Supporting Information

Reaction of $N$-Heterocyclic Carbenes with 13-Vertex *closo*-Carboranes: Synthesis and Structural Characterization of Zwitterionic Salts of 13-Vertex *nido*-Carboranes

Fangrui Zheng and Zuowei Xie*

*Department of Chemistry, Center of Novel Functional Molecules and State Key Laboratory of Synthetic Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China

E-mail: zxie@cuhk.edu.hk

Table of Contents

General Procedures S-2
Experimental Section S-2
References S-18
**General Procedures.** All experiments were performed under an atmosphere of dry argon with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents were refluxed over sodium benzophenone ketyl for several days and freshly distilled prior to use. CH₂Cl₂ was refluxed over CaH₂ for several days and distilled immediately before use. All chemicals were purchased from either Aldrich or Acros Chemical Co. and used as received unless otherwise noted. 1,2-(CH₂)₃-1,2-C₂B₁₁H₁₁, ¹, 1,2-(CH₂)₄-1,2-C₂B₁₁H₁₁, ² 1,2-(CH₂)₃-3-Ph-1,2-C₂B₁₁H₁₀, ¹ and 1,2-(CH₂)₄-3-Ph-1,2-C₂B₁₁H₁₀ ² were prepared according to literature methods. Infrared spectra were obtained from KBr pellets on a Perkin-Elmer 1600 Fourier transform spectrometer. ¹H NMR spectra were recorded on either a Bruker DPX 300 spectrometer at 300 MHz or a Bruker DPX 400 spectrometer at 400 MHz. ¹³C{¹H} NMR spectra were recorded on either a Bruker DPX 300 spectrometer at 75 MHz or a Bruker DPX 400 spectrometer at 100 MHz. ¹¹B NMR spectra were recorded on either a Bruker DPX 300 spectrometer at 96 MHz or a Bruker DPX 400 spectrometer at 128 MHz. All chemical shifts were reported in δ units with references to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts, to external BF₃·OEt₂ (0.00 ppm) for boron chemical shifts. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry, CAS, China.

**Preparation of 2,8-(CH₂)₃-9-(2"-{1',3'-[2'',6''-iPr₂(C₆H₃)]₂-1',3'-N₂C₃H₂})-2,8-C₂B₁₁H₁₁ (1).**

A THF solution (5 mL) of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (78 mg, 0.2 mmol) was slowly added to a stirring solution of 1,2-(CH₂)₃-1,2-C₂B₁₁H₁₁ (39 mg, 0.2 mmol) in THF (5 mL) at room temperature, and the mixture was stirred for 1 d. After removal of the solvent, the residue was subject to chromatographic separation (SiO₂, 300-400 mesh, n-hexane/CH₂Cl₂ 3:1), giving 1 as a white solid (96 mg, 82%). X-ray-quality crystals were obtained by recrystallization.
from acetone. $^1$H NMR (acetone-$d_6$): $\delta$ 8.02 (s, 2H, imidazolium NCH), 7.56 (t, $J$ = 7.8 Hz, 2H, C$_6$H$_3$), 7.44 (d, $J$ = 7.6 Hz, 2H, C$_6$H$_3$), 7.37 (d, $J$ = 7.6 Hz, 2H, C$_6$H$_3$), 2.72 (m, 2H, CH(CH$_3$)$_2$), 2.58 (m, 2H, CH(CH$_3$)$_2$), 2.52 (m, 1H, CH$_2$), 2.14 (m, 1H, CH$_2$), 1.61 (m, 1H, CH$_2$), 1.46 (d, $J$ = 6.8 Hz, 6H, CH(CH$_3$)$_2$), 1.40 (m, 3H, CH$_2$), 1.34 (d, $J$ = 6.8 Hz, 6H, CH(CH$_3$)$_2$), 1.20 (d, $J$ = 6.8 Hz, 6H, CH(CH$_3$)$_2$), 1.15 (d, $J$ = 6.8 Hz, 6H, CH(CH$_3$)$_2$). $^{13}$C{$^1$H} NMR (acetone-$d_6$): $\delta$ 146.7, 146.3, 134.4, 132.0, 127.1, 125.1, 124.9 (C$_6$H$_3$ & imidazolium NCH), 76.0 ($v_{1/2}$ = 40 Hz), 48.5 ($v_{1/2}$ = 36 Hz) (cage C), 44.3, 35.6, 21.3 (CH$_2$), 30.0, 29.9 (CH(CH$_3$)$_2$), 26.3, 26.2, 22.4, 22.2 (CH(CH$_3$)$_2$), the imidazolium NCN carbon was not observed. $^{11}$B NMR (acetone-$d_6$): $\delta$ 7.5 (d, $J$ = 142 Hz, 1B), -1.9 (d, $J$ = 64 Hz, 1B), -3.5 (d, $J$ = 151 Hz, 2B), -9.0 (d, $J$ = 131 Hz, 1B), -16.7 (d, $J$ = 148 Hz, 2B), -18.4 (d, $J$ = 211 Hz, 2B), -23.5 (d, $J$ = 132 Hz, 1B), -35.2 (d, $J$ = 132 Hz, 1B). IR (KBr, cm$^{-1}$): $\nu$$_{BH}$ 2545 (vs). HRMS: $m/z$ calcd for C$_{32}$H$_{53}$B$_{11}$N$_2$ [M – 2H]$^+$: 582.5160. Found: 582.5183. Anal. Calcd for C$_{32}$H$_{53}$B$_{11}$N$_2$: C, 65.73; H, 9.14; N, 4.79. Found: C, 65.77; H, 9.13; N, 4.78.

