Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION

Hypoelectronic Isomeric Diiridaboranes $[(Cp^*Ir)_2B_6H_6]$: The "Rule-Breakers" ($Cp^* = \eta^5\text{-}C_5Me_5$)

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I Experimental Details

I.1 Synthesis

Scheme S1 Synthesis of compounds **1, 2** and **3**

I.2 Spectroscopic details

Fig. S1 ^{1}H NMR spectrum of **1**

Fig. S2 $^{11}B\{^{1}H\}$ NMR spectrum of **1**

Fig. S3 ^{11}B NMR spectrum of **1**

Fig. S4 $^{1}H\{^{11}B\}$-$^{11}B\{^{1}H\}$ HSQC spectrum of **1**

Fig. S5 ^{1}H NMR spectrum of **2**

Fig. S6 $^{11}B\{^{1}H\}$ NMR spectrum of **2**

Fig. S7 ^{11}B NMR spectrum of **2**

Fig.S8 ^{1}H NMR spectrum of **3**

Fig. S9 $^{11}B\{^{1}H\}$ NMR spectrum of **3**

Fig. S10 ^{11}B NMR spectrum of **3**

I.3 X-ray analysis details

I.4 Computational details

II Supplementary data

Table S1 DFT calculated and experimental NMR chemical shifts δ (ppm) **1'**-**3'**

Table S2. DFT calculated energies of the HOMO and LUMO (eV), HOMO-LUMO gaps ($\Delta E = E_{LUMO} - E_{HOMO}$, eV), relative electronic energy (E_R, kcal/mol) and relative thermal energy ($H_{R,}$ kcal/mol) for **1'** and **2'**

Fig. S11 Selected molecular orbitals of **1'** and **2',** where **(a)** shows the HOMO of **1'** and **(b)** shows the LUMO of **2'**

Fig. S12 Molecular orbital scheme resulting from Fenske-Hall calculation on **1'**

Fig.S13 Molecular orbital scheme resulting from Fenske-Hall calculation on **2'**

Fig.S14 Frontier molecular orbitals of **1'** obtained from Fenske-Hall calculation

Fig.S15 Frontier molecular orbitals of **2'** obtained from Fenske-Hall calculation

I. Experimental details

I.1 Synthesis

General procedures and instrumentation. All the syntheses were carried out under argon atmosphere with standard Schlenk and glove box techniques. Solvents were dried by common methods and distilled under N_2 before use. $[Cp^*IrCl_2]_2$ was prepared according to literature method[1]while other chemicals ($NaBH_4$, BH_3.THF) were obtained commercially and used as received. The external reference for the ^{11}B NMR, $[Bu_4N(B_3H_8)]$ was synthesized according to literature method.[2] Thin layer chromatography was carried on aluminum supported silica gel TLC plates (MERCK TLC Plates) with layer thickness of 250-μm and L x W 20 cm x 20 cm. NMR spectra were recorded on 400 and 500 MHz Bruker FT-NMR spectrometers. The residual solvent protons were used as reference (δ, ppm, d_6-benzene, 7.16, $CDCl_3$, 7.26), while a sealed tube containing $[Bu_4N(B_3H_8)]$ in d_6-benzene (δ_B, ppm, –30.07) was used as an external reference for the ^{11}B NMR. Electrospray mass (ESI-MS) spectra were recorded on a Qtof Micro YA263 HRMS instrument.

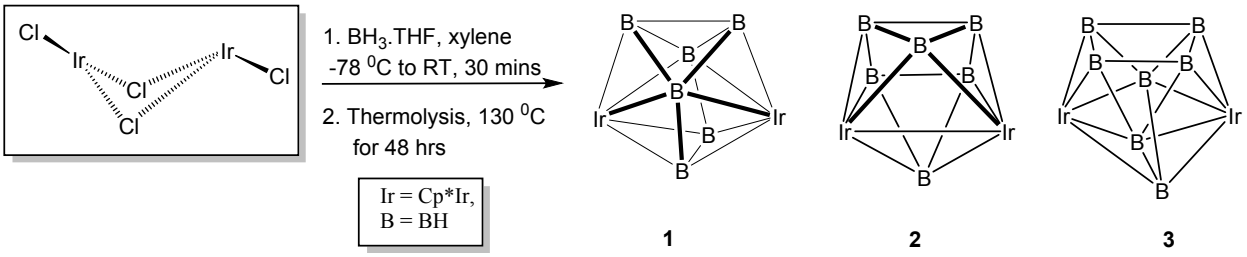
Synthesis of 1, 2 and 3: In a flame-dried Schlenk tube, $[Cp^*IrCl_2]_2$ (0.2g, 0.25 mmol) was suspended in xylene (15 mL) and cooled to -78 ˚C. To it BH_3.THF (4.00 mL, 4.01 mmol) was added, the reaction mixture was slowly warmed to room temperature and allowed to stir for 30 min at room temperature and then kept on thermolysis for three days. The solvent was removed under vacuum and the residue was extracted into hexane and passed through Celite. The mother liquor was concentrated and the residue was subjected to chromatographic work up using silica-gel TLC plates. Elution with a hexane/CH_2Cl_2 (70:30) mixture afforded yellow **1**(0.053 g, 18%), red **2** (0.048 g, 24 %) and brown **3** (0.033, 32 %).

1: R_f = 0.42 (7:3 Hexane/CH_2Cl_2); HRMS (ESI) calcd for $C_{20}H_{37}Ir_2B_6^+$ $[M+H]^+$ m/z 729.2712, found m/z 729.2723; ^{11}B NMR (160 MHz, $CDCl_3$, 22 °C): δ = 92.1 (d, J_{B-H} = 151 Hz, 2B), 64.6 (d, J_{B-H} = 148 Hz, 2B), -23.1 (d, J_{B-H} = 133 Hz, 2B); ^1H NMR (400MHz, $CDCl_3$, 22 °C): δ = 12.31-10.77 (m, 4H, BH*t*), 1.93(s, 30H, Cp*), -3.47 (q, 2H, BH*t*); ^{13}C NMR (100 MHz, $CDCl_3$, 22 °C): δ = 98.9 (s, C_5Me_5), 10.9 (s, C_5Me_5).

2: R_f = 0.30 (7:3 Hexane/CH_2Cl_2); HRMS (ESI) calcd for $C_{20}H_{36}Ir_2B_6^+$ $[M+H]^+$ m/z 729.2712, found m/z 729.2719; ^{11}B NMR (160 MHz, $CDCl_3$, 22 °C): δ = 73.1 (d, J_{B-H} = 149 Hz, 4B), 51.8

(d, J_{B-H} = 116 Hz, 2B); ^{1}H NMR (400MHz, $CDCl_3$, 22 °C): δ = 9.09-8.24(m, 6H, BH*t*), 1.97 ppm (s, 30H, Cp*); ^{13}C NMR (100 MHz, $CDCl_3$, 22 °C): δ = 101.9 (s, C_5Me_5), 11.3 ppm (s, C_5Me_5).

3: R_f = 0.48 (7:3 Hexane/CH_2Cl_2); HRMS (ESI) calcd for $C_{20}H_{37}Ir_2B_7^+$ $[M]^+$ m/z 740.2805, found m/z 740.6362; ^{11}B NMR (160 MHz, $CDCl_3$, 22 °C): δ = 102.6 (d, J_{B-H} = 159 Hz, 1B), 63.2 (d, J_{B-H} = 144 Hz, 4B), -4.9 (d, J_{B-H} = 131 Hz, 2B); ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C): δ = 16.98 (d, 2H, BH*t*), 9.78-8.99 (m, 5H,BH*t*), 1.927 (s, 30H, Cp*); ^{13}C NMR (100 MHz, $CDCl_3$, 22 °C): δ = 98.4 (s, C_5Me_5), 8.6 ppm (s, C_5Me_5).



Scheme S1. Synthesis of compounds **1, 2** and **3**.

