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Supporting Information

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

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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. CH_2Cl_2 was refluxed over CaH_2 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-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$,[1] 1,2-$(CH_2)_4$-1,2-$C_2B_{11}H_{11}$,[2] 1,2-$(CH_2)_3$-3-Ph-1,2-$C_2B_{11}H_{10}$,[1] and 1,2-$(CH_2)_4$-3-Ph-1,2-$C_2B_{11}H_{10}$[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. $^{13}C\{^1H\}$ NMR spectra were recorded on either a Bruker DPX 300 spectrometer at 75 MHz or a Bruker DPX 400 spectrometer at 100 MHz. ^{11}B 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 $BF_3·OEt_2$ (0.00 ppm) for boron chemical shifts. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry, CAS, China.

Preparation of 2,8-$(CH_2)_3$-9-(2'-{1',3'-[2'',6''-^{i}$Pr_2(C_6H_3)]_2$-1',3'-$N_2C_3H_2$})-2,8-$C_2B_{11}H_{11}$ (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-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ (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 (SiO_2, 300-400 mesh, *n*-hexane/CH_2Cl_2 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): δ 8.02 (s, 2H, imidazolium NCH), 7.56 (t, J = 7.8 Hz, 2H, C_6H_3), 7.44 (d, J = 7.6 Hz, 2H, C_6H_3), 7.37 (d, J = 7.6 Hz, 2H, C_6H_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): δ 146.7, 146.3, 134.4, 132.0, 127.1, 125.1, 124.9 (C_6H_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): δ 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}): ν_{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.

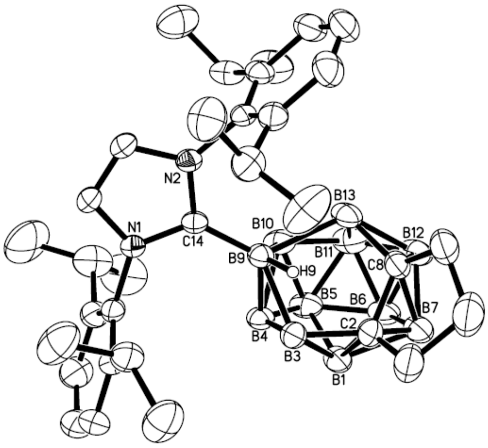

Figure S1. Molecular structure of 2,8-(CH$_2$)$_3$-9-(2'-{1',3'-[2'',6''-^{i}Pr$_2$(C$_6$H$_3$)]$_2$-1',3'-N$_2$C$_3$H$_2$})-2,8-C$_2$B$_{11}$H$_{11}$ (**1**).

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 NC*H*), 7.16 (s, 2H, C_6H_2), 7.08 (s, 2H, C_6H_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_6H_2 & imidazolium N*C*H), 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 N*C*N 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''-^{i}Pr$_2$(C_6H_3)]$_2$-1',3'-$N_2C_3H_4$)})-2,8-$C_2B_{11}H_{11}$ (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-$C_2B_{11}H_{11}$ (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_2Cl_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_6H_3), 7.34 (d, *J* = 7.2 Hz, 2H, C_6H_3), 7.29 (d, *J* = 7.2 Hz, 2H, C_6H_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, 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (acetone-*d*$_6$): δ 147.5, 147.2, 134.9, 131.1, 125.5 (*C*$_6$H$_3$), 76.3 ($v_{1/2}$ = 36 Hz), 51.0 ($v_{1/2}$ = 36 Hz) (cage *C*), 55.0 (imidazolium N*C*H$_2$), 44.4, 36.2, 21.4 (*C*H$_2$), 26.9, 26.8, 23.3, 23.1 (CH(*C*H$_3$)$_2$), the imidazolium N*C*N carbon was not observed. ^{11}B NMR (acetone-*d*$_6$): 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}): ν_{BH} 2534 (vs). HRMS: *m/z* calcd for $C_{32}H_{55}B_{11}N_2$ [M]$^+$: 586.5456. Found: 586.5450. Anal. Calcd for $C_{32}H_{55}B_{11}N_2$: C, 65.51; H, 9.45; N, 4.77. Found: C, 65.51; H, 9.07; N, 4.58.