Figure S1. Molecular structure of 2,8-(CH$_2$)$_3$-9-(2’-{1’,3’-[2’’,6’’-Pr$_2$(C$_6$H$_3$)]$_2$-1’,3’-N$_2$C$_3$H$_2$})-2,8-C$_2$B$_{11}$H$_{11}$ (1).

Preparation of 2,8-(CH$_2$)$_3$-9-(2’-{1’,3’-[2’’,4’’,6’’-Me$_3$(C$_6$H$_2$)]$_2$-1’,3’-N$_2$C$_3$H$_2$})-2,8-C$_2$B$_{11}$H$_{11}$ (2). This complex was prepared as a white solid from 1,2-(CH$_2$)$_3$-1,2-C$_2$B$_{11}$H$_{11}$ (39 mg, 0.2 mmol)
and 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (61 mg, 0.2 mmol) in THF using the same procedure reported for 1: yield 80 mg (80%). $^1$H NMR (acetone-$d_6$): δ 7.82 (s, 2H, imidazolium NCH), 7.16 (s, 2H, C$_6$H$_2$), 7.08 (s, 2H, C$_6$H$_2$), 2.37 (s, 6H, CH$_3$), 2.32 (m, 1H, CH$_2$), 2.21 (s, 6H, CH$_3$), 2.12 (m, 1H, CH$_2$), 2.08 (s, 6H, CH$_3$), 1.59 (m, 1H, CH$_2$), 1.34 (m, 2H, CH$_2$), 0.76 (m, 1H, CH$_2$). $^{13}$C($^1$H) NMR (acetone-$d_6$): δ 141.3, 136.8, 136.1, 134.3, 130.2, 130.0, 125.7 (C$_6$H$_2$ & imidazolium NCH), 77.0 (v$_{1/2}$ = 38 Hz), 48.5 (v$_{1/2}$ = 36 Hz) (cage C), 44.1, 35.0, 21.4 (CH$_2$), 21.1, 18.2, 18.1 (CH$_3$), the imidazolium NCN carbon was not observed. $^{11}$B NMR (acetone-$d_6$): δ 6.8 (d, J = 163 Hz, 1B), -2.8 (d, J = 74 Hz, 1B), -4.9 (d, J = 144 Hz, 1B), -9.5 (d, J = 124 Hz, 2B), -16.3 (d, J = 131 Hz, 2B), -18.8 (d, J = 128 Hz, 2B), -23.8 (d, J = 133 Hz, 1B), -35.4 (d, J = 138 Hz, 1B). IR (KBr, cm$^{-1}$): ν$_{BH}$ 2529 (vs). HRMS: m/z calcd for C$_{26}$H$_{41}$B$_{11}$N$_2$ [M]$^+$: 500.4374. Found: 500.4368. Anal. Calcd for C$_{26}$H$_{41}$B$_{11}$N$_2$: C, 62.39; H, 8.26; N, 5.60. Found: C, 62.39; H, 8.28; N, 5.31.

**Preparation of 2,8-(CH$_2$)$_3$-9-(2’-{1’,3’-[2'',6''-Pr$_2$(C$_6$H$_3$)]$_2$-1’,3’-N$_2$C$_3$H$_4$})]-2,8-C$_2$B$_{11}$H$_{11}$ (3).**

A THF solution (5 mL) of 1,3-bis(2,6-di-i-propylphenyl)imidazolidin-2-ylidene (78 mg, 0.2 mmol) was slowly added to a stirring solution of 1,2-(CH$_2$)$_3$-1,2-C$_2$B$_{11}$H$_{11}$ (39 mg, 0.2 mmol) in THF (5 mL) at room temperature, and the mixture was heated at 50 °C for 36 h in a sealed tube to give a brown solution. After removal of the solvent, the residue was subject to chromatographic separation (SiO$_2$, 300-400 mesh, n-hexane/CH$_2$Cl$_2$ 3:1), giving 3 as a white solid (92 mg, 78%). X-ray-quality crystals were obtained by recrystallization from acetone. $^1$H NMR (acetone-$d_6$): δ 7.42 (t, J = 7.7 Hz, 2H, C$_6$H$_3$), 7.34 (d, J = 7.2 Hz, 2H, C$_6$H$_3$), 7.29 (d, J = 7.2 Hz, 2H, C$_6$H$_3$), 4.44 (brs, 4H, imidazolium NCH$_2$), 3.30 (m, 2H, CH(CH$_3$)$_2$), 3.24 (m, 2H, CH(CH$_3$)$_2$), 2.62 (m, 1H, CH$_2$), 2.15 (m, 1H, CH$_2$), 1.63 (m, 1H, CH$_2$), 1.52 (d, J = 6.2 Hz, 6H, CH(CH$_3$)$_2$), 1.47 (m, 2H, CH$_2$), 1.42 (d, J = 6.2 Hz, 6H, CH(CH$_3$)$_2$), 1.31 (d, J = 6.2 Hz, 6H, CH(CH$_3$)$_2$), 1.30 (m, 1H, CH$_2$), 1.29 (d, J = 6.2 Hz, 1B), -2.8 (d, J = 74 Hz, 1B), -4.9 (d, J = 144 Hz, 1B), -9.5 (d, J = 124 Hz, 2B), -16.3 (d, J = 131 Hz, 2B), -18.8 (d, J = 128 Hz, 2B), -23.8 (d, J = 133 Hz, 1B), -35.4 (d, J = 138 Hz, 1B). IR (KBr, cm$^{-1}$): ν$_{BH}$ 2529 (vs). HRMS: m/z calcd for C$_{26}$H$_{41}$B$_{11}$N$_2$ [M]$^+$: 500.4374. Found: 500.4368. Anal. Calcd for C$_{26}$H$_{41}$B$_{11}$N$_2$: C, 62.39; H, 8.26; N, 5.60. Found: C, 62.39; H, 8.28; N, 5.31.
Hz, 6H, CH(CH₃)₂). ¹³C{¹H} NMR (acetone-δ₆): δ 147.5, 147.2, 134.9, 131.1, 125.5 (C₆H₃), 76.3
(v½ = 36 Hz), 51.0 (v½ = 36 Hz) (cage C), 55.0 (imidazolium NCH₂), 44.4, 36.2, 21.4 (CH₂), 26.9,
26.8, 23.3, 23.1 (CH(CH₃)₂), the imidazolium NCN carbon was not observed. ¹¹B NMR
(acetone-δ₆): δ 8.0 (d, J = 137 Hz, 1B), -1.9 (d, J = 52 Hz, 1B), -2.5 (d, J = 104 Hz, 2B), -9.1 (d, J =
131 Hz, 1B), -16.3(d, J = 113 Hz, 1B), -17.1 (d, J = 125 Hz, 2B), -17.9 (d, J = 115 Hz, 1B), -23.2
(d, J = 130 Hz, 1B), -34.0 (d, J = 134 Hz, 1B). IR (KBr, cm⁻¹): νBH 2534 (vs). HRMS: m/z calcd for
4.77. Found: C, 65.51; H, 9.07; N, 4.58.

