Electronic Supplementary Information

Synthesis and Structure of a Carbene-Stabilized Iminocarboranylboron(I) Compound

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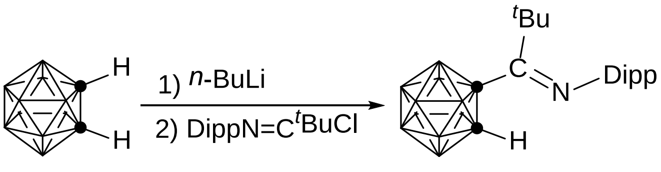
Experimental Section

General Procedures. All operations were carried out under a dry argon or nitrogen atmosphere with standard Schlenk and glovebox techniques. ^{1}H, ^{13}C and ^{11}B NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400 MHz, 100 MHz and 128 MHz, respectively. All chemical shifts were reported in δ units with references to the residual solvent resonance of the deuterated solvents for proton and carbon chemical shifts, and to external $BF_3 \cdot OEt_2$ (0.00 ppm) for boron chemical shifts. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal. Elemental analyses were performed by MEDAC Ltd, U.K., or the Shanghai Institute of Organic Chemistry, CAS, China. Mass spectra were obtained on a Thermo Finnigan MAT 95 XL spectrometer. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. Compounds (Dipp)N=C(^{t}Bu)Cl (Dipp = 2,6-$^{i}Pr_2C_6H_3$)[1] and 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene[2] were prepared according to literature procedure. All other chemicals were purchased from either Aldrich, J&K or Acros Chemical Co. and used as received unless otherwise specified.



1

Preparation of 1. To a solution of o-$C_2B_{10}H_{12}$ (2.3 g, 16.0 mmol) in Et_2O (50 mL) was slowly added via syringe n-BuLi (1.6 M in n-hexane, 10.0 mL, 16.0 mmol) at 0 °C under stirring. The mixture was allowed to slowly warm up to room temperature and stirred at room temperature for 3 h, to which was slowly added (Dipp)N=C(^{t}Bu)Cl (4.5 g, 16.0 mmol). The reaction mixture was stirred at room temperature overnight. After removal of solvents, the residue was purified by column chromatography on silica gel using AcOEt/n-hexane (1:40 in V/V) as elute to give **1** as a pale yellow solid (5.0 g, 81%). X-ray quality colorless crystals were obtained by recrystallization from hexane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (d, J = 6.8 Hz, 6H; CHMe_2), 1.20 (s, 9H; CMe_3), 1.26 (d, J = 6.8 Hz, 6H; CHMe_2), 2.48 (m, 2H;

*CH*Me$_2$), 4.52 (s, 1H; cage C*H*), 6.95-6.98 (m, 1H; aromatic C*H*), 7.02-7.04 (m, 2H; aromatic C*H*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 21.7, 24.7, 28.5 (CH*Me*$_2$, C*Me*$_3$), 30.0 (*C*HMe$_2$), 45.8 (*C*Me$_3$), 63.6, 78.4 (cage *C*), 122.8, 123.2, 132.2, 144.0 (aromatic *C*), 161.4 (*C*N). ^{11}B NMR (128 MHz, CDCl$_3$): δ -14.1 (d, J_{BH} = 164 Hz; 2B), -11.5 (d, J_{BH} = 162 Hz; 2B), -10.3 (d, J_{BH} = 145 Hz; 2B), -9.2 (d, J_{BH} = 148 Hz; 2B), -3.5 (d, J_{BH} = 146 Hz; 1B), -2.4 (d, J_{BH} = 133 Hz; 1B). HRMS (EI) calcd for $C_{19}H_{37}B_{10}N^+$: 387.3933. Found: 387.3936.