I.2 Spectroscopic details

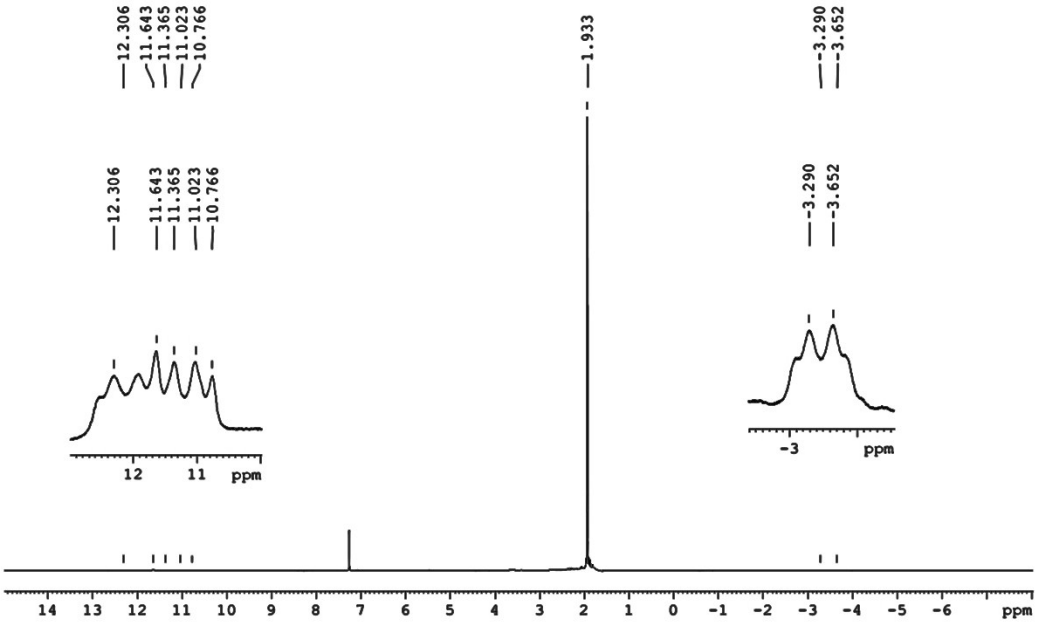


Fig. S1.[1]H NMR spectrum of **1**

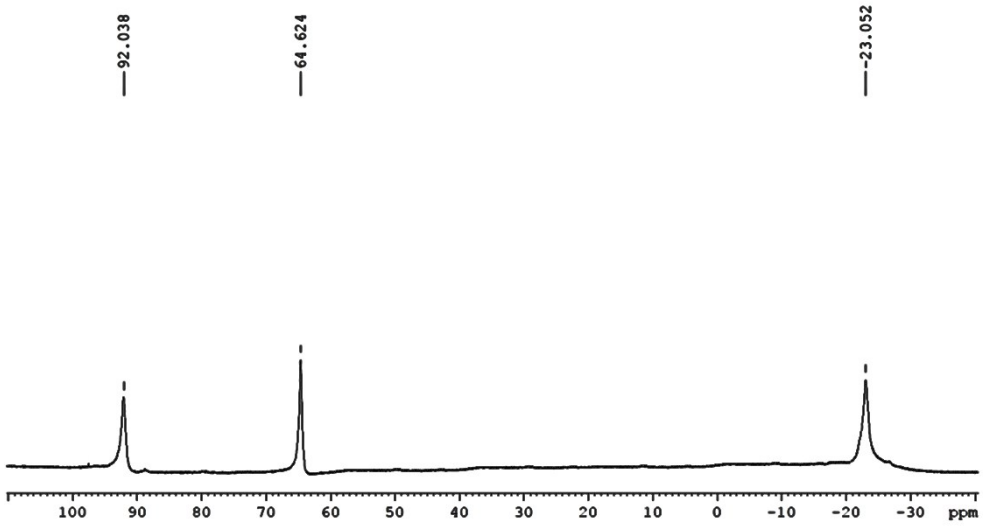


Fig. S2. [11]B{[1]H} NMR spectrum of **1**

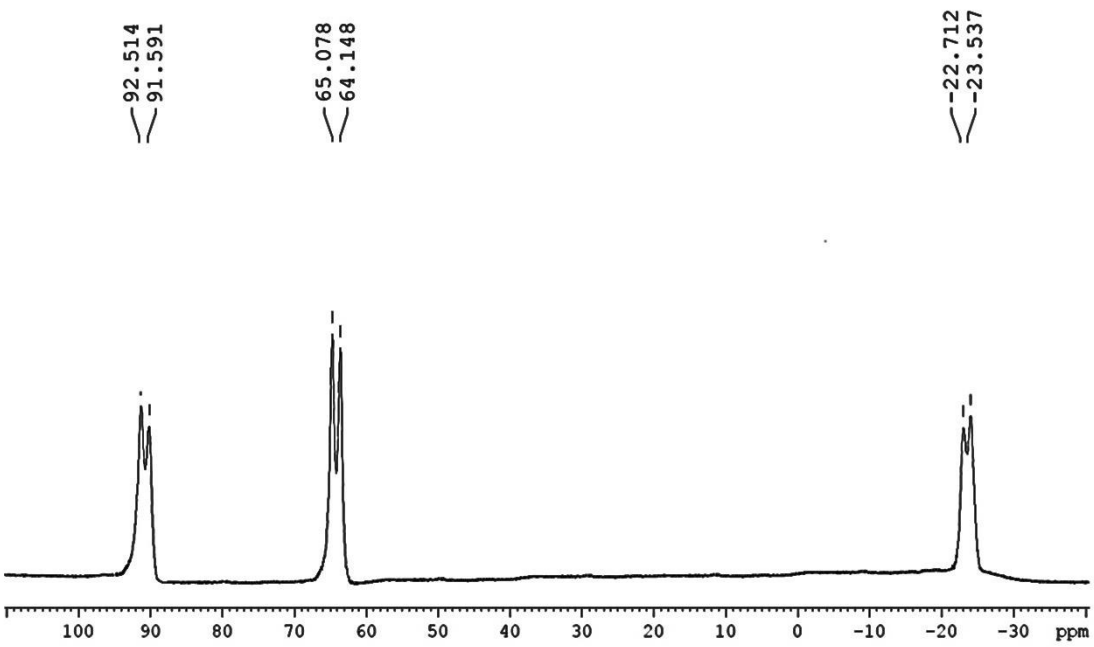


Fig. S3. ^{11}B NMR spectrum of **1**

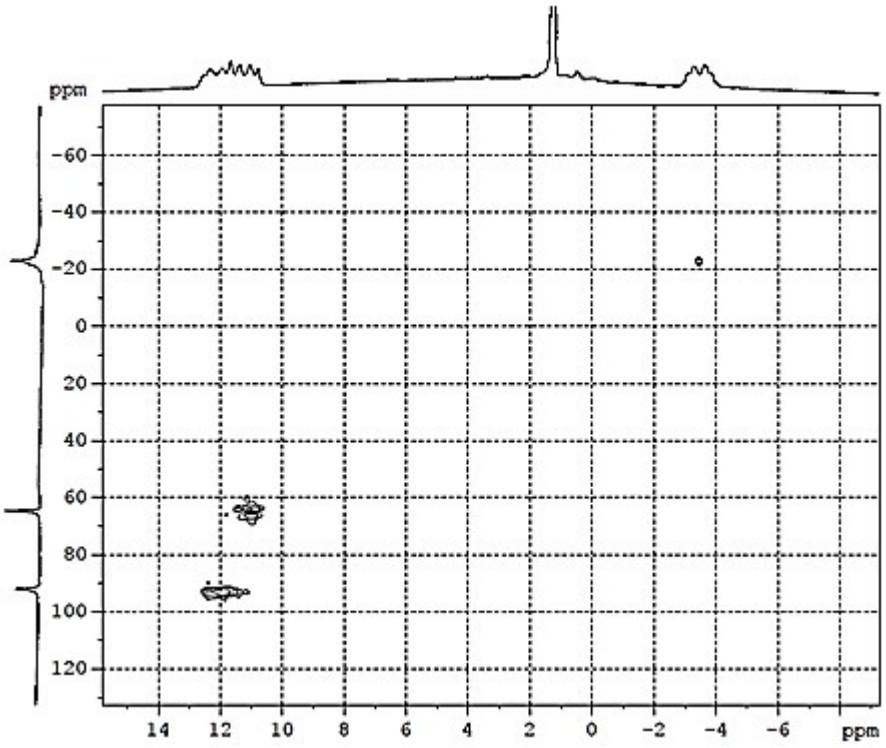


Fig.S4. ^{1}H{^{11}B}-^{11}B{^{1}H} HSQC spectrum of **1**

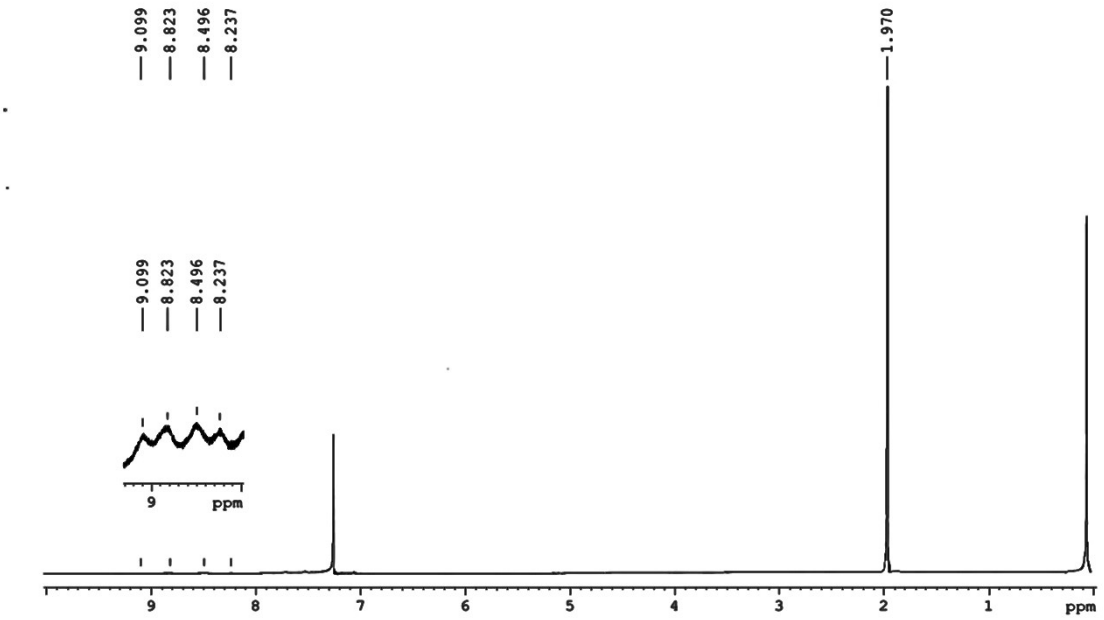


Fig. S5. ^{1}H NMR spectrum of **2**

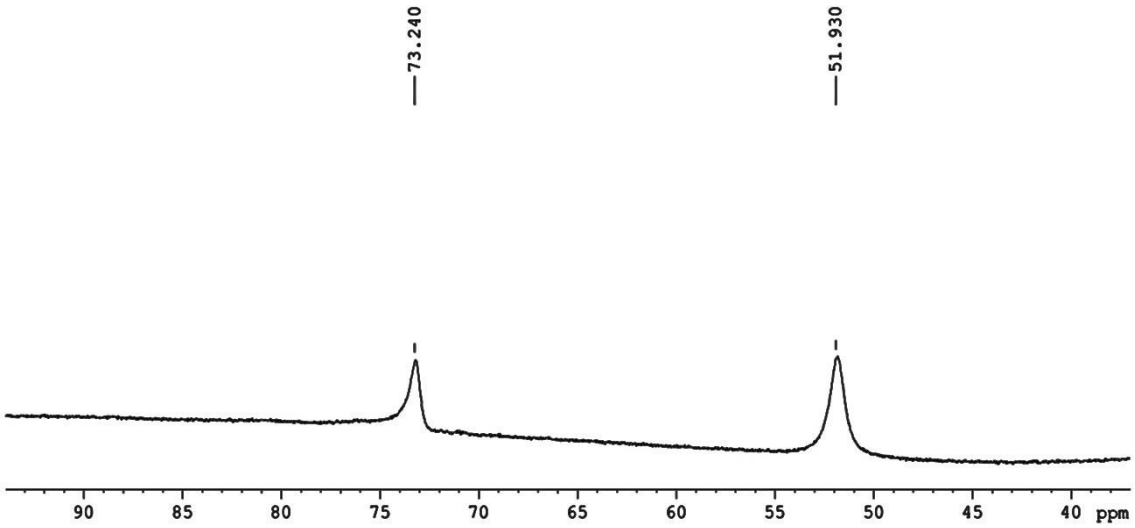


Fig. S6. $^{11}B\{^{1}H\}$ NMR spectrum of **2**

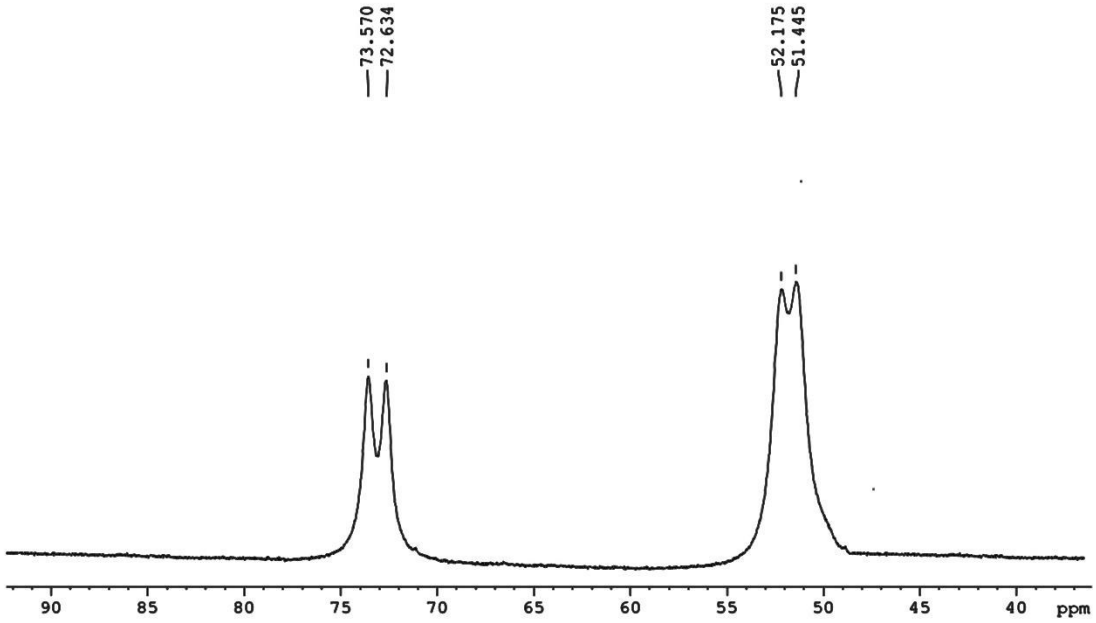


Fig. S7. ^{11}B NMR spectrum of **2**

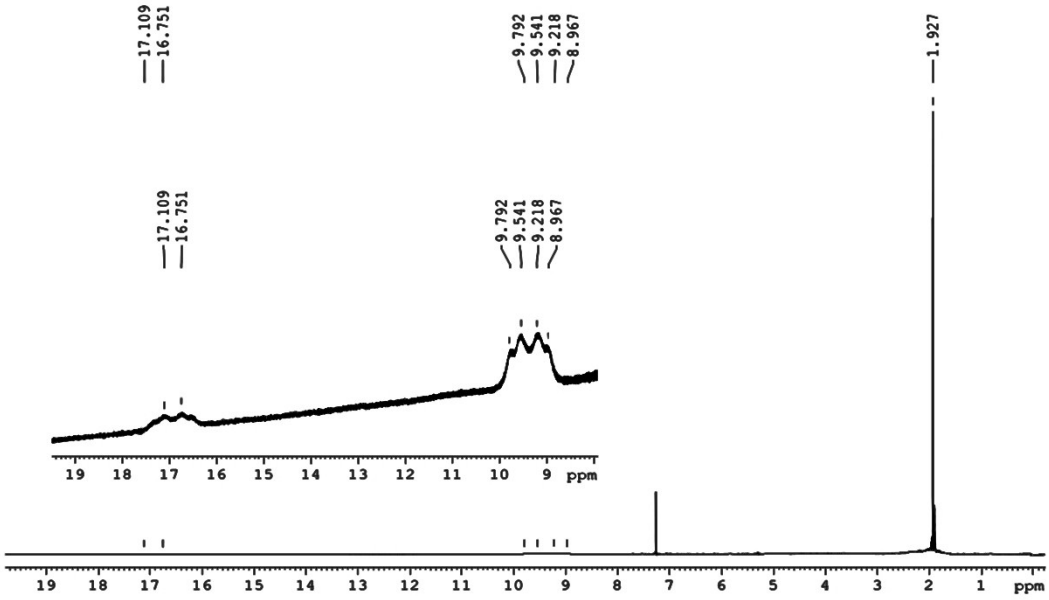


Fig.S8.^{1}H NMR spectrum of **3**

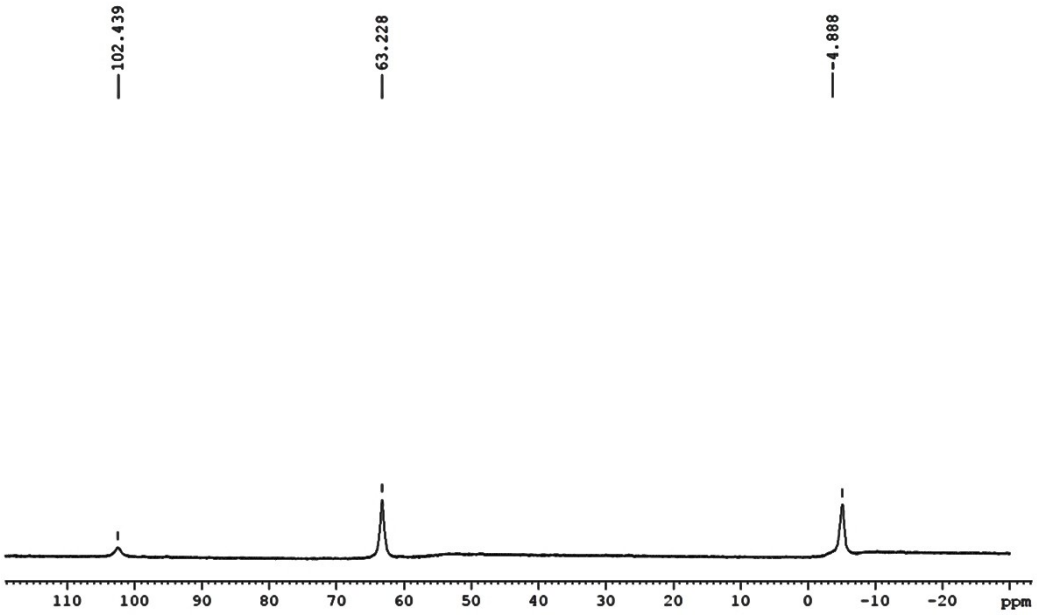


Fig. S9.$^{11}B\{^{1}H\}$ NMR spectrum of **3**

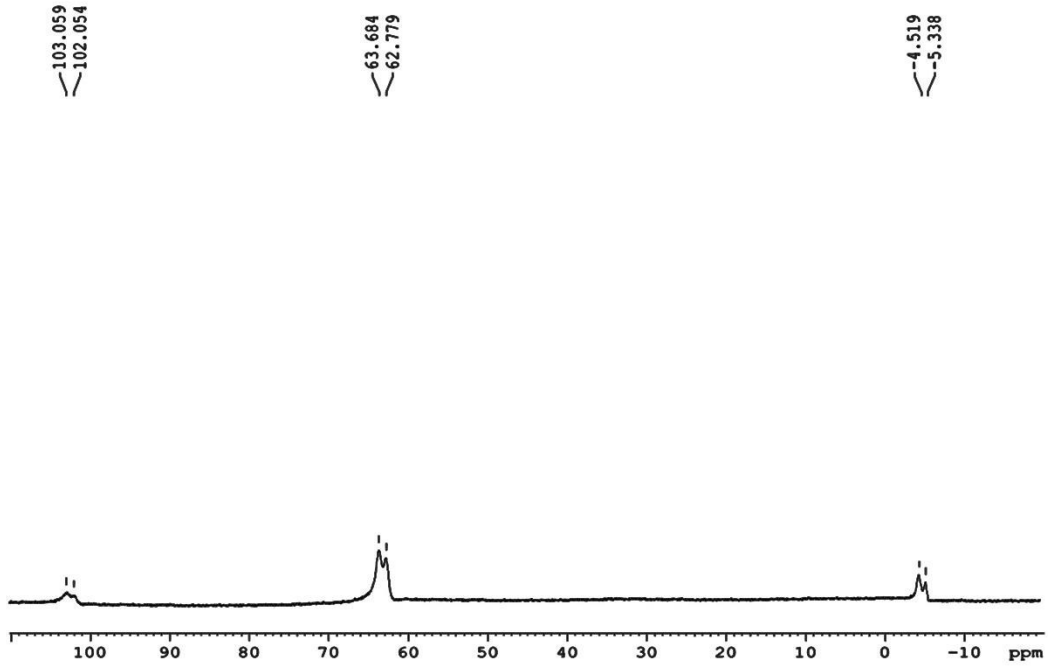