*Figure S2.* Molecular structure of 2,8-(CH₂)₃-12-(2'-{1',3'-[2''',6'''-Pr₂(C₆H₃)]₂-1',3'-
N₂C₃H₄})-2,8-C₂B₁₁H₁₁ (3).

**Preparation of 2,8-(CH₂)₃-9-(2'-{1',3'-[2''',6'''-Me₃(C₆H₂)]₂-1',3'-N₂C₃H₄})-2,8- C₂B₁₁H₁₁
(4).** A THF solution (5 mL) of 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2- ylidene (61
mg, 0.2 mmol) was slowly added to a stirring solution of 1,2-(CH₂)₃-1,2-C₂B₁₁H₁₁ (39 mg, 0.2
mmol) in THF (5 mL) at room temperature, and the mixture was stirred for 3 d. After removal of
the solvent, the residue was subject to chromatographic separation (SiO₂, 300-400 mesh, 
n-hexane/CH₂Cl₂ 3:1), giving 4 as a white solid (81 mg, 81%). X-ray-quality crystals were obtained
by recrystallization from acetone. $^1$H NMR (acetone-$d_6$): $\delta$ 7.05 (s, 2H, C$_6$H$_2$), 6.99 (s, 2H, C$_6$H$_2$), 4.35 (m, 4H, imidazolium NCH$_2$), 2.46 (s, 6H, CH$_3$), 2.42 (m, 1H, CH$_2$), 2.35 (s, 6H, CH$_3$), 2.30 (s, 6H, CH$_3$), 2.14 (m, 1H, CH$_2$), 1.58 (m, 1H, CH$_2$), 1.34 (m, 2H, CH$_2$), 0.79 (m, 1H, CH$_2$). $^{13}$C{$^1$H}$^1$ NMR (acetone-$d_6$): $\delta$ 140.3, 137.5, 136.8, 134.6, 130.6, 130.3 (C$_6$H$_2$), 52.0 (imidazolium NCH$_2$), 44.2, 35.3, 21.5 (CH$_2$), 21.1, 18.6, 18.5 (CH$_3$), the imidazolium NCN and cage C atoms were not observed. $^{11}$B NMR (acetone-$d_6$): $\delta$ 7.7 (d, $J = 142$ Hz, 1B), -2.1 (d, $J = 84$ Hz, 1B), -3.2 (d, $J = 165$ Hz, 1B), -6.6 (d, $J = 115$ Hz, 1B), -9.5 (d, $J = 131$ Hz, 1B), -16.1 (d, $J = 147$ Hz, 2B), -17.4 (d, $J = 114$ Hz, 1B), -18.1 (d, $J = 143$ Hz, 1B), -22.5 (d, $J = 143$ Hz, 1B), -34.3 (d, $J = 143$ Hz, 1B). IR (KBr, cm$^{-1}$): $\nu_{B}$H 2530 (vs). HRMS: m/z calcd for C$_{26}$H$_{43}$B$_{11}$N$_2$ [M]$^+$: 502.4531. Found: 500.4522.

Anal. Calcd for C$_{26}$H$_{43}$B$_{11}$N$_2$: C, 62.14; H, 8.62; N, 5.57. Found: C, 61.93; H, 8.64; N, 5.28.

Figure S3. Molecular structure of 2,8-(CH$_2$)$_3$-9-(2’-{1’,3’-[2’’,4’’,6’’-Me$_3$(C$_6$H$_2$)]$_2$-1’,3’-N$_2$C$_3$H$_4$})-2,8-C$_2$B$_{11}$H$_{11}$ (4).