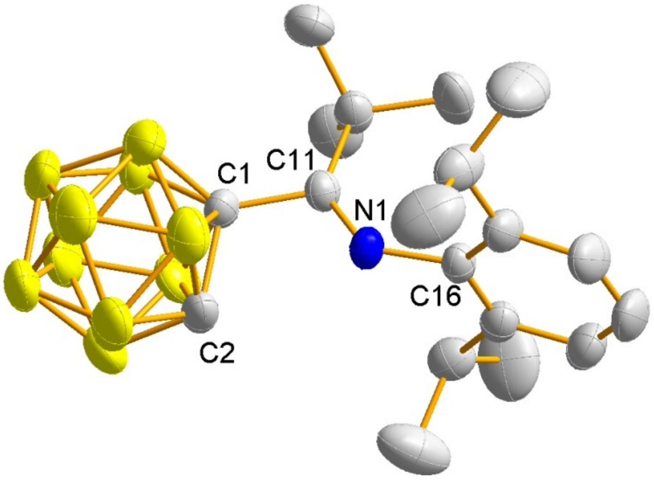
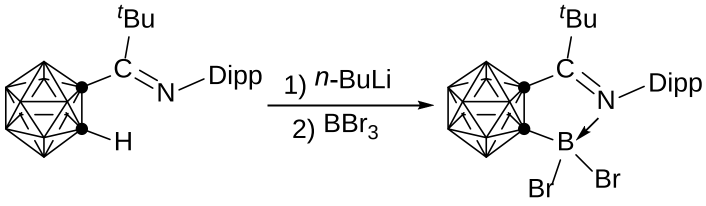


Figure S1. Molecular Structure of **1.**



1 **2**

Preparation of 2. To a toluene solution (30 mL) of **1** (0.93 g, 2.4 mmol) was slowly added via syringe a hexane solution of n-BuLi (1.6 M, 1.5 mL, 2.4 mmol) at 0 °C under stirring. The reaction mixture was allowed to warm up to room temperature and stirred overnight. A CH_2Cl_2 solution of BBr_3 (1.0 M, 2.4 mL, 2.4 mmol) was then added via syringe at -78 °C. The resulting mixture was allowed to warm to room temperature and stirred overnight. After removal of precipitate by filtration, the filtrate was concentrated to about 5 mL, to which was added n-hexane (2 mL). Compound **2** was isolated as colorless crystals after the solution stood at room temperature overnight (1.15 g, 79%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 1.30 (d, *J* = 6.4 Hz, 6H; CH*Me*$_2$), 1.38 (s, 9H; C*Me*$_3$), 1.45 (d, *J* = 6.4 Hz, 6H; CH*Me*$_2$), 3.14 (m, 2H; *CH*Me$_2$), 7.31 (d, *J* = 7.6 Hz, 2H; aromatic C*H*), 7.47 (t, *J* = 7.6 Hz, 1H; aromatic C*H*). $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_2Cl_2): δ 25.8, 27.5, 29.8 (CH*Me*$_2$, C*Me*$_3$), 31.2 (*C*HMe$_2$), 46.8 (*C*Me$_3$), 80.4 (cage *C*), 126.6, 131.1, 136.2, 145.4 (aromatic *C*), 194.6 (*C*N). ^{11}B NMR (128 MHz, CD_2Cl_2): δ -9.9 (d, J_{BH} = 169 Hz; 2B), -8.4 (d, unresolved; 3B), -6.9 (d, J_{BH} = 154 Hz; 3B), -3.2 (d, J_{BH} = 148 Hz; 1B), -0.2 (d, unresolved; 1B), 0.6 (s, 1B). Anal. Calcd for $C_{22.5}H_{40}B_{11}Br_2N$ (**2** + $0.5C_7H_8$): C 44.80, H 6.68, N 2.32. Found: C 45.09, H 6.77, N 2.30.

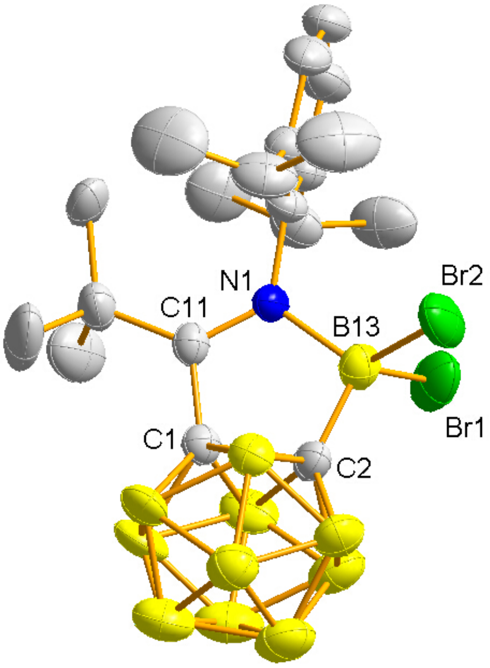
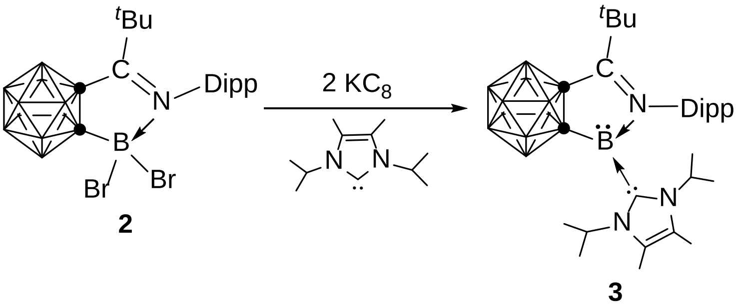