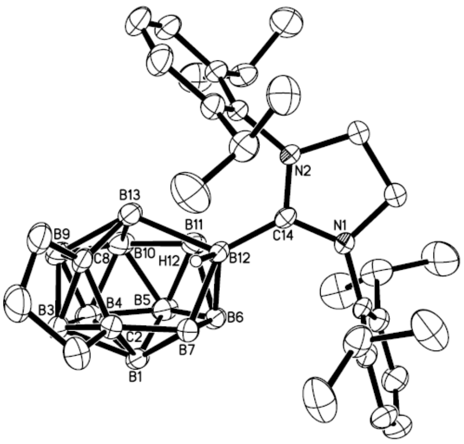

Figure S2. Molecular structure of 2,8-(CH$_2$)$_3$-12-(2'-{1',3'-[2'',6''-^{i}Pr$_2$(C$_6$H$_3$)]$_2$-1',3'-N$_2$C$_3$H$_4$)})-2,8-C$_2$B$_{11}$H$_{11}$ (**3**).

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$_4$})-2,8- C$_2$B$_{11}$H$_{11}$ (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-(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 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$_2$ 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): δ 7.05 (s, 2H, C_6H_2), 6.99 (s, 2H, C_6H_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} NMR (acetone-d_6): δ 140.3, 137.5, 136.8, 134.6, 130.6, 130.3 (C_6H_2), 52.0 (imidazolium NCH_2), 44.2, 35.3, 21.5 (CH_2), 21.1, 18.6, 18.5 (CH_3), the imidazolium N*C*N and cage *C* atoms were not observed. ^{11}B NMR (acetone-d_6): δ 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}): ν_{BH} 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.

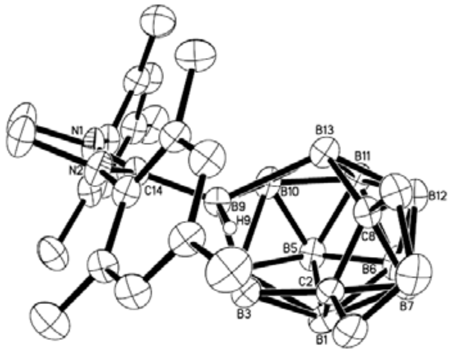

Figure S3. Molecular structure of 2,8-$(CH_2)_3$-9-(2'-{1',3'-[2'',4'',6''-$Me_3(C_6H_2)]_2$-1',3'-$N_2C_3H_4$})-2,8-$C_2B_{11}H_{11}$ (**4**).

Preparation of 2,8-$(CH_2)_3$-9-(2'-{1',3'-[2'',6''-$^{i}Pr_2(C_6H_3)]_2$-1',3'-$N_2C_3H_2$)-12-Ph-2,8-$C_2B_{11}H_{10}$ (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-$C_2B_{11}H_{10}$ (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 (SiO_2, 300-400 mesh, *n*-hexane/CH_2Cl_2 5:2), giving **5** as a white solid (91 mg, 69%). X-ray-quality crystals were obtained by recrystallization from acetone. ^{1}H NMR (acetone-d_6): δ 8.06 (s, 2H, imidazolium NC*H*), 7.54 (t, J = 8.0 Hz, 2H, C_6H_3), 7.45 (d, J = 7.6 Hz, 2H, C_6H_3), 7.37 (d, J = 7.6 Hz, 2H, C_6H_3), 7.32 (m, 2H, C_6H_5), 7.12 (m, 3H, C_6H_5), 2.75 (m, 2H, C*H*(CH_3)$_2$), 2.61 (m, 2H, C*H*(CH_3)$_2$), 2.51 (m, 1H, CH_2), 2.14 (m, 1H, CH_2), 1.49 (d, J = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.38 (d, J = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.30 (m, 3H, CH_2), 1.22 (d, J = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.17 (d, J = 6.8 Hz, 6H, CH(CH_3)$_2$), 0.75 (m, 1H, CH_2). ^{13}C{^{1}H} NMR (acetone-d_6): δ 146.8, 146.3, 134.5, 133.6, 132.0, 127.6, 127.3, 127.1, 125.0, 124.9 (C_6H_5 & C_6H_3 & imidazolium N*C*H), 77.5 ($v_{1/2}$ = 36 Hz), 46.0 ($v_{1/2}$ = 36 Hz) (cage *C*), 44.2, 32.2, 21.3 (*C*H_2), 30.0, 26.3, 26.2, 22.5, 22.2 (CH(*C*H_3)$_2$), the imidazolium N*C*N carbon was not observed. ^{11}B NMR (acetone-d_6): δ 13.9 (s, 1B, *B*Ph), -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). IR (KBr, cm^{-1}): ν_{BH} 2533 (vs). HRMS: *m/z* calcd for $C_{38}H_{57}B_{11}N_2$ [M]$^+$: 660.5617. Found: 660.5614. Anal. Calcd for $C_{38}H_{57}B_{11}N_2$: C, 69.07; H, 8.69; N, 4.24. Found: C, 69.00; H, 8.76; N, 4.25.