Preparation of 2,8-(CH$_2$)$_3$-9-(2’-{1’,3’-[2’’,6’’-Pr$_2$(C$_6$H$_3$)]$_2$-1’,3’-N$_2$C$_3$H$_2$)-12-Ph-2,8-C$_2$B$_{11}$H$_{10}$ (5). A THF solution (5 mL) of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (78 mg, 0.2 mmol) was slowly added to a stirring solution of 1,2-(CH$_2$)$_3$-3-Ph-1,2-C$_2$B$_{11}$H$_{10}$ (55 mg, 0.2 mmol) in THF (5 mL) at room temperature, and the mixture was heated at 50 °C for 1 d in a sealed tube to give a brown solution. After removal of the solvent, the residue was subject to
chromatographic separation (SiO₂, 300-400 mesh, n-hexane/CH₂Cl₂ 5:2), giving 5 as a white solid (91 mg, 69%). X-ray-quality crystals were obtained by recrystallization from acetone. ¹H NMR (acetone-d₆): δ 8.06 (s, 2H, imidazolium NCH), 7.54 (t, J = 8.0 Hz, 2H, C₆H₃), 7.45 (d, J = 7.6 Hz, 2H, C₆H₃), 7.37 (d, J = 7.6 Hz, 2H, C₆H₃), 7.32 (m, 2H, C₆H₃), 7.12 (m, 3H, C₆H₃), 2.75 (m, 2H, CH(CH₃)₂), 2.61 (m, 2H, CH(CH₃)₂), 2.51 (m, 1H, CH₂), 2.14 (m, 1H, CH₂), 1.49 (d, J = 6.8 Hz, 6H, CH(CH₃)₂), 1.38 (d, J = 6.8 Hz, 6H, CH(CH₃)₂), 1.30 (m, 3H, CH₂), 1.22 (d, J = 6.8 Hz, 6H, CH(CH₃)₂), 1.17 (d, J = 6.8 Hz, 6H, CH(CH₃)₂), 0.75 (m, 1H, CH₂). ¹³C{¹H} NMR (acetone-d₆): δ 146.8, 146.3, 134.5, 133.6, 132.0, 127.6, 127.3, 127.1, 125.0, 124.9 (C₆H₅ & C₆H₃ & imidazolium NCH), 77.5 (v₁/₂ = 36 Hz), 46.0 (v₁/₂ = 36 Hz) (cage C), 44.2, 32.2, 21.3 (CH₂), 30.0, 26.3, 26.2, 22.5, 22.2 (CH(CH₃)₂), the imidazolium NCN carbon was not observed. ¹¹B NMR (acetone-d₆): δ 13.9 (s, 1B, BPh), -1.4 (d, J = 55 Hz, 1B), -2.1 (d, J = 141 Hz, 1B), -8.5 (d, J = 124 Hz, 2B), -15.9 (d, J = 143 Hz, 2B), -16.8 (d, J = 151 Hz, 2B), -21.4 (d, J = 138 Hz, 1B), -35.4 (d, J = 138 Hz, 1B).


**Figure S4.** Molecular structure of 2,8-(CH₂)₃-9-(2’-{1’,3’-[2’’,6’’-iPr₂(C₆H₃)]₂-1’,3’-N₂C₃H₂}-12-Ph-2,8-C₂B₁₁H₁₁ (5).
Preparation of 2,8-(CH$_2$)$_3$-9-(2’-{1’,3’-[2’’’,4’’’-Me$_3$(C$_6$H$_2$)]$_2$-1’,3’-N$_2$C$_3$H$_2$})-12-Ph-2,8-C$_2$B$_{11}$H$_{10}$ (6). A THF solution (5 mL) of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (61 mg, 0.2 mmol) was slowly added to a stirring solution of 1,2-(CH$_2$)$_3$-3-Ph-1,2-C$_2$B$_{11}$H$_{10}$ (55 mg, 0.2 mmol) in THF (5 mL) at room temperature, and the mixture was stirred for 3 d. After removal of the solvent, the residue was subject to chromatographic separation (SiO$_2$, 300-400 mesh, n-hexane/CH$_2$Cl$_2$ 2:5), giving 6 as a white solid (77 mg, 80%). $^1$H NMR (acetone-$d_6$): $\delta$ 7.84 (s, 2H, imidazolium NCH), 7.38 (m, 2H, aromatic CH), 7.14 (m, 5H, aromatic CH), 7.07 (s, 2H, aromatic CH), 2.36 (s, 6H, CH$_3$), 2.31 (m, 1H, CH$_2$), 2.24 (s, 6H, CH$_3$), 2.14 (m, 1H, CH$_2$), 2.09 (s, 6H, CH$_3$), 1.23 (m, 3H, CH$_2$), 0.45 (m, 1H, CH$_2$). $^{13}$C{$^1$H} NMR (acetone-$d_6$): $\delta$ 141.3, 136.8, 136.1, 134.4, 133.8, 130.5, 130.2, 130.0, 127.6, 127.3, 125.8 (C$_6$H$_5$ & C$_6$H$_2$ & imidazolium NCH), 77.0 ($v_{1/2}$ = 36 Hz), 48.0 ($v_{1/2}$ = 36 Hz) (cage C), 44.1, 31.6, 21.4 (CH$_2$), 21.1, 18.3, 18.1 (CH$_3$), the imidazolium NCN carbon was not observed. $^{11}$B NMR (acetone-$d_6$): $\delta$ 13.5 (s, 1B, BPh), -2.3 (d, $J$ = 49 Hz, 1B), -3.5 (d, $J$ = 127 Hz, 1B), -9.2 (d, $J$ = 133 Hz, 2B), -15.4 (d, $J$ = 132 Hz, 3B), -18.1 (d, $J$ = 176 Hz, 1B), -21.4 (d, $J$ = 125 Hz, 1B), -35.4 (d, $J$ = 139 Hz, 1B). IR (KBr, cm$^{-1}$): $\nu _{BH}$ 2531 (vs). HRMS: m/z calcd for C$_{32}$H$_{45}$B$_{11}$N$_2$ [M]$^+$: 576.4690. Found: 576.4703. Anal. Calcd for C$_{32}$H$_{45}$B$_{11}$N$_2$: C, 66.65; H, 7.87; N, 4.86. Found: C, 66.82; H, 8.00; N, 4.41.