Figure S2. Molecular Structure of **2.**



Preparation of 3. A toluene solution (30 mL) of **2** (302 mg, 0.5 mmol) was slowly added to a mixture of KC_8 (135 mg, 1.0 mmol) and 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (90 mg, 0.5 mmol) in toluene (10 mL) at room temperature, and the reaction mixture was stirred overnight. The color of the solution was changed to dark blue. After filtration, the dark blue filtrate was concentrated to about 5 mL. Compound **3** was isolated as dark purple crystals after this solution stood at -30 °C overnight (165 mg, 57%). ^{1}H NMR (400 MHz, THF-d$_8$): δ 0.40 (br s, 6H; CH*Me*$_2$), 0.99 (br s, 9H; C*Me*$_3$), 1.04 (br s, 3H; CH*Me*$_2$), 1.14 (br s, 6H; CH*Me*$_2$), 1.39 (br s, 3H; CH*Me*$_2$), 1.57 (br s, 3H; CH*Me*$_2$), 1.72 (br s, 3H; CH*Me*$_2$), 2.16 (br s, 3H; *Me*), 2.38 (br s, 3H; *Me*), 3.51 (br s, 1H; *CH*Me$_2$), 3.65 (br s, 1H; *CH*Me$_2$), 3.73 (br s, 1H; *CH*Me$_2$), 4.85 (br s, 1H; *CH*Me$_2$), 7.03 (br s, 1H; aromatic C*H*), 7.15 (br s, 2H; aromatic C*H*). ^{13}C{^{1}H} NMR (100 MHz, THF-d$_8$): δ 10.3, 10.7, 19.2, 20.2, 22.1, 25.8, 26.7, 27.9 (CH*Me*$_2$, C*Me*$_3$, *Me*), 29.6, 52.4, 54.3 (*C*HMe$_2$), 39.9 (*C*Me$_3$), 88.2 (cage *C*), 125.1, 126.7, 127.6, 128.1, 129.6, 142.0 (aromatic *C*, N*CC*N), 143.3, 147.7 (N*C*N, *C*N). ^{11}B NMR (128 MHz, THF-d$_8$): δ -18.8 (d, J_{BH} = 137 Hz; 2B), -15.1 (d, unresolved; 1B), -13.5 (d, unresolved; 2B), -12.0 (d, J_{BH} = 145 Hz; 2B), -10.0 (d, J_{BH} = 151 Hz; 2B), -7.1 (d, J_{BH} = 129 Hz; 1B), 17.7 (s, 1B). Anal. Calcd for $C_{30}H_{56}B_{11}N_3$ (**3**): C 62.37, H 9.77, N 7.27. Found: C 62.32, H 10.01, N 7.66.