Fig. S10. ^{11}B NMR spectrum of **3**

I.3 X-ray analysis details

The crystal data of **1** and **3** were collected and integrated using a Bruker Axs kappa apex2 CCD diffractometer with graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation.The crystal data for **2** was collected and integrated using Super Nova (Mo) X-ray Source, with graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation at 293 K. The structures were solved by heavy atom methods using SHELXS-97 or SIR92 and refined using SHELXL-97.[3] CCDC 1429317(**1**), 1429319 (**2**), 1429318(**3**) 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.

Crystal data for **1**: $C_{20}H_{36}B_6Ir_2$, M_r = 725.75, Monoclinic, $P2_1/n$, a = 9.1413(2)Å, b = 19.4335(7)Å, c = 28.6894(9)Å, β = 98.9110(10)°, V = 5035.1(3)Å^3, Z = 8, ρ_{calcd} = 1.915 mg/m^3, μ = 10.565 mm^{-1}, F(000) = 2720, R_1 = 0.0437, wR_2 = 0.0858, 8865 independent reflections [2θ≤49.99°] and 524 parameters.

Crystal data for **2**: $C_{20}H_{36}B_6Ir_2$, M_r = 725.75, Monoclinic, $P2_1/c$, a = 16.4805(14) Å, b = 19.9995(11) Å, c = 16.6991(14) Å, β = 117.242(11)°, V = 4893.5(8)Å^3, Z = 8, ρ_{calcd} = 1.970mg/m^3, μ = 10.870mm^{-1}, F(000) = 2720, R_1 = 0.0831, wR_2 = 0.2211, 8552 independent reflections [2θ≤49.98°] and 525 parameters.

Crystal data for **3**: $C_{20}H_{37}B_7Ir_2$, M_r = 737.56, Triclinic, *P-1*, a = 9.1768(2) Å, b = 9.2116(2)Å, c = 16.3496(4) Å, α = 99.3790(10)°, β = 101.7600(10)°, γ = 102.7410(10)°, V = 1288.09(5)Å^3, Z = 2, ρ_{calcd} = 1.902 mg/m^3, μ = 10.325mm^{-1}, F(000) = 692, R_1 = 0.0330, wR_2 = 0.0860, 4514 independent reflections [2θ≤50.00°] and 353 parameters.