Preparation of 2,8-(CH$_2$)$_3$-9-(2’-{1’,3’-[2’’’,6’’’-Pr$_2$(C$_6$H$_3$)]$_2$-1’,3’-N$_2$C$_3$H$_2$})-12-Ph-2,8-C$_2$B$_{11}$H$_{10}$ (7). A THF solution (5 mL) of 1,3-bis(2,6-di-i-propylphenyl)imidazolidin-2-ylidene (78 mg, 0.2 mmol) was slowly added to a stirring solution of 1,2-(CH$_2$)$_3$-3-Ph-1,2-C$_2$B$_{11}$H$_{10}$ (55 mg, 0.2 mmol) in THF (5 mL) at room temperature, and the mixture was heated at 60 °C for 12 h in a sealed tube to give a brown solution. After removal of the solvent, the residue was subject to chromatographic separation (SiO$_2$, 300-400 mesh, n-hexane/CH$_2$Cl$_2$ 5:2), giving 7 as a white solid.
(86 mg, 65%). $^1$H NMR (acetone-$d_6$): $\delta$ 7.40 (t, $J = 7.6$ Hz 2H, aromatic CH), 7.30 (m, 6H, aromatic CH), 7.11 (m, 3H, aromatic CH), 4.47 (s, 4H, imidazolium NCH$_2$), 3.35 (m, 2H, CH(CH$_3$)$_2$), 3.27 (m, 2H, CH(CH$_3$)$_2$), 2.60 (m, 1H, CH$_2$), 2.15 (m, 1H, CH$_2$), 1.54 (d, $J = 6.7$ Hz, 6H, CH(CH$_3$)$_2$), 1.47 (d, $J = 6.7$ Hz, 6H, CH(CH$_3$)$_2$), 1.39 (m, 1H, CH$_2$), 1.33 (d, $J = 6.7$ Hz, 6H, CH(CH$_3$)$_2$), 1.31 (d, $J = 6.7$ Hz, 6H, CH(CH$_3$)$_2$), 1.26 (m, 2H, CH$_2$), 1.05 (m, 1H, CH$_2$). $^{13}$C{$^1$H}NMR (acetone-$d_6$): $\delta$ 147.6, 147.2, 135.0, 133.5, 131.1, 127.6, 127.2, 125.4 (C$_6$H$_5$ & C$_6$H$_3$), 55.0 (imidazolium NCN), 44.3, 32.7, 21.3 (CH$_2$), 26.9, 26.8, 23.4, 23.1 (CH(CH$_3$)$_2$), the imidazolium NCN and cage C atoms were not observed. $^{11}$B NMR (acetone-$d_6$): $\delta$ 13.2 (s, 1B, BPh), -2.0 (d, $J = 108$ Hz, 2B), -2.6 (d, $J = 65$ Hz, 1B), -10.0 (d, $J = 122$ Hz, 2B), -17.0 (d, $J = 131$ Hz, 3B), -21.9 (d, $J = 145$ Hz, 1B), -35.2 (d, $J = 139$ Hz, 1B). IR (KBr, cm$^{-1}$): $\nu_{BH}$ 2533 (vs). HRMS: $m/z$ calcd for C$_{38}$H$_{59}$B$_{11}$N$_2$ [M]$^+$: 662.5774. Found: 662.5769. Anal. Calcd for C$_{38}$H$_{59}$B$_{11}$N$_2$: C, 68.86; H, 8.97; N, 4.23. Found: C, 68.95; H, 9.22; N, 3.81.

**Preparation of 2,8-(CH$_2$)$_3$-9-(2’-{1’,3’-[2’’,4’’,6’’-Me$_3$(C$_6$H$_2$)]$_2$-1’,3’-N$_2$C$_3$H$_4$})-12-Ph-2,8-C$_2$B$_{11}$H$_{10}$ (8).** A THF solution (5 mL) of 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene (61 mg, 0.2 mmol) was slowly added to a stirring solution of 1,2-(CH$_2$)$_3$-3-Ph-1,2-C$_2$B$_{11}$H$_{10}$ (55 mg, 0.2 mmol) in THF (5 mL) at room temperature, and the mixture was stirred for 7 d. After removal of the solvent, the residue was subject to chromatographic separation (SiO$_2$, 300-400 mesh, $n$-hexane/CH$_2$Cl$_2$ 5:2), giving 8 as a white solid (70 mg, 60%). $^1$H NMR (acetone-$d_6$): $\delta$ 7.34 (m, 2H, C$_6$H$_5$), 7.13 (m, 3H, C$_6$H$_5$), 7.05 (s, 2H, C$_6$H$_2$), 6.98 (s, 2H, C$_6$H$_2$), 4.35 (m, 4H, imidazolium NCH$_2$), 2.48 (s, 6H, CH$_3$), 2.37 (s, 6H, CH$_3$), 2.34 (m, 1H, CH$_2$), 2.28 (s, 6H, CH$_3$), 2.11 (m, 1H, CH$_2$), 1.23 (m, 3H, CH$_2$), 0.44 (m, 1H, CH$_2$). $^{13}$C{$^1$H}NMR (acetone-$d_6$): $\delta$ 140.3, 137.6, 136.9, 134.6, 133.7, 130.6, 130.3, 127.6, 127.3 (C$_6$H$_5$ & C$_6$H$_2$),
51.9 (imidazolium NCH₂), 44.2, 31.6, 21.4 (CH₂), 21.0, 18.6, 18.5 (CH₃), the imidazolium NCN and cage C atoms were not observed. ¹¹B NMR (acetone-d₆): δ 13.6 (s, 1B, BPh), -2.5 (d, J = 49 Hz, 1B), -2.9 (d, J = 102 Hz, 1B), -6.8 (d, J = 125 Hz, 1B), -9.9 (d, J = 129 Hz, 1B), -16.0 (d, J = 138 Hz, 3B), -18.2 (d, J = 157 Hz, 1B), -21.2 (d, J = 143 Hz, 1B), -35.6 (d, J = 152 Hz, 1B). IR (KBr, cm⁻¹): νBH 2520 (vs). HRMS: m/z calcd for C₃₂H₄₇B₁₁N₂ [M]⁺: 578.4847. Found: 578.4849. Anal. Calcd for C₃₂H₄₇B₁₁N₂: C, 66.42; H, 8.19; N, 4.84. Found: C, 66.81; H, 8.50; N, 4.38.

