Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic supplementary information

Decaborane anion tautomerism: ion pairing and proton transfer control

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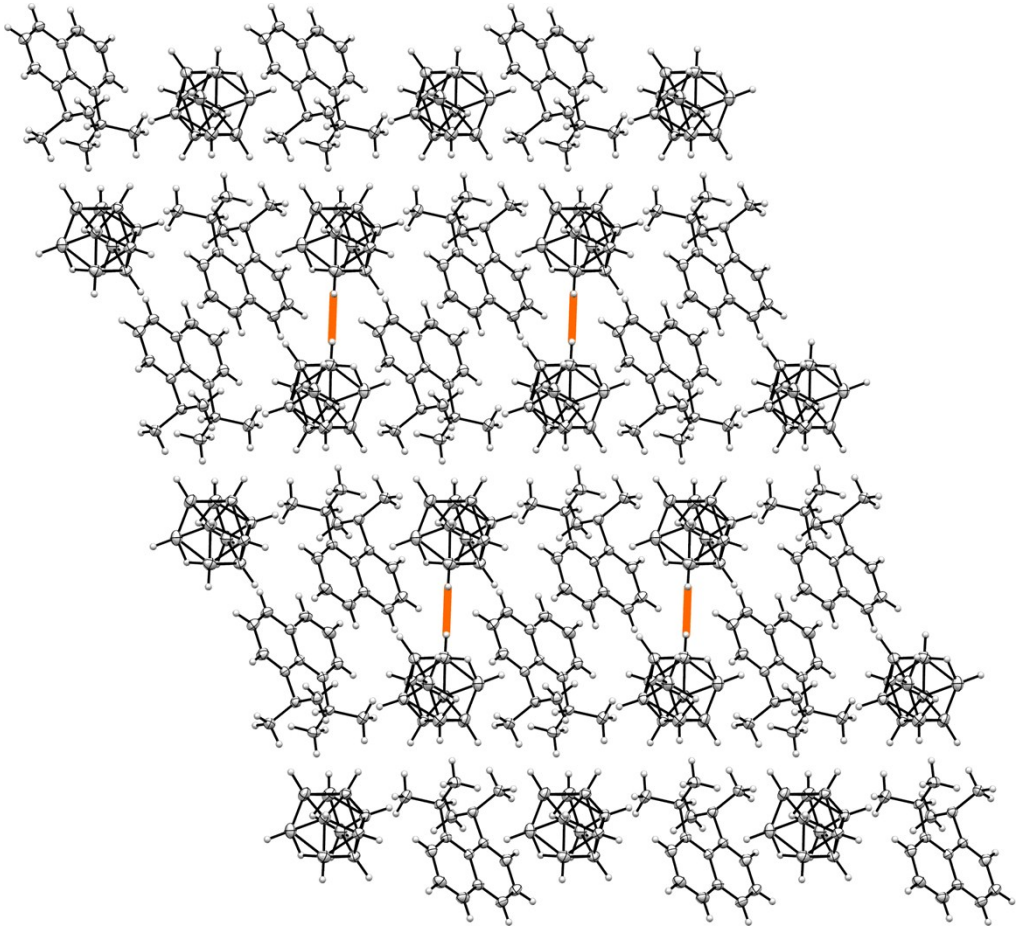

Figure S1 Packing of salt **1** along the *bc* plane. H(7)···H(7). The cations and anions form chains along the *a* axis; contacts between inversion-centre related chains are highlighted in orange.