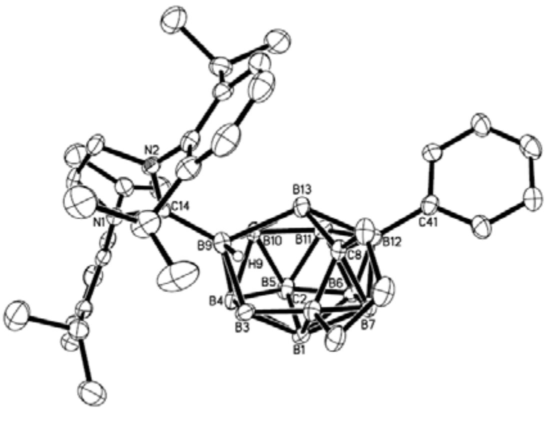

Figure S4. Molecular structure of 2,8-(CH_2)$_3$-9-(2'-{1',3'-[2'',6''-^{i}Pr$_2$(C_6H_3)]$_2$-1',3'-$N_2C_3H_2$)-12-Ph-2,8-$C_2B_{11}H_{11}$ (**5**).

Preparation of 2,8-$(CH_2)_3$-9-(2'-{1',3'-[2'',4'',6''-$Me_3(C_6H_2)]_2$-1',3'-$N_2C_3H_2$})-12-Ph-2,8-$C_2B_{11}H_{10}$ (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-$C_2B_{11}H_{10}$ (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_2Cl_2 2:5), giving **6** as a white solid (77 mg, 80%). ^1H NMR (acetone-d_6): δ 7.84 (s, 2H, imidazolium NC*H*), 7.38 (m, 2H, aromatic C*H*), 7.14 (m, 5H, aromatic C*H*), 7.07 (s, 2H, aromatic C*H*), 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). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 141.3, 136.8, 136.1, 134.4, 133.8, 130.5, 130.2, 130.0, 127.6, 127.3, 125.8 (C_6H_5 & C_6H_2 & imidazolium N*C*H), 77.0 ($v_{1/2}$ = 36 Hz), 48.0 ($v_{1/2}$ = 36 Hz) (cage *C*), 44.1, 31.6, 21.4 (*C*H_2), 21.1, 18.3, 18.1 (*C*H_3), the imidazolium N*C*N carbon was not observed. ^{11}B NMR (acetone-d_6): δ 13.5 (s, 1B, *B*Ph), -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}): ν_{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''-$^iPr_2(C_6H_3)]_2$-1',3'-$N_2C_3H_4$)-12-Ph-2,8-$C_2B_{11}H_{10}$ (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-$C_2B_{11}H_{10}$ (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_2Cl_2 5:2), giving **7** as a white solid

(86 mg, 65%). ^{1}H NMR (acetone-d_6): δ 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): δ 147.6, 147.2, 135.0, 133.5, 131.1, 127.6, 127.2, 125.4 (C_6H$_5$ & C_6H$_3$), 55.0 (imidazolium NCH$_2$), 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): δ 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}): ν_{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): δ 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$), 4.35 (m, 4H, imidazolium NCH_2), 2.48 (s, 6H, CH_3), 2.37 (s, 6H, CH_3), 2.34 (m, 1H, CH_2), 2.28 (s, 6H, CH_3), 2.11 (m, 1H, CH_2), 1.23 (m, 3H, CH_2), 0.44 (m, 1H, CH_2). ^{13}C{^{1}H} NMR (acetone-d_6): δ 140.3, 137.6, 136.9, 134.6, 133.7, 130.6, 130.3, 127.6, 127.3 (C_6H$_5$ & C_6H$_2$), 51.9 (imidazolium N*C*H$_2$), 44.2, 31.6, 21.4 (*C*H$_2$), 21.0, 18.6, 18.5 (*C*H$_3$), the imidazolium N*C*N and cage *C* atoms were not observed. ^{11}B NMR (acetone-d_6): δ 13.6 (s, 1B, *B*Ph), -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}): ν_{BH} 2520 (vs). HRMS: *m/z* calcd for $C_{32}H_{47}B_{11}N_2$ [M]$^+$: 578.4847. Found: 578.4849. Anal. Calcd for $C_{32}H_{47}B_{11}N_2$: C, 66.42; H, 8.19; N, 4.84. Found: C, 66.81; H, 8.50; N, 4.38.