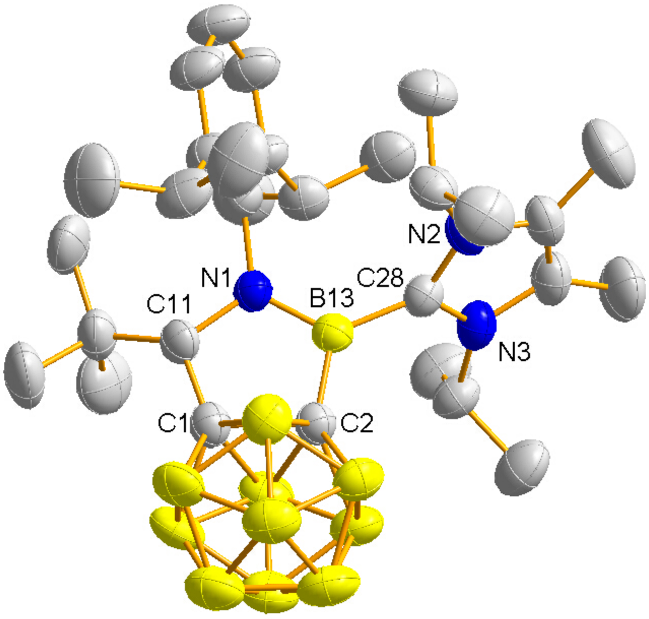
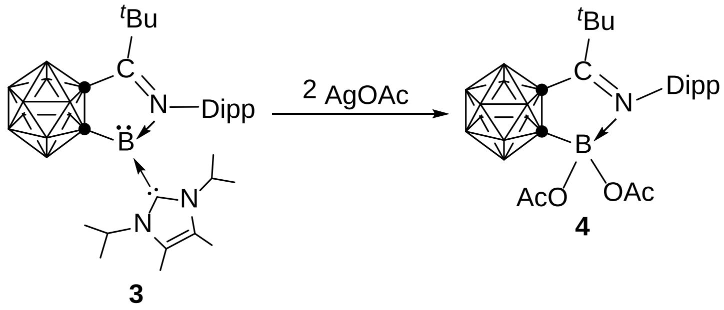


Figure S3. Molecular Structure of **3.**



Preparation of 4. To a THF solution (15 mL) of **3** (58.0 mg, 0.1 mmol) was added AgOAc (33.4 mg, 0.2 mmol) at room temperature, and the mixture was stirred at room temperature overnight. The color of solution was changed from dark purple to light brown with the formation of black precipitate (silver). The ^{11}B NMR spectrum indicated a complete conversion of **3**. After removal of precipitate and solvent, the resulting yellow oil was dissolved in toluene (20 mL). After removal of toluene and extraction with n-hexane (3 x 20 mL), the hexane solution was concentrated to about 25 mL. Compound **4** was isolated as colorless crystals after slow evaporation of the solvent (15.0 mg, 29%). ^{1}H NMR (400 MHz, C_6D_6): δ 0.86 (s, 9H; C*Me*$_3$), 1.00 (d, *J* = 6.8 Hz, 6H; CH*Me*$_2$), 1.23 (d, *J* = 6.0 Hz, 6H; CH*Me*$_2$), 1.89 (s, 6H; OC*Me*), 2.92 (m, 2H; *CH*Me$_2$), 6.86 (d, *J* = 7.6 Hz, 2H; aromatic C*H*), 7.01 (t, *J* = 7.6 Hz, 1H; aromatic C*H*). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 23.5, 24.6, 26.0, 28.5 (CH*Me*$_2$, C*Me*$_3$, OC*Me*), 30.3 (*C*HMe$_2$), 45.0 (*C*Me$_3$), 77.8 (cage *C*), 125.1, 129.9, 136.7, 143.3 (aromatic *C*), 169.6 (*C*N), 189.6 (*C*O). ^{11}B NMR (128 MHz, C_6D_6): δ -9.7 (d, unresolved; 5B), -7.0 (d, J_{BH} = 155 Hz; 3B), -2.8 (d, J_{BH} = 141 Hz; 1B), 1.3 (d, J_{BH} = 132 Hz; 1B), 5.2 (s, 1B). Anal. Calcd for $C_{23}H_{42}B_{11}NO_4$ (**4**): C 53.59, H 8.21, N 2.72. Found: C 53.66, H 8.92, N 3.04.