**Preparation of 2,8-(CH₂)₄-9-(2'-{1',3'-[2'',6''-iPr₂(C₆H₃)]₂-1',3'-N₂C₃H₂})-7,8-C₂B₁₁H₁₁ (9).**

A THF solution (5 mL) of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (78 mg, 0.2 mmol) was slowly added to a stirring solution of 1,2-(CH₂)₄-1,2-C₂B₁₁H₁₁ (42 mg, 0.2 mmol) in THF (5 mL) at room temperature, and the mixture was heated at 80 °C for 2 d in a sealed tube to give a brown solution. After removal of the solvent, the residue was subject to chromatographic separation (SiO₂, 300-400 mesh, n-hexane/CH₂Cl₂ 3:1), giving 9 as a white solid (77 mg, 64%). X-ray-quality crystals were obtained by recrystallization from acetone. ¹H NMR (acetone-d₆): δ 8.04 (s, 2H, imidazolium NCH), 7.58 (t, J = 8.0 Hz, 2H, C₆H₃), 7.48 (d, J = 7.6 Hz, 2H, C₆H₃), 7.39 (d, J = 7.6 Hz, 2H, C₆H₃), 2.72 (m, 2H, CH(CH₃)₂), 2.63 (m, 2H, CH(CH₃)₂), 2.44 (m, 1H, CH₂), 1.99 (m, 1H, CH₂), 1.57 (m, 1H, CH₂), 1.51 (d, J = 6.8 Hz, 6H, CH(CH₃)₂), 1.46 (m, 1H, CH₂), 1.36 (d, J = 6.8 Hz, 6H, CH(CH₃)₂), 1.23 (d, J = 6.8 Hz, 6H, CH(CH₃)₂), 1.18 (m, 3H, CH₂), 1.15 (d, J = 6.8 Hz, 6H, CH(CH₃)₂), 0.97 (m, 1H, CH₂). ¹³C{¹H} NMR (acetone-d₆): δ 146.8, 146.4, 134.5, 132.1, 127.2, 125.2, 125.1 (C₆H₃ & imidazolium NCH), 42.2, 33.7, 23.0, 22.0 (CH₂), 26.4, 26.3, 22.6, 22.2 (CH(CH₃)₂), the imidazolium NCN and cage C atoms were not observed. ¹¹B NMR (acetone-d₆): δ 7.8 (d, J = 158 Hz, 1B), -2.4 (d, J = 48 Hz, 1B), -2.2 (d, J = 100 Hz, 1B), -6.9 (d, J = 126 Hz, 2B), -13.7 (d, J = 149 Hz, 1B), -16.0 (d, J = 140 Hz, 2B), -18.4 (d, J = 149 Hz, 1B), -23.3 (d, J = 136 Hz,

Alternative Method for Preparation of 9. To a stirring THF (15 mL) solution of 1,2-(CH₂)₄-1,2-C₂B₁₁H₁₁ (105 mg, 0.50 mmol) was added a THF solution (5 mL) of 1,3,4,5-tetramethylimidazol-2-ylidene (62 mg, 0.50 mmol) at room temperature, to which was added 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (213 mg, 0.50 mmol). The mixture was heated at 80 °C for 2 d in a sealed flask to give a brown solution. After removal of the solvent, the residue was subject to chromatographic separation (SiO₂, 300-400 mesh, n-hexane/CH₂Cl₂ 3:1), giving 9 as a white solid (195 mg, 65%).

Figure S5. Molecular structure of 2,8-(CH₂)₄-9-(2’-{1’,3’-[2’’,6’’-Pr₂(C₆H₃)]₂-1’,3’-N₂C₃H₂})-7,8-C₂B₁₁H₁₁ (9).