Preparation of 2,8-(CH$_2$)$_4$-9-(2'-{1',3'-[2'',6''-^{i}Pr$_2$(C$_6$H$_3$)]$_2$-1',3'-N$_2$C$_3$H$_2$})-7,8-C$_2$B$_{11}$H$_{11}$ (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-(CH$_2$)$_4$-1,2-C$_2$B$_{11}$H$_{11}$ (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 (SiO$_2$, 300-400 mesh, *n*-hexane/CH$_2$Cl$_2$ 3:1), giving **9** as a white solid (77 mg, 64%). X-ray-quality crystals were obtained by recrystallization from acetone. ^{1}H NMR (acetone-d_6): δ 8.04 (s, 2H, imidazolium NC*H*), 7.58 (t, J = 8.0 Hz, 2H, C$_6$*H*$_3$), 7.48 (d, J = 7.6 Hz, 2H, C$_6$*H*$_3$), 7.39 (d, J = 7.6 Hz, 2H, C$_6$*H*$_3$), 2.72 (m, 2H, C*H*(CH$_3$)$_2$), 2.63 (m, 2H, C*H*(CH$_3$)$_2$), 2.44 (m, 1H, C*H*$_2$), 1.99 (m, 1H, C*H*$_2$), 1.57 (m, 1H, C*H*$_2$), 1.51 (d, J = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.46 (m, 1H, C*H*$_2$), 1.36 (d, J = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.23 (d, J = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.18 (m, 3H, C*H*$_2$), 1.15 (d, J = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 0.97 (m, 1H, C*H*$_2$). ^{13}C{^{1}H} NMR (acetone-d_6): δ 146.8, 146.4, 134.5, 132.1, 127.2, 125.2, 125.1 (*C*$_6$H$_3$ & imidazolium N*C*H), 42.2, 33.7, 23.0, 22.0 (*C*H$_2$), 26.4, 26.3, 22.6, 22.2 (CH(*C*H$_3$)$_2$), the imidazolium N*C*N and cage *C* atoms were not observed. ^{11}B NMR (acetone-d_6): 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, 1B), -35.5 (d, *J* = 147 Hz, 1B). IR (KBr, cm^{-1}): ν_{BH} 2539 (vs). HRMS: *m/z* calcd for $C_{33}H_{55}B_{11}N_2$ $[M]^+$: 598.5473. Found: 598.5461. Anal. Calcd for $C_{33}H_{55}B_{11}N_2$: C, 66.20; H, 9.26; N, 4.68. Found: C, 66.47; H, 9.44; N, 4.24.

Alternative Method for Preparation of 9. To a stirring THF (15 mL) solution of 1,2-$(CH_2)_4$-1,2-$C_2B_{11}H_{11}$ (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 (SiO_2, 300-400 mesh, *n*-hexane/CH_2Cl_2 3:1), giving **9** as a white solid (195 mg, 65%).

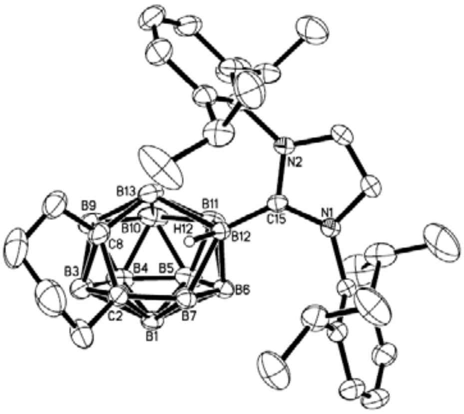

Figure S5. Molecular structure of 2,8-$(CH_2)_4$-12-(2’-{1’,3’-[2’’,6’’-$^iPr_2(C_6H_3)]_2$-1’,3’-$N_2C_3H_2$})-7,8-$C_2B_{11}H_{11}$ (**9**).