I.4 Computational details

Geometry optimizations without symmetry constraints were carried out using Gaussin09[4] software suite. The calculations were performed using density functional theory at the BP86[5] level in conjunction with def2-TZVP[6] basis sets. The 60 core electrons of iridium were replaced by the quasi-relativistic effective core potential def2-ECP[7] for iridium. To save computing time all the calculations were carried out with the Cp analogue model compounds, instead of Cp*. The model compounds were fully optimized in gaseous state (no solvent effect). Stationary

points were characterized as minima by calculating the Hessian matrix analytically at the same level. Thermodynamic corrections and Kohn-Sham orbitals have been taken from these calculations. The NMR chemical shifts were calculated using the hybrid Becke−Lee−Yang−Parr (B3LYP) functional,[8] using the BP86/def2-TZVP optimized geometries. Computation of the NMR shielding tensors employed gauge-including atomic orbitals (GIAOs),[9-11] using the implementation of Schreckenbach, Wolff, Ziegler, and co-workers.[12-16] The ^{11}B NMR chemical shifts were calculated relative to B_2H_6 (B3LYP B shielding constant 84.23 ppm) and converted to the usual [BF3.OEt_2] scale using the experimental δ(^{11}B) value of B_2H_6, 16.6 ppm[17] TMS ($SiMe_4$) was used as internal standard for the ^{1}H NMR chemical shift calculations. Bonding analysis was carried out using the NBO[18-19] routine within the Gaussian09 package at the same level of theory. Wiberg bond indexes (WBI)[20] and NBO second order perturbation energy values on some selected bonds are obtained on natural bond orbital (NBO) analysis. Molecular orbital analyses were performed with the aid of Jimp 2,[21] which employs Fenske-Hall[22] calculations and visualization using MOPLOT.[23] Fenske-Hall calculations were carried out on the DFT optimized geometries of **1'** and **2'** (Cp analog). The minimal AO basis set calculations were transformed into a fragment basis set for 2 CpIr and [B_6H_6] fragments.

II. Supplementary Data

Table S1. DFT calculated and experimental NMR chemical shifts δ (ppm) **1'- 3'**.

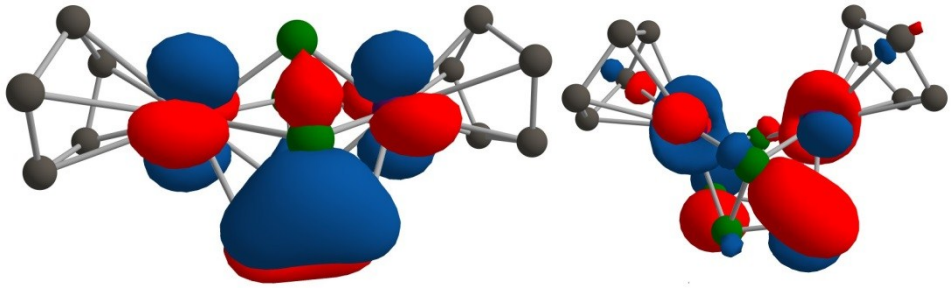
	1'		**2'**		**3'**	
^{11}B NMR	Exp.[a]	Cal.	Exp.	Cal.	Exp.	Cal.
B1	92.0	114.2	73.2	77.5	102.4	121.4
B2	92.0	114.2	51.9[a]	8.0	-4.9	6.2
B3	-23.0	-12.6	51.9[a]	104.2	-4.9	6.2
B4	64.6	64.6	51.9[a]	8.0	63.2[a]	106.9
B5	64.6	64.6	51.9[a]	104.2	63.2[a]	28.4
B6	-23.0	-12.6	73.2	76.6	63.2[a]	106.9
B7	-	-	-	-	63.2[a]	28.4

^{1}H NMR						
B<u>H</u>$_t$	-3.26, 11.64, 10.76	-2.98, 10.86, 9.97	8.82	8.45	17.10, 9.79	16.28,9.21

[a]Fluxional behavior

Table S2. DFT calculated energies of the HOMO and LUMO (eV), HOMO-LUMO gaps ($\Delta E = E_{LUMO} - E_{HOMO}$, eV), relative electronic energy (E_R, kcal/mol) and relative thermal energy (H_R, kcal/mol) for **1'**and **2'.**

Molecule	**E_{HOMO} (eV)**	**E_{LUMO} (eV)**	**E_{HOMO}-E_{LUMO} (eV)**	**E_R (kcal/mol)**	**H_R, (kcal/mol)**
1'	-5.68	-2.93	2.75	0	0
$(1')^{2-}$	3.99	5.51	1.52	20.50	21.86
2'	-5.69	-3.16	2.53	0	0
$(2')^{2-}$	4.01	5.40	1.39	16.0	16.95
$[B_8H_8]$	-7.81	-5.43	2.38	29.75	29.81
$[B_8H_8]^{2-}$	7.57	4.17	3.40	0	0



(a) **(b)**

Fig. S11. Selected molecular orbitals of **1'** and **2',** where **(a)** shows the HOMO of **1'** and **(b)** shows the LUMO of **2'**

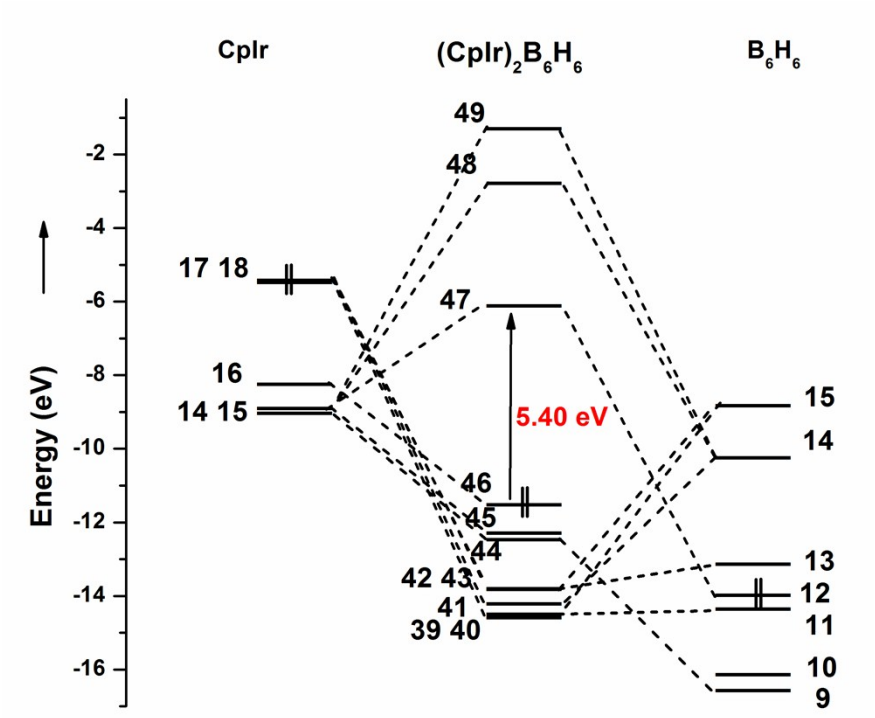


Fig S12. Molecular orbital scheme resulting from Fenske-Hall calculation on **1'**

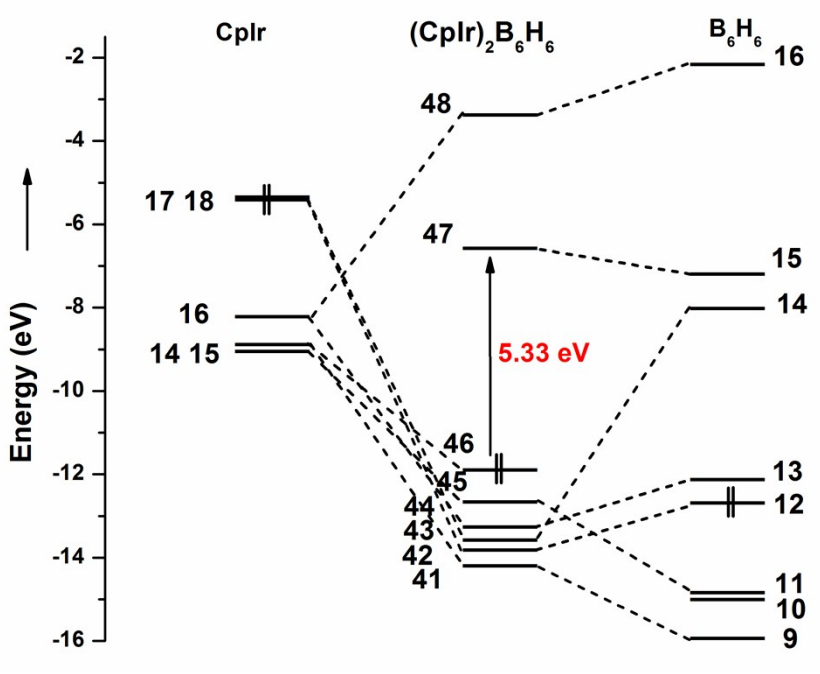


Fig.S13. Molecular orbital scheme resulting from Fenske-Hall calculation on **2'**