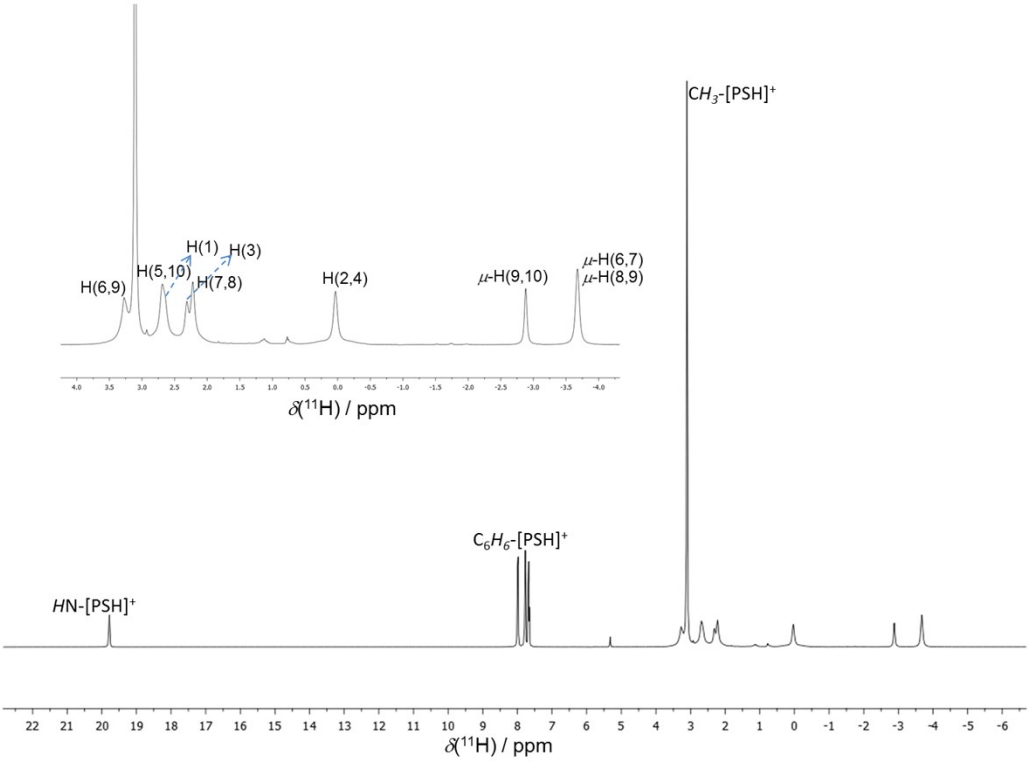

Figure S2 500 MHz ^{1}H-{^{11}B} NMR spectra of salt **1** in CD_2Cl_2 at 178 K.

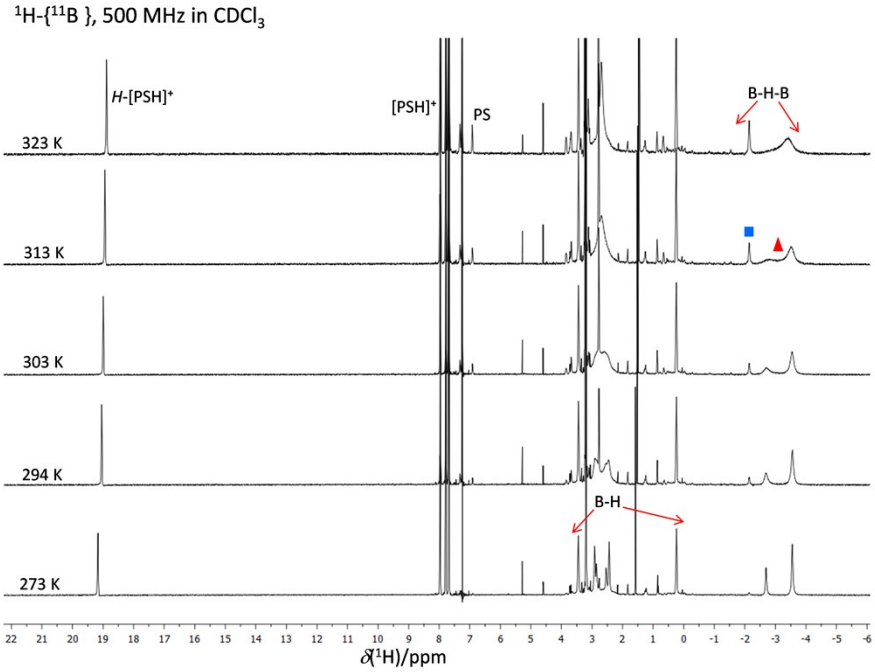

Figure S3 Variable temperature (VT): 500 MHz ^{1}H-{^{11}B} NMR spectra of salt **1** in $CDCl_3$. The signals of neutral $B_{10}H_{14}$ and anionic $[B_{10}H_{13}]^-$ are highlighted in blue squares and red triangles, respectively.