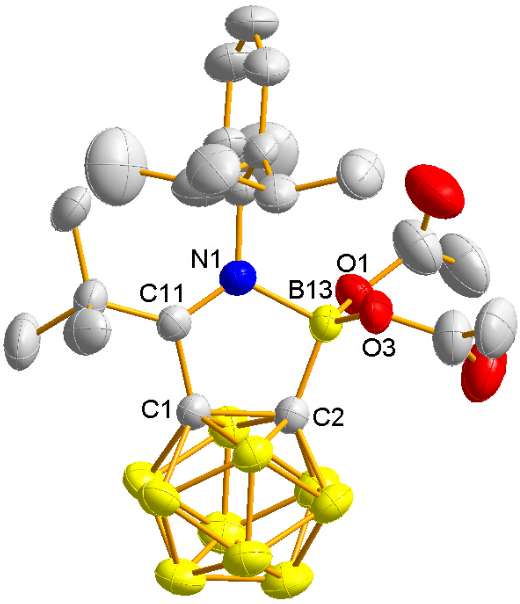


Figure S4. Molecular Structure of **4.**

X-ray Structure Determination. Single crystals were immersed in Paraton-N oil and sealed under argon in thin-walled glass capillaries. All data were collected at 296 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 calculations on F^2 using the SHELXTL program package.[4] All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and refinement are given in Table S1. Details of the crystal structures were deposited in the Cambridge Crystallographic Data Centre with CCDC 1404022-1404025 for **1** - **4**.

Table S1. Crystal Data and Summary of Data Collection and Refinement for **1-4**

compounds	**1**	**2**·0.5C_7H_8	**3**	**4**·0.25C_6H_{14}
formula	$C_{19}H_{37}B_{10}N$	$C_{22.50}H_{40}B_{11}Br_2N$	$C_{30}H_{56}B_{11}N_3$	$C_{24.50}H_{45.50}B_{11}NO_4$
Mw	387.60	603.29	577.69	537.03
crystal size (mm^3)	0.50x0.40x0.30	0.50x0.40x0.30	0.08x0.06x0.05	0.40x0.30x0.20
crystal system	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	P-1
a, Å	10.515(1)	8.889(1)	9.990 (1)	9.856(1)
b, Å	20.272(2)	16.193(3)	23.386(3)	17.248(1)
c, Å	12.191(1)	21.266(3)	18.285(2)	19.285(1)
α, deg	90	90	90	97.064(2)
β,deg	108.02(1)	94.99(1)	96.64(1)	93.41(1)
γ, deg	90	90	90	102.491(2)
V, Å^3	2471.0(5)	3049.6(8)	4243.1(10)	3163.89(14)
Z	4	4	4	4
D_{calcd}, Mg/m^3	1.042	1.314	0.904	1.127
Radiation (Å)	0.71073	0.71073	0.71073	0.71073
2θ range, deg	4.02 to 50.48	3.16 to 50.50	3.48 to 55.22	2.14 to 50.50
μ, mm^{-1}	0.053	2.673	0.048	0.067
F(000)	832	1228	1248	1146
No. of obsd reflns	4469	5521	9822	11399
No. of params refnd	272	344	397	715
Goodness of fit	1.025	0.976	0.908	1.037
R1	0.0841	0.0993	0.0777	0.0723
wR2	0.2165	0.2273	0.1834	0.1936

Computational Details. The geometry optimization of compound **3** is performed using the Gaussian09 program, Revision D.01,[5] at the B3LYP[6]-D3[7] theoretical level using 6-31g(d,p) basis set. Frequency calculations were made to determine the characteristics of all stationary points as energy minima. Orbital energies of compound **3** are calculated at the same level of theory. NBO analysis was also carried out using the NBO program implemented in the Gaussian 09 package. The graphic of molecular orbital were produced by using the visualizing software VMD.[8]

Table S2. The Cartesian coordinate of compound **3**

0 1

N	-0.70668800	-0.49406200	0.34382200
N	2.38913400	-0.05342700	-1.12833900
N	2.44731000	1.62186200	0.26867800
B	0.05756300	0.63951700	-0.11766600
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H	-1.35934200	2.24759400	1.98993600
B	-1.04139900	3.51727800	-0.26579200
H	-0.07057800	4.12491200	0.02197400
B	-2.02313300	1.23004500	-1.71626700
H	-1.68132700	0.25769500	-2.28997900
B	-1.14577400	2.73375800	-1.86290300
H	-0.22378700	2.78260000	-2.61177000
B	-3.51274100	2.28431500	0.49530000
H	-4.31549200	2.05090100	1.33071100
B	-2.68257000	3.85206900	0.30254100
H	-2.91277500	4.75898100	1.03542900
B	-2.26330300	4.05317300	-1.42159500
H	-2.19037900	5.12549300	-1.92839400
B	-2.87345300	2.63530000	-2.30255800
H	-3.22232500	2.66210000	-3.43838500