Preparation of 2,8-$(CH_2)_4$-9-(2’-{1’,3’-[2’’,4’’,6’’-$Me_3(C_6H_2)]_2$-1’,3’-$N_2C_3H_2$})-2,8- $C_2B_{11}H_{11}$ (10). This complex was prepared as a white solid from 1,2-$(CH_2)_4$-1,2-$C_2B_{11}H_{11}$ (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-d_6): δ 7.81 (s, 2H, imidazolium NC*H*), 7.17 (s, 2H, C_6H_2), 7.07 (s, 2H, C_6H_2), 2.45 (m, 1H, CH_2), 2.36 (s, 6H, CH_3), 2.27 (s, 6H, CH_3), 2.07 (s, 6H, CH_3), 1.98 (m, 1H, CH_2), 1.61 (m, 1H, CH_2), 1.51 (m, 1H, CH_2), 1.34 (m, 1H, CH_2), 1.20 (m, 2H, CH_2), 0.77 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 141.2, 137.1, 135.7, 134.3, 130.3, 130.2, 125.8 (C_6H_2 & imidazolium N*C*H), 42.8, 33.3, 22.8, 22.4 (CH_2), 21.1, 18.3, 18.1 (CH_3), the imidazolium N*C*N and cage *C* atoms were not observed. ^{11}B NMR (acetone-d_6): 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}): ν_{BH} 2527 (vs). HRMS: *m/z* calcd for $C_{27}H_{43}B_{11}N_2$ $[M]^+$: 513.4453. Found: 513.4454. Anal. Calcd for $C_{27}H_{43}B_{11}N_2$: C, 63.02; H, 8.42; N, 5.44. Found: C, 63.26; H, 8.79; N, 4.99.

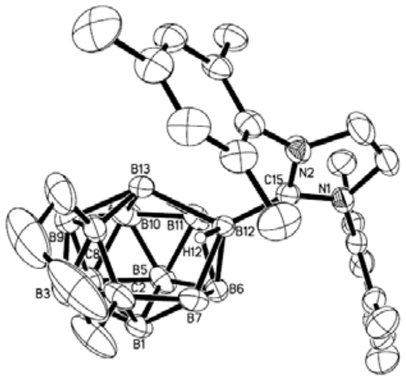

Figure S6. Molecular structure of 2,8-$(CH_2)_4$-12-(2'-{1',3'-[2'',4'',6''-$Me_3(C_6H_2)]_2$-1',3'-$N_2C_3H_2$})-2,8-$C_2B_{11}H_{11}$ (**10**).

Preparation of 2,8-$(CH_2)_4$-9-(2'-{1',3'-[2'',6''-$^iPr_2(C_6H_3)]_2$-1',3'-$N_2C_3H_2$)-12-Ph-2,8-$C_2B_{11}H_{10}$ (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-$(CH_2)_4$-3-Ph-1,2-$C_2B_{11}H_{10}$ (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 (SiO_2, 300-400 mesh, *n*-hexane/CH_2Cl_2 3:1), giving **11** as a white solid (80 mg, 59%). X-ray-quality crystals were obtained by recrystallization from acetone. ^1H NMR (acetone-d_6): δ 8.08 (s, 2H, imidazolium NC*H*), 7.56 (t, *J* = 8.0 Hz, 2H, aromatic C*H*), 7.49 (d, *J* = 7.6 Hz, 2H, aromatic C*H*), 7.37 (m, 4H, aromatic C*H*), 7.12 (m, 3H, aromatic C*H*), 2.76 (m, 2H, $CH(CH_3)_2$), 2.66 (m, 2H, $CH(CH_3)_2$), 2.39 (m, 1H, CH_2), 2.02 (m, 1H, CH_2), 1.55 (m, 2H, CH_2), 1.54 (d, *J* = 6.8 Hz, 6H, $CH(CH_3)_2$), 1.38 (d, *J* = 6.8 Hz, 6H, $CH(CH_3)_2$), 1.25 (d, *J* = 6.8 Hz, 6H, $CH(CH_3)_2$), 1.16 (d, *J* = 6.8 Hz, 6H, $CH(CH_3)_2$), 1.01 (m, 3H, CH_2), 0.50 (m, 1H, CH_2). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 146.9, 146.4, 134.5, 133.9, 132.0, 127.5, 127.2, 127.1, 125.2, 125.0 (C_6H_5 & C_6H_3 & imidazolium N*C*H), 70.5 ($v_{1/2}$ = 35 Hz), 33.0 ($v_{1/2}$ = 33 Hz) (cage *C*), 42.6, 23.4, 22.0 (CH_2), 26.4, 26.3, 22.6, 22.1 ($CH(CH_3)_2$), the imidazolium N*C*N carbon was not observed. ^{11}B NMR (acetone-d_6): δ 13.0 (s, 1B, *B*Ph), -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}): ν_{BH} 2531 (vs). HRMS: *m/z* calcd for $C_{39}H_{59}B_{11}N_2$ $[M]^+$: 674.5774. Found: 674.5781. Anal. Calcd for $C_{39}H_{59}B_{11}N_2$: C, 69.41; H, 8.81; N, 4.15. Found: C, 69.09; H, 9.28; N, 3.92.