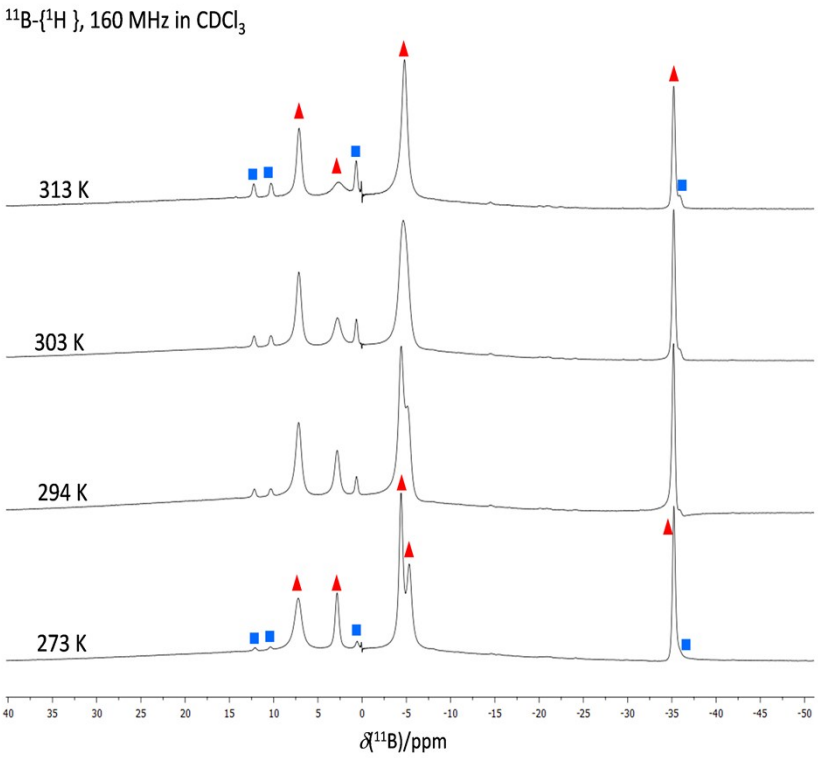

Figure S4 Variable temperature (VT): 160 MHz ^{11}B-{^{1}H} NMR spectra of salt **1** in $CDCl_3$. The signals of neutral $B_{10}H_{14}$ and anionic $[B_{10}H_{13}]^-$ are highlighted in blue squares and red triangles, respectively.

Thermodynamic data

Table S1 The equilibrium ratios of the anionic *versus* the neutral species measured by ^{1}H-{^{11}B} NMR

Temperature (K)	1/T(K) 10^3	K_{eq} = $[B_{10}H_{13}^-][PSH^+]/[B_{10}H_{14}][PS]$	ln K_{eq}
273	3.66	2500	7. 2
294	3.40	302.46	5.7
303	3.30	82.64	4.4
313	3.19	51.02	3.9
323	3.09	28.44	3.4

$\Delta G = -RT \ln K_{eq}$ ($R = 8.314$ J K^{-1} mol^{-1})

$\Delta G = \Delta H - T\Delta S$

$\ln K_{eq} = -\Delta H/RT + \Delta S/R$

$-\Delta H/R = 6975.2$; $\Delta H = -57.992$ kJ K^{-1} mol^{-1} = -13.85 ± 0.25 kcal K^{-1} mol^{-1}