Preparation of 2,8-(CH₂)₄-9-(2’-{1’,3’-[2’’,4’’,6’’-Me₃(C₆H₂)]₂-1’,3’-N₂C₃H₂})-2,8- C₂B₁₁H₁₁ (10). This complex was prepared as a white solid from 1,2-(CH₂)₄-1,2-C₂B₁₁H₁₁ (42 mg, 0.2 mmol) and 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (61 mg, 0.2 mmol) in THF using the same procedure reported for 9: yield 70 mg (68%). X-ray-quality crystals were obtained by recrystallization from acetone. ¹H NMR (acetone-d₆): δ 7.81 (s, 2H, imidazolium NCH), 7.17 (s,
2H, C6H2), 7.07 (s, 2H, C6H2), 2.45 (m, 1H, CH2), 2.36 (s, 6H, CH3), 2.27 (s, 6H, CH3), 2.07 (s, 6H, CH3), 1.98 (m, 1H, CH2), 1.61 (m, 1H, CH2), 1.51 (m, 1H, CH2), 1.34 (m, 1H, CH2), 1.20 (m, 2H, CH2), 0.77 (m, 2H, CH2). 13C{1H} NMR (acetone-d6): δ 141.2, 137.1, 135.7, 134.3, 130.3, 130.2, 125.8 (C6H2 & imidazolium NCH), 42.8, 33.3, 22.8, 22.4 (CH2), 21.1, 18.3, 18.1 (CH3), the imidazolium NCN and cage C atoms were not observed. 11B NMR (acetone-d6): δ 6.1 (d, J = 139 Hz, 1B), -3.8 (d, J = 40 Hz, 1B), -4.0 (d, J = 122 Hz, 1B), -8.6 (d, J = 121 Hz, 2B), -14.7 (d, J = 162 Hz, 1B), -16.7 (d, J = 135 Hz, 2B), -19.4 (d, J = 151 Hz, 1B), -24.2 (d, J = 144 Hz, 1B), -36.2 (d, J = 137 Hz, 1B). IR (KBr, cm⁻¹): νBH 2527 (vs). HRMS: m/z calcd for C27H43B11N2 [M]⁺: 513.4453. Found: 513.4454. Anal. Calcd for C27H43B11N2: C, 63.02; H, 8.42; N, 5.44. Found: C, 63.26; H, 8.79; N, 4.99.

**Figure S6.** Molecular structure of 2,8-(CH2)4-12-(2'-{1',3'-[2'',4'',6''-Me3(C6H2)]2-1',3'-N2C3H2})-2,8-C2B11H11 (10).

**Preparation of 2,8-(CH2)4-9-(2'-{1',3'-[2'',6''-Pr2(C6H3)]2-1',3'-N2C3H2})-12-Ph-2,8-C2B11H10 (11).** A THF solution (5 mL) of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (78 mg, 0.2 mmol) was slowly added to a stirring solution of 1,2-(CH2)4-3-Ph-1,2-C2B11H10 (57 mg, 0.2 mmol) in THF (5 mL) at room temperature, and the mixture was heated at 80 °C for 9 d in a sealed tube to give a brown solution. After removal of the solvent, the residue was subject to
chromatographic separation (SiO₂, 300-400 mesh, n-hexane/CH₂Cl₂ 3:1), giving 11 as a white solid (80 mg, 59%). X-ray-quality crystals were obtained by recrystallization from acetone. ¹H NMR (acetone-d₆): δ 8.08 (s, 2H, imidazolium NCH), 7.56 (t, J = 8.0 Hz, 2H, aromatic CH), 7.49 (d, J = 7.6 Hz, 2H, aromatic CH), 7.37 (m, 4H, aromatic CH), 7.12 (m, 3H, aromatic CH), 2.66 (m, 2H, CH(CH₃)₂), 2.39 (m, 1H, CH₂), 2.02 (m, 1H, CH₂), 1.55 (m, 2H, CH₂), 1.54 (d, J = 6.8 Hz, 6H, CH(CH₃)₂), 1.38 (d, J = 6.8 Hz, 6H, CH(CH₃)₂), 1.25 (d, J = 6.8 Hz, 6H, CH(CH₃)₂), 1.16 (d, J = 6.8 Hz, 6H, CH(CH₃)₂), 1.01 (m, 3H, CH₂), 0.50 (m, 1H, CH₂). ¹³C{¹H} NMR (acetone-d₆): δ 146.9, 146.4, 134.5, 133.9, 132.0, 127.5, 127.2, 127.1, 125.2, 125.0 (C₆H₅ & C₆H₃ & imidazolium NCH), 70.5 (v₁/₂ = 35 Hz), 33.0 (v₁/₂ = 33 Hz) (cage C), 42.6, 23.4, 22.0 (CH₂), 26.4, 26.3, 22.6, 22.1 (CH(CH₃)₂), the imidazolium NCN carbon was not observed. ¹¹B NMR (acetone-d₆): δ 13.0 (s, 1B, BPh), -1.4 (d, J = 118 Hz, 1B), -2.8 (d, J = 58 Hz, 1B), -7.2 (d, J = 131 Hz, 2B), -13.5 (d, J = 150 Hz, 1B), -15.7 (d, J = 133 Hz, 2B), -19.3 (d, J = 133 Hz, 1B), -21.9 (d, J = 141 Hz, 1B) -36.7 (d, J = 150 Hz, 1B). IR (KBr, cm⁻¹): ν₃H₂ 2531 (vs). HRMS: m/z calcd for C₃₉H₅₉B₁₁N₂ [M]⁺: 674.5774. Found: 674.5781. Anal. Calcd for C₃₉H₅₉B₁₁N₂: C, 69.41; H, 8.81; N, 4.15. Found: C, 69.09; H, 9.28; N, 3.92.

