0.082
wR2	0.063	0.115	0.164	0.148

References

1. L. Deng, H.-S. Chan and Z. Xie, *J. Am. Chem. Soc.*, 2006, **128**, 5219-5230.
2. G. M. Sheldrick, *SADABS: Program for Empirical Absorption Correction of Area Detector Data*, (1996) University of Göttingen, Germany.
3. G. M. Sheldrick, *SHELXTL 5.10 for Windows NT: Structure Determination Software Programs*, (1997) Bruker Analytical X-ray systems, Inc., Madison, Wisconsin, USA.