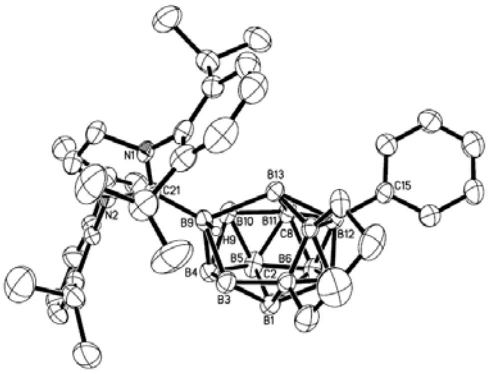

Figure S7. Molecular structure of 2,8-$(CH_2)_4$-9-(2'-{1',3'-[2'',6''-$^iPr_2(C_6H_3)]_2$-1',3'-$N_2C_3H_2$)-12-Ph-2,8-$C_2B_{11}H_{11}$ (**11**).

Preparation of 2,8-$(CH_2)_4$-9-(2'-{1',3'-[2'',4'',6''-$Me_3(C_6H_3)]_2$-1',3'-$N_2C_3H_2$})-12-Ph-2,8-$C_2B_{11}H_{10}$ (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-$C_2B_{11}H_{10}$ (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_2Cl_2 1:3), giving **12** as a white solid (65 mg, 55%). ^1H NMR (acetone-d_6): δ 7.84 (s, 2H, imidazolium NC*H*), 7.41 (m, 2H, aromatic C*H*), 7.15 (m, 5H, aromatic C*H*), 7.06 (s, 2H, aromatic C*H*), 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_2), 0.33 (m, 1H, CH_2). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 141.3, 137.2, 135.8, 134.4, 134.2, 130.4, 130.2, 127.5, 127.3, 125.9 (C_6H_5 & C_6H_2 & imidazolium N*C*H), 43.5, 23.2, 22.6 (CH_2), 21.1, 18.4, 18.1 (CH_3), the imidazolium N*C*N and cage *C* atoms were not observed. ^{11}B NMR (acetone-d_6): δ 11.5 (s, 1B, *B*Ph), -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}): ν_{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-$C_2B_{11}H_{11}$][1',3',4',5'-Me_4-1',3'-N_2C_3H] (13). To a stirring CH_2Cl_2 (15 mL) solution of 1,2-$(CH_2)_4$-1,2-$C_2B_{11}H_{11}$ (105 mg, 0.50 mmol) was added a CH_2Cl_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%). ^1H NMR (CD_2Cl_2): δ 8.30 (s, 1H, NC*H*N), 5.82 (t, *J* = 4.8 Hz, 1H, C*H*), 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, $CH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 152.0 (*C*H), 134.5 (N*C*HN), 128.3 (N*C*CH_3), 79.2 (cage *C*CH), 52.9 (cage *C*CH_2), 42.2 (C*C*H_2), 34.4 (N*C*H_3), 29.0 (CH*C*H_2), 19.2 ($CH_2CH_2CH_2$), 8.7 (C*C*H_3). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ 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}): ν_{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-Kα 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

1. L. Deng, H.-S. Chan and Z. Xie, *J. Am. Chem. Soc.*, 2006, **128**, 5219.
2. F. Zheng, J. Zhang, X. Fu and Z. Xie, *Chem. Asian J.*, 2013, **8**, 1886.
3. G. M. Sheldrick, *SADABS*, *Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Germany, 1996.
4. G. M. Sheldrick, *SHELXTL 5.10 for Windows NT*: *Structure Determination Software Programs*. Bruker Analytical X-ray systems, Inc., Madison, WI, 1997.