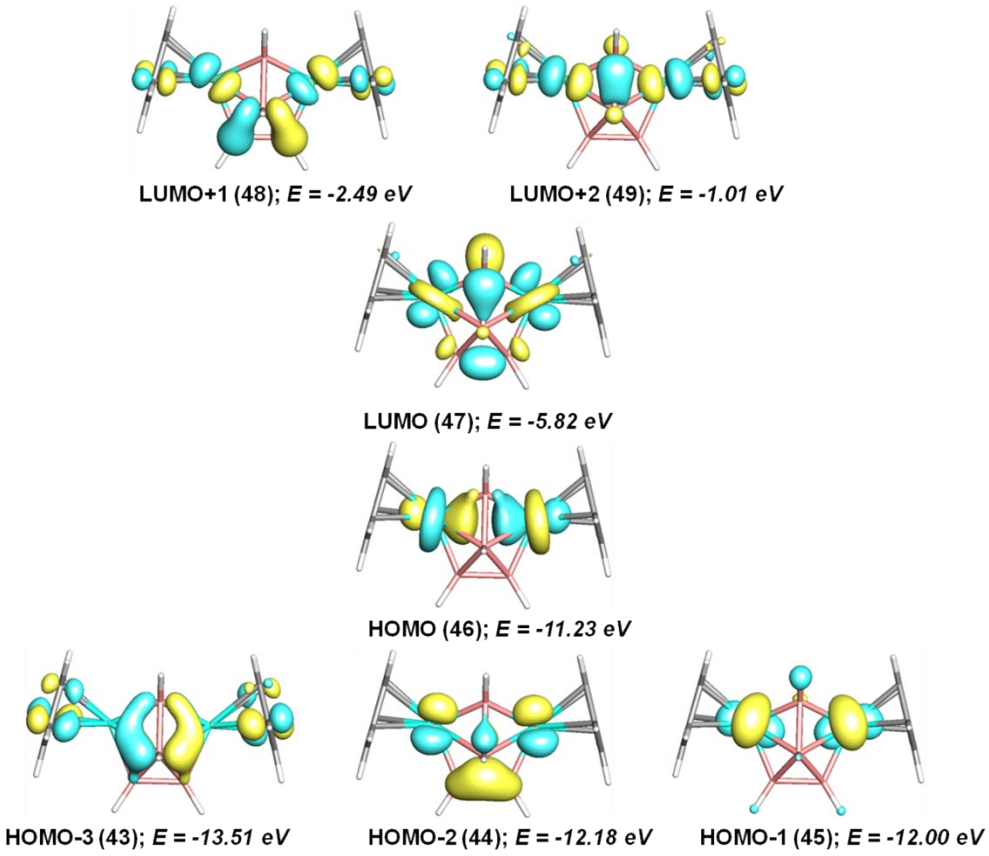


Fig. S14. Frontiermolecular orbitalsof **1'**obtained from Fenske-Hall calculation

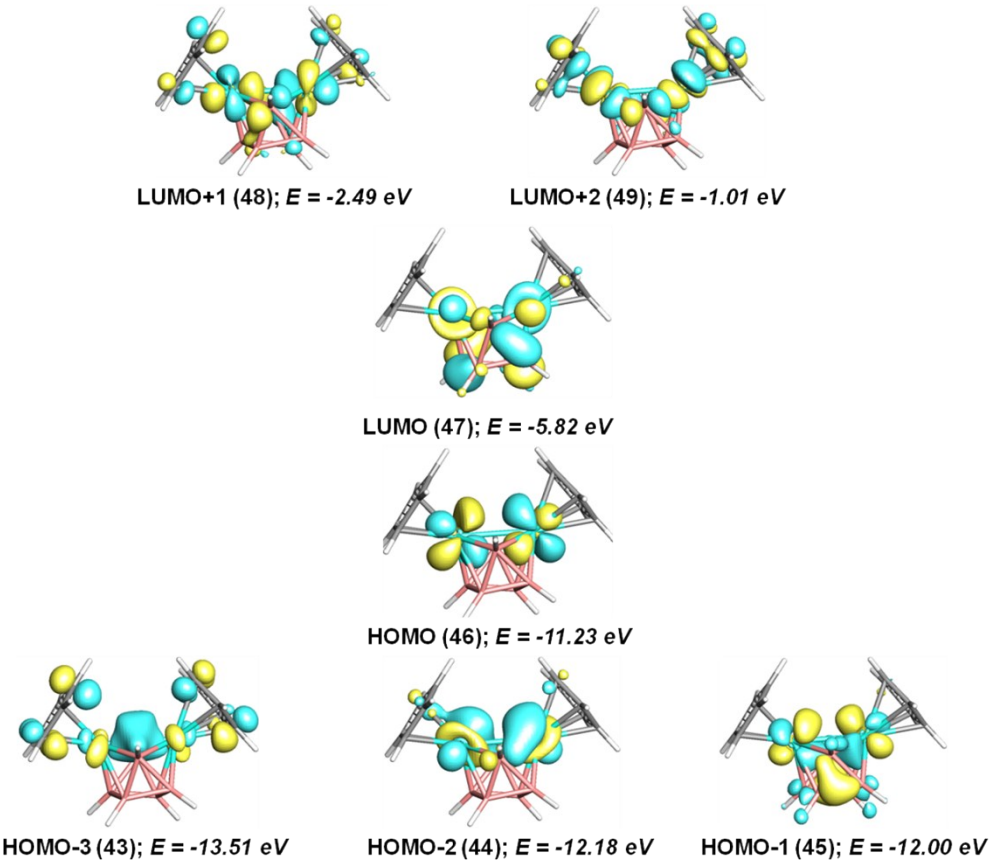
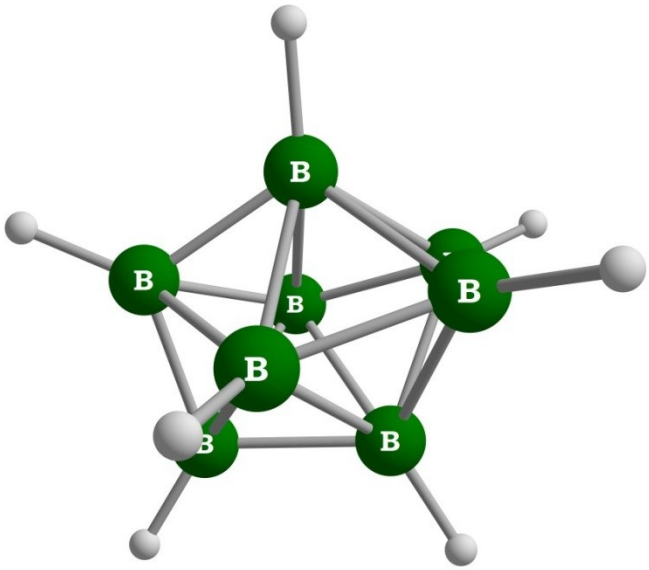


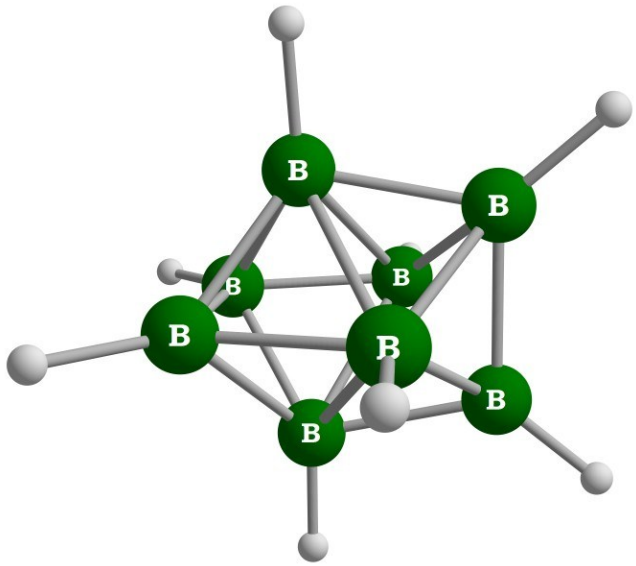
Fig. S15. Frontier molecular orbitals of **2'** obtained from Fenske-Hall calculation

Cartesian coordinates of the optimized molecules along with their total energies (in hartrees) including zero point vibrational correction.