$\Delta S/R = -18.293$; $\Delta S = -152.089$ J K^{-1} mol^{-1} = -36.33 ± 0.25 calK^{-1} mol^{-1}

$\Delta G_{298} = -13{,}850 - 298*(-36.33) = -3.02 \pm 0.25$ kcal mol^{-1}

Calculation of free energy of activation by the coalescence temperature:

at The B-H terminal resonances:

δ_H at +2.91 (2H), +2.86 (1H), +2.53 (1H) and +2.43 (1H). These peaks coalesce in pairs at 303 K in a 11.7467 Tesla magnetic field. The fraction of these nuclei at 243 K is: P_A = 0.50 and P_B = 0.50, ΔP = 0.00 equal populated sites, and $\delta\upsilon$ = 238.5 Hz for the peaks of relative intensity two, and 162.3 Hz for the peaks of intensity one.

$\Delta G^{\ddagger} = -RT_C[\ln(\pi\delta\upsilon h/2^{1/2}\kappa_B T_C)] = RT_c[22.8 + \ln(T_c/\delta\upsilon)] = 8.3145\times303[22.8 + \ln(303/238)$ = 58.1 kJ mol^{-1} = 13.9 kcal mol^{-1}.

R = 8.3145 J K^{-1} mol
h = 6.626.10^{-34} J s
κ_B = 1.381×10^{-23} J/K

at the B–H–B proton nuclei:

Based on the treatment by Shanan-Atidi and Bar-Eli (*J. Phy. Chem*. **1970**, *74*, 961), and Egan and Mislow (Thesis Princeton University, 1971).

P_A, P_B = factional populations of nuclei in sites A and B: at 243 K P_A = 1/3 and P_B = 2/3; ΔP = 0.33. These correspond to the signals of relative intensity ratio at –2.70 and –3.54 ppm.

$\delta\upsilon$ = 422 Hz, T_c = 318 K and X = 2.0823]

$$\Delta G_A^{\ddagger} = 4.57T_c[10.62 + \log X/2(1\ \Delta P) + \log T_c/\delta\upsilon]$$

$$\Delta G_B^{\ddagger} = 4.57T_c[10.62 + \log X/2(1 + \Delta P) + \log T_c/\delta\upsilon]$$

$\Delta G_A^{\ddagger} = 4.57\times318[10.62 + \log2.0823/2(1 + 0.33) + \log318/422] = 4.57\times318[10.62 - 0.43]$ = 14.8 kcal mol^{-1}.

$\Delta G_A^{\ddagger} = 4.57\times318[10.62 + \log2.0823/2(1 + 0.33) + \log318/422] = 4.57\times318[10.62 - 0.73]$ = 14.4 kcal mol^{-1}.