B	-3.64778700	1.53243600	-1.13632200
H	-4.49783300	0.74014500	-1.36597700
B	-3.82781900	3.28229000	-0.94693900
H	-4.87965000	3.81237000	-1.10250500
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C	-2.93535900	-0.91600900	1.64562400
C	-2.53919600	-2.35758400	2.03627500
H	-1.54031100	-2.42028100	2.46437900
H	-2.58124900	-3.05388300	1.20107500
H	-3.24342700	-2.70945100	2.79756900
C	-2.82959700	-0.08319600	2.95572200
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H	-3.39700200	-0.56586400	3.76070100
H	-3.21912800	0.92725400	2.83775100
C	-4.41451000	-0.98246100	1.19760600
H	-4.51661200	-1.60985500	0.30725800
H	-4.82734900	-0.00249100	0.96419200
H	-5.02636900	-1.41620400	1.99674700
C	1.59944000	0.72778400	-0.33425700
C	3.72293400	0.33760400	-1.01978400
C	3.75953800	1.38809500	-0.14569900
C	4.86064800	-0.33732300	-1.71393900
H	5.78699600	0.20715300	-1.52567700
H	4.72149300	-0.37763800	-2.79745700
H	4.99586900	-1.36310000	-1.35764700
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H	5.86555100	1.63482600	0.02433400
H	4.97775200	2.30287400	1.38632500

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H	1.34417800	-0.80550300	-4.28869400
H	2.87654900	-0.02832400	-3.87850200
C	1.99865200	2.64637100	1.24734100
H	0.91396000	2.60268200	1.19913200
C	2.40058600	2.31429600	2.68750400
H	1.95172300	1.37766900	3.01670800
H	2.03441300	3.11071500	3.34184900
H	3.48331200	2.24690800	2.81807300
C	2.43129200	4.05642400	0.83125000
H	2.26418900	4.22098700	-0.23546500
H	3.47958500	4.25386500	1.06449800
H	1.82760900	4.78409400	1.37949300
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H	-0.49489700	-4.82016500	-1.27078300
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C	1.31155700	-3.52588300	1.27119400
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C	0.81852000	-2.21302700	1.29396400

C	1.35335600	-1.27905500	2.37689100
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H	3.24202900	-0.87133300	1.33576500
H	3.35604800	-2.14387700	2.55325900
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H	1.30832700	-1.03118000	4.53963400
H	1.27591900	-2.72322700	4.02183600
C	-1.78812300	-2.52590900	-1.59483200
H	-2.21928600	-1.55344400	-1.35764300
C	-1.26770000	-2.49485400	-3.04410600
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H	-3.74830600	-3.25021000	-2.17334400
H	-3.34474100	-3.62791000	-0.49725400
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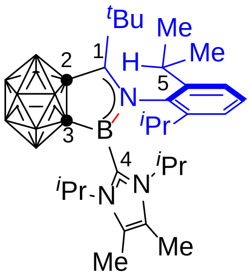
Table S3. Results of the NBO Analysis



3

		Occupancy	Coefficients	
C1-C2	σ	1.97	0.6669* C1	0.7451* C2
	π	1.60	0.7718* C1	0.6358* C2
	π*	0.88	-0.6358* C1	0.7718* C2
C1-C(^{t}Bu)	σ	1.97	0.7080* C1	0.7062* C(^{t}Bu)
C1-N	σ	1.97	0.5990* C1	0.8007* N
C5-N	σ	1.98	0.6140* C5	0.7893* N
B-N	σ	1.96	0.4778* B	0.8785* N
	π	1.85	0.4725* B	0.8813* N
B-C3	σ	1.87	0.5443* B	0.8389* C3
B-C4	σ	1.96	0.5707* B	0.8212* C4
C2-C3	σ	1.73	0.7013* C2	0.7128* C3