$[B_8H_8]^{2-}$,T. E. = -203.555051

5	-0.316270000	-0.873130000	-0.920305000
5	-1.341809000	-0.587964000	0.557897000
5	-1.341809000	0.587963000	-0.557898000
5	-0.316270000	0.873130000	0.920305000
5	0.316270000	0.920306000	-0.873129000
5	0.316270000	-0.920305000	0.873130000
5	1.341809000	-0.557898000	-0.587963000
5	1.341809000	0.557898000	0.587963000
1	-0.615167000	-1.690954000	-1.780971000
1	2.263418000	-1.108022000	-1.166320000
1	2.263416000	1.108022000	1.166321000
1	-0.615167000	1.690954000	1.780970000
1	0.615167000	1.780972000	-1.690952000
1	-2.263417000	1.166320000	-1.108022000
1	-2.263417000	-1.166320000	1.108022000
1	0.615167000	-1.780973000	1.690951000



[B_8H_8],T. E. = -203.530104

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5	0.251106000	0.976452000	1.203541000
5	1.159404000	-0.323780000	0.464125000
5	0.378070000	1.112642000	-0.532498000
5	-0.367876000	-1.203345000	-0.284765000
5	-0.821544000	0.121010000	-1.332457000
5	0.853793000	-0.407940000	-1.252854000
1	-2.312509000	0.782538000	0.340374000
1	-1.535032000	0.250419000	-2.274272000
1	1.589913000	-0.738727000	-2.125513000
1	2.301270000	-0.682552000	0.560536000
1	0.745778000	2.244007000	-0.695821000
1	0.472283000	1.797894000	2.033685000
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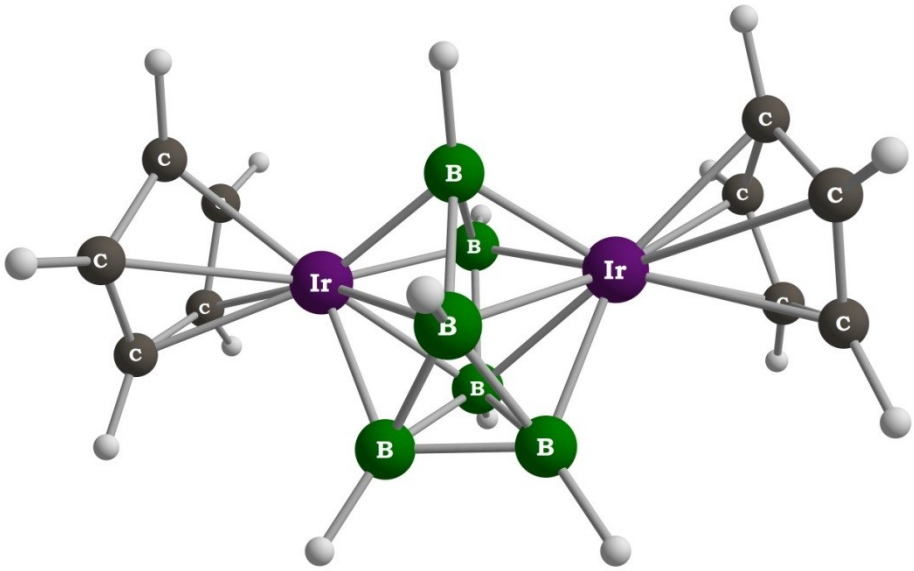
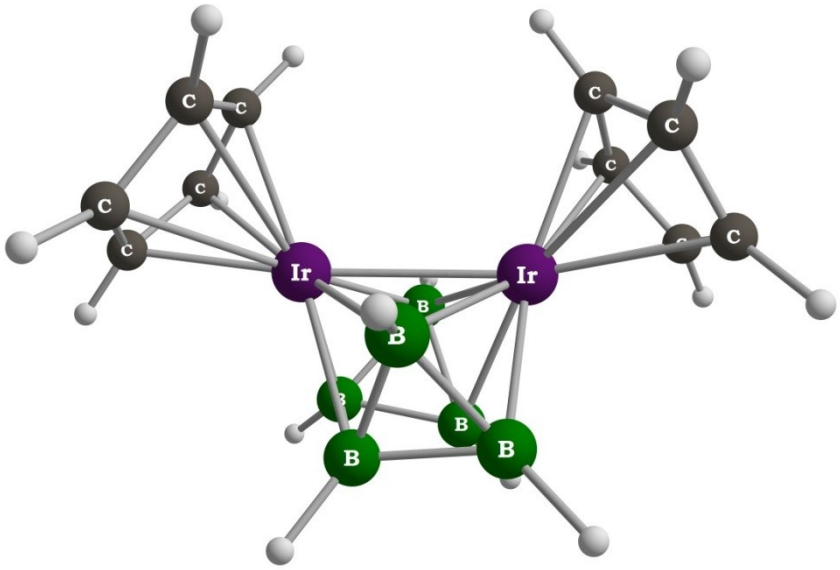


1', T. E. = -748.927982

77	-1.682631000	0.010221000	0.000045000
77	1.682609000	0.009777000	-0.000348000
6	3.376825000	-1.266269000	0.831576000
5	-0.000111000	-0.788742000	0.955066000
1	-0.001845000	-1.655287000	1.786802000
6	-3.731396000	0.096796000	-1.106364000
6	3.349563000	-1.432624000	-0.596247000
6	-3.376912000	-1.266680000	-0.830986000
6	3.730469000	0.097410000	1.107149000
6	3.914993000	0.768611000	-0.140055000
6	3.672121000	-0.169425000	-1.192607000
6	-3.915477000	0.767914000	0.140962000
6	-3.348637000	-1.433051000	0.596780000
5	-0.000139000	-0.788212000	-0.956024000
1	0.001188000	-1.654488000	-1.788036000
5	-0.003288000	1.008222000	-1.247678000
1	-0.005533000	1.143663000	-2.443478000
5	0.003414000	1.007678000	1.247839000
1	0.005716000	1.142772000	2.443667000
6	-3.671427000	-0.170007000	1.193347000
5	0.843964000	1.941433000	-0.003715000
1	1.480232000	2.955860000	-0.004034000
5	-0.843726000	1.941626000	0.004206000
1	-1.479694000	2.956245000	0.005054000