**Figure S7.** Molecular structure of 2,8-(CH₂)₄-9-(2’-{1’,3’-[2’”,6’”-Pr₂(C₆H₃)]₂-1’,3’-N₂C₃H₂})-12-Ph-2,8-C₂B₁₁H₁₁ (11).
Preparation of 2,8-(CH$_2$)$_4$-9-(2'-{1',3'-[2'',4'',6''-Me$_3$(C$_6$H$_3$)]$_2$-1',3'-N$_2$C$_3$H$_2$})-12-Ph-2,8-C$_2$B$_{11}$H$_{10}$ (12). A THF solution (5 mL) of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (61 mg, 0.2 mmol) was slowly added to a stirring solution of 1,2-(CH$_2$)$_4$-3-Ph-1,2-C$_2$B$_{11}$H$_{10}$ (57 mg, 0.2 mmol) in THF (5 mL) at room temperature, and the mixture was heated at 80 °C for 3 d in a sealed tube to give a brown solution. After removal of the solvent, the residue was subject to chromatographic separation (SiO$_2$, 300-400 mesh, $n$-hexane/CH$_2$Cl$_2$ 1:3), giving 12 as a white solid (65 mg, 55%). $^1$H NMR (acetone-$d_6$): $\delta$ 7.84 (s, 2H, imidazolium NC$_H$), 7.41 (m, 2H, aromatic CH), 7.15 (m, 5H, aromatic CH), 7.06 (s, 2H, aromatic CH), 2.39 (m, 1H, CH$_2$), 2.34 (s, 6H, CH$_3$), 2.30 (s, 6H, CH$_3$), 2.13 (m, 1H, CH$_2$), 2.09 (s, 6H, CH$_3$), 1.61 (m, 1H, CH$_2$), 1.34 (m, 1H, CH$_2$), 1.06 (m, 3H, CH$_3$), 0.33 (m, 1H, CH$_2$). $^{13}$C {$^1$H} NMR (acetone-$d_6$): $\delta$ 141.3, 137.2, 135.8, 134.4, 134.2, 130.4, 130.2, 127.5, 127.3, 125.9 (C$_6$H$_5$ & C$_6$H$_2$ & imidazolium NCH), 43.5, 23.2, 22.6 (CH$_2$), 21.1, 18.4, 18.1 (CH$_3$), the imidazolium NCN and cage C atoms were not observed. $^{11}$B NMR (acetone-$d_6$): $\delta$ 11.5 (s, 1B, BPh), -3.4 (d, $J$ = 62 Hz, 2B), -4.0 (d, $J$ = 115 Hz, 1B), -8.9 (d, $J$ = 142 Hz, 2B), -14.5 (d, $J$ = 174 Hz, 1B), -16.0 (d, $J$ = 152 Hz, 1B), -17.0 (d, $J$ = 131 Hz, 1B), -20.5 (d, $J$ = 119 Hz, 1B), -22.9 (d, $J$ = 152 Hz, 1B), -37.8 (d, $J$ = 131 Hz, 1B). IR (KBr, cm$^{-1}$): $\nu_{BH}$ 2521 (vs). HRMS: $m/z$ calcd for C$_{33}$H$_{47}$B$_{11}$N$_2$ [M – H]$^+$: 589.4769. Found: 589.4759. Anal. Calcd for C$_{33}$H$_{47}$B$_{11}$N$_2$: C, 67.10; H, 8.02; N, 4.74. Found: C, 67.28; H, 8.12; N, 4.38.

Preparation of [1,2-CH(CH$_2$)$_3$-1,2-C$_2$B$_{11}$H$_{11}$][1',3',4',5'-Me$_4$-1',3'-N$_2$C$_3$H] (13). To a stirring CH$_2$Cl$_2$ (15 mL) solution of 1,2-(CH$_2$)$_4$-1,2-C$_2$B$_{11}$H$_{11}$ (105 mg, 0.50 mmol) was added a CH$_2$Cl$_2$ solution (5 mL) of 1,3,4,5-tetramethylimidazol-2-ylidene (62 mg, 0.50 mmol) at room temperature. Removal of the solvent afforded 13 as a white solid (165 mg, 99%). $^1$H NMR (CD$_2$Cl$_2$): $\delta$ 8.30 (s, 1H, NCHN), 5.82 (t, $J$ = 4.8 Hz, 1H, CH), 3.75 (s, 6H, NCH$_3$), 2.25 (s, 6H, CCH$_3$), 2.18 (m, 2H,
CHCH$_2$, 2.10 (m, 2H, CCH$_2$), 1.58 (m, 2H, CH$_2$CH$_2$CH$_2$). $^{13}$C{$^{1}$H} NMR (CD$_2$Cl$_2$): $\delta$ 152.0 (CH), 134.5 (NCHN), 128.3 (NCCH$_3$), 79.2 (cage CCH), 52.9 (cage CCH$_2$), 42.2 (CCH$_2$), 34.4 (NCH$_3$), 29.0 (CHCH$_2$), 19.2 (CH$_2$CH$_2$CH$_2$), 8.7 (CCH$_3$). $^{1}$B{$^{1}$H} NMR (CD$_2$Cl$_2$): $\delta$ 6.3 (d, $J$ = 138 Hz, 1B), -1.5 (d, $J$ = 149 Hz, 5B), -21.8 (d, $J$ = 136 Hz, 5B). IR (KBr, cm$^{-1}$): v$_{BH}$ 2530 (vs). Anal. Calcd for C$_{13}$H$_{31}$B$_{11}$N$_2$: C, 46.70; H, 9.35; N, 8.38. Found: C, 46.61; H, 9.03; N, 8.39.

**X-ray Structure Determination.** All single crystals were immersed in Paratone-N oil and sealed under nitrogen in thin-walled glass capillaries. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo-K$\alpha$ radiation. An empirical absorption correction was applied using the SADABS program.$^3$ 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 on $F^2$ using the SHELXTL program package.$^4$ All hydrogen atoms were geometrically fixed using the riding model.

CCDC 1032166-1032172 (1, 3 – 5, 9 – 11) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**References**