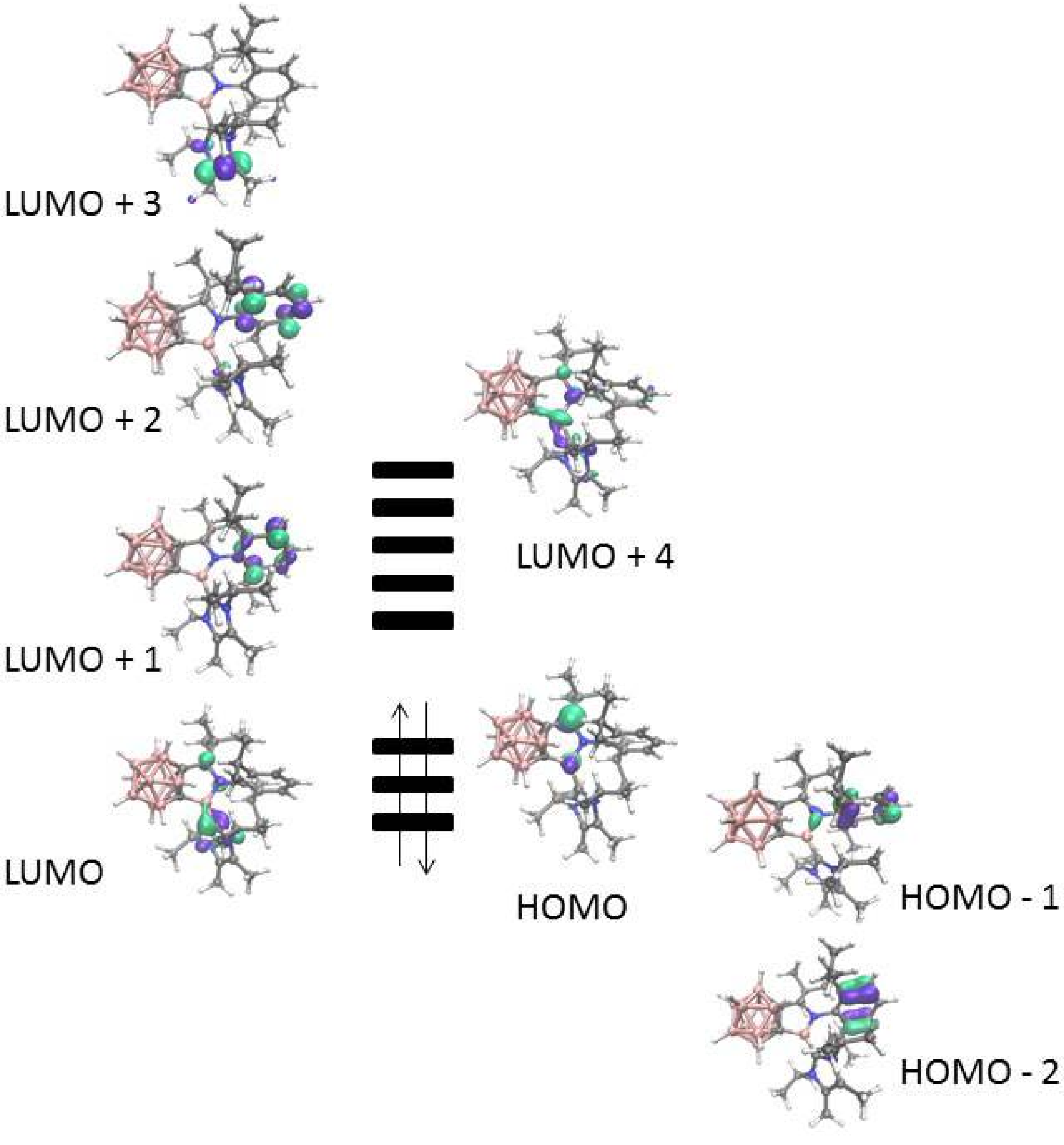


Figure S5. Plots of frontier molecular orbitals of **3** calculated at B3LYP-D3/6-31G(d,p) level of theory. HOMO and LUMO + 4 show the orbital features of an allyl-like BNC moiety. HOMO - 1 and HOMO - 2 are π-bonding molecular orbitals on the aryl ring of the Dipp substituent while LUMO, LUMO + 1, LUMO + 2 and LUMO + 3 are mainly contributed by the NHC moiety and π* molecular orbitals on the aryl ring of the Dipp substituent.

References

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