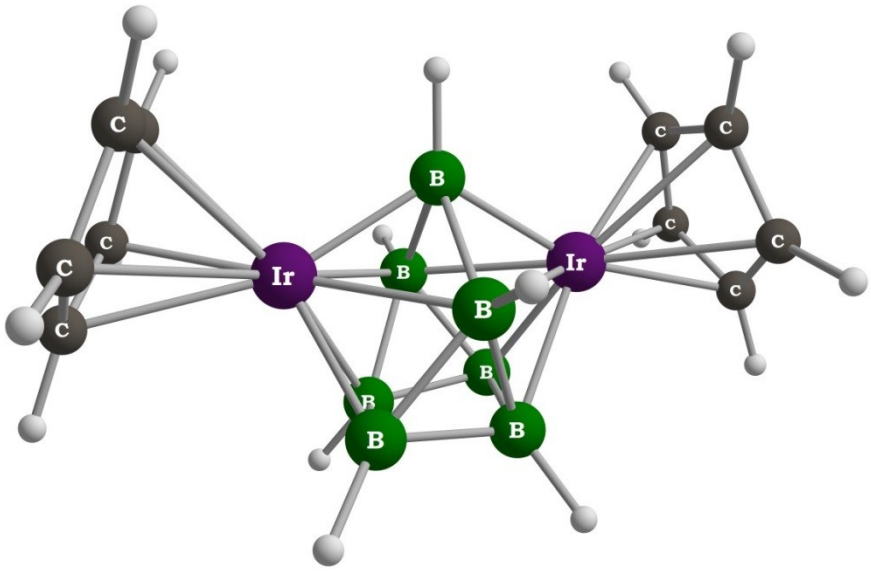
1	4.163539000	1.818163000	-0.268084000
1	3.725048000	0.036741000	-2.258184000
1	3.830964000	0.541906000	2.093693000
1	3.192825000	-2.040378000	1.571176000
1	3.129222000	-2.352445000	-1.130878000
1	-3.192885000	-2.040656000	-1.570720000
1	-3.127338000	-2.352722000	1.131280000
1	-3.723743000	0.036113000	2.258960000
1	-4.164488000	1.817340000	0.269162000
1	-3.832773000	0.541230000	-2.092849000



2', T. E. = -748.926744

77	1.375689000	0.115076000	-0.031864000
77	-1.377458000	0.115877000	0.031432000
6	2.254720000	-1.985192000	-0.449361000
6	2.379414000	-1.751851000	0.962274000
6	-3.483964000	-0.272167000	-0.750354000
6	3.049318000	-1.008659000	-1.131396000
6	3.218906000	-0.613301000	1.148204000
6	-2.686141000	-1.356448000	-1.244496000
5	0.093273000	0.659032000	1.529372000
5	-0.094520000	0.656483000	-1.534058000
5	-1.044797000	1.924904000	1.009237000
6	-2.180667000	-2.079916000	-0.122392000
6	3.627839000	-0.139080000	-0.148259000
6	-3.486976000	-0.339439000	0.685960000

5	1.045242000	1.921468000	-1.015518000
5	0.638789000	2.155489000	0.722832000
6	-2.672104000	-1.458557000	1.073014000
5	-0.639754000	2.153923000	-0.731564000
1	-2.481933000	-1.571346000	-2.289437000
1	-4.011939000	0.461065000	-1.353910000
1	-4.023110000	0.327618000	1.354859000
1	-2.473805000	-1.784941000	2.090083000
1	-1.532949000	-2.951489000	-0.162901000
1	1.899971000	-2.325314000	1.750548000
1	1.685914000	-2.781464000	-0.920538000
1	3.161967000	-0.918351000	-2.208540000
1	4.288507000	0.700566000	-0.343839000
1	3.494417000	-0.170876000	2.101636000
1	-1.817072000	2.610085000	1.615159000
1	-1.346550000	3.027966000	-1.159175000
1	1.819653000	2.600397000	-1.625723000
1	1.347301000	3.028497000	1.149737000
1	-0.158781000	0.316215000	-2.684453000
1	0.171429000	0.319138000	2.679127000



3', T. E. = -774.390359

77	1.777563000	-0.033122000	-0.010335000
77	-1.777551000	-0.033074000	0.010288000
6	3.312320000	1.573758000	-0.676979000
6	3.789582000	0.290738000	-1.115655000
6	4.057246000	-0.501942000	0.042365000

6	3.716399000	0.274908000	1.199179000
6	3.282533000	1.568827000	0.749702000
6	-3.716551000	0.274701000	-1.199039000
6	-4.057232000	-0.501989000	-0.042074000
6	-3.789410000	0.290830000	1.115809000
6	-3.312253000	1.573799000	0.676912000
6	-3.282678000	1.568678000	-0.749783000
5	0.079540000	-0.263912000	1.386536000
5	0.707876000	-1.806880000	0.754804000
5	0.981432000	-1.637018000	-1.046450000
5	-0.079472000	-0.264031000	-1.386525000
1	-0.118976000	0.135388000	-2.520130000
5	-0.707978000	-1.806870000	-0.754703000
5	-0.981505000	-1.636877000	1.046595000
5	0.000003000	1.016676000	-0.000187000
1	0.119001000	0.135647000	2.520077000
1	-1.589936000	-2.426399000	1.710364000
1	0.000029000	2.221175000	-0.000084000
1	1.285266000	-2.709720000	1.296159000
1	-1.285273000	-2.709734000	-1.296122000
1	1.589766000	-2.426719000	-1.710097000
1	-4.415634000	-1.527816000	-0.045101000
1	-3.808589000	-0.045439000	-2.233090000
1	-2.958086000	2.388500000	-1.384891000
1	-3.027234000	2.401815000	1.320158000
1	-3.928125000	-0.018134000	2.148210000
1	4.415788000	-1.527720000	0.045582000
1	3.928435000	-0.018333000	-2.148003000
1	3.808261000	-0.045096000	2.233289000
1	3.027310000	2.401670000	-1.320367000
1	2.957885000	2.388741000	1.384658000

References

1 U. Koelle and J. Kossakowski, *Inorg. Synth.,* 1992, **29**, 225.

2 G. E. Ryschkewitsch and K. C. Nainan, *Inorg. Synth.,* 1974, **15**, 113.

3 (a) G. M. Sheldrick, SHELXS-97, University of Göttingen, Germany, 1997; (b) G. M. Sheldrick, SHELXL-97, University of Göttingen, Germany, 1997; (c) A. Altornare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Cryst.,* 1993, **26**, 343.

4 Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

5 (a) H. L. Schmider and A. D. Becke, *J. Chem. Phys.*, 1998, **108**, 9624; (b) J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822.

6 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys*., 2005, **7**, 3297.

7 D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H. Preuss, *Theor. Chim. Acta*., 1990, **77**, 123.

8 (a) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098; (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*,1988, **37**, 785; (c) A. D. Becke, *J. Chem. Phys.*,1993, **98**, 5648.

9 F. J. London, *J. Phys. Radium*, 1937, **27**, 397.

10 R. Ditchfield, *Mol. Phys.*,1974, **27**, 789.

11 K. Wolinski, J. F. Hinton and P. Pulay, *J. Am. Chem. Soc.*, 1990, **112**, 8251.

12 G. Schreckenbach and T. Ziegler, *J. Phys. Chem.*, 1995, **99**, 606.

13 G. Schreckenbach and T. Ziegler, *Int. J. Quantum Chem.*, 1997, **61**, 899.

14 G. Schreckenbach and T. Ziegler, *Int. J. Quantum Chem.,* 1996, **60**, 753.

15 S. K. Wolff and T. Ziegler, *J. Chem. Phys.*, 1998, **109**, 895.

16 S. K. Wolff, T. Ziegler, E. van Lenthe and E. J. Baerends, *J. Chem. Phys.*, 1999, **110**, 7689.

17 T. P. Onak, H. L.Landesman, R. E. Williams and I.Shapiro, *J. Phys.Chem.*, 1959, **63**, 1533.

18 F. Weinhold and C. R. Landis, *Valency and bonding: A natural bond orbital donor-acceptor perspective*, Cambridge University Press: Cambridge; U.K, 2005.

19 A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899.

20 K. Wiberg, *Tetrahedron*, 1968, **24**, 1083.

21 J. M. B. Manson, C. E. Webster and M. B. Hall, Jimp 2 Version 0.089, 2006, Department of Chemistry, Texas A&M University, College Station, TX 77842, (http://www.chem.tamu.edu/jimp2/).

22 (a) R. F. Fenske, *Pure Appl. Chem.,* 1988, **27**, 61; (b) M. B. Hall and R. F. Fenske, *Inorg. Chem.*, 1972, **11**, 768.

23 Version 2.0, June 1993; Lichtenberger, D. L. Department of Chemistry, University of Arizona, Tuscon, AZ 85721.