Boron-11 selective decoupling experiments

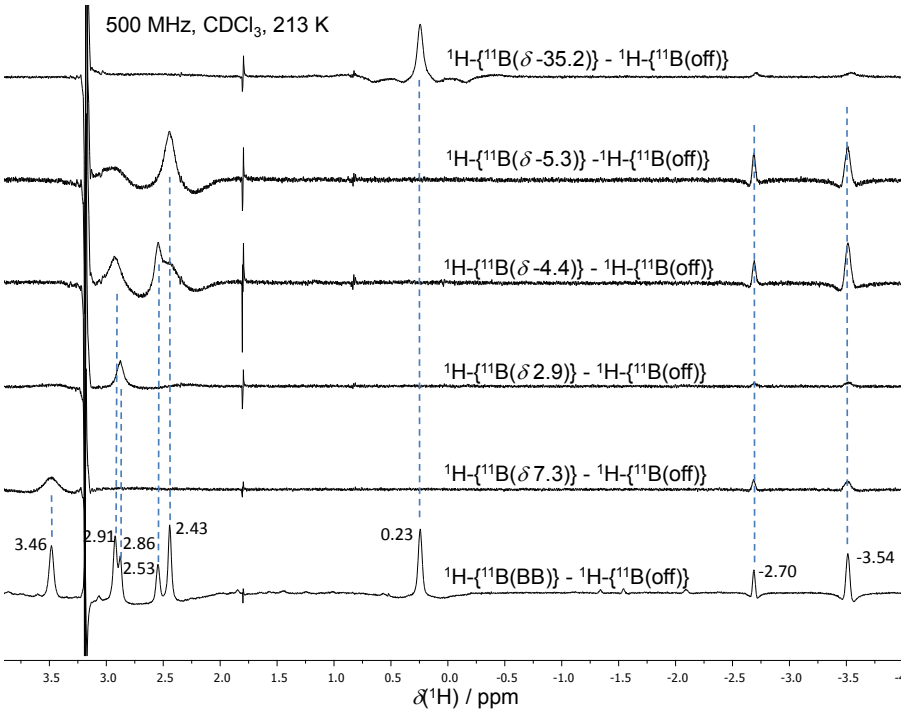

Figure S5 Subtraction of the off-decoupled spectrum, ^{1}H-{^{11}B(off)}, from the Broad Band (BB) decoupled spectrum, ^{1}H-{^{11}B(BB)} (bottom trace); and subtractions of the ^{1}H-{^{11}B(off)} spectrum from the ^{11}B-selectively decoupled spectra, ^{1}H-{^{11}B(δ_B)} for compound **1**.

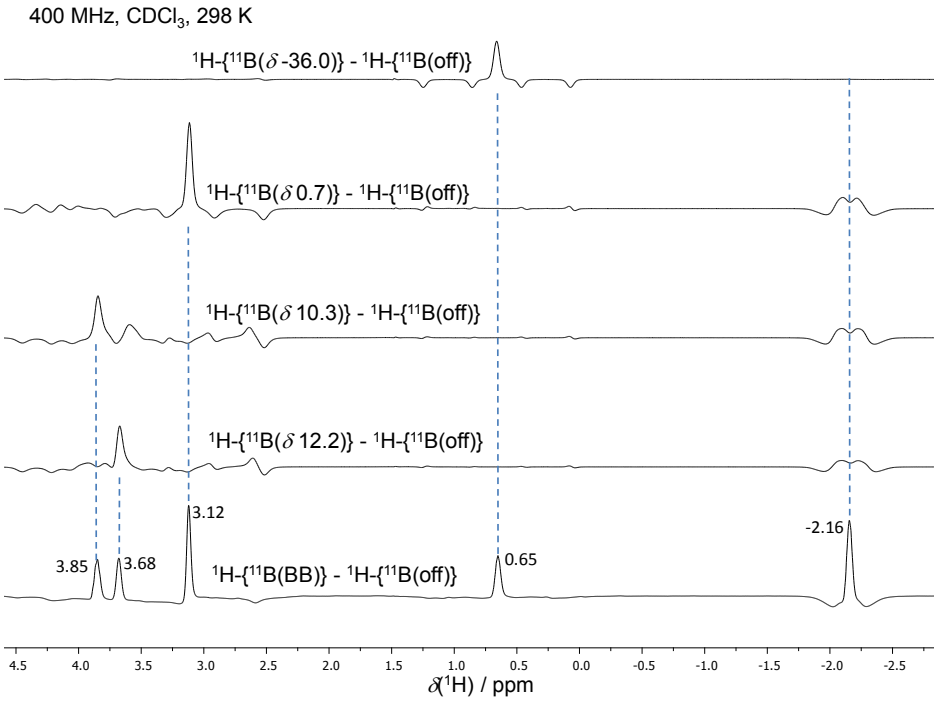

Figure S6 Subtraction of the off-decoupled spectrum, ^{1}H-{^{11}B(off)}, from the Broad Band (BB) decoupled spectrum, ^{1}H-{^{11}B(BB)} (bottom trace); and subtractions of the

^{1}H-{^{11}B(off)} spectrum from the ^{11}B-selectively decoupled spectra, ^{1}H-{^{11}B(δ_B)} for decaborane, *nido*-$B_{10}H_{14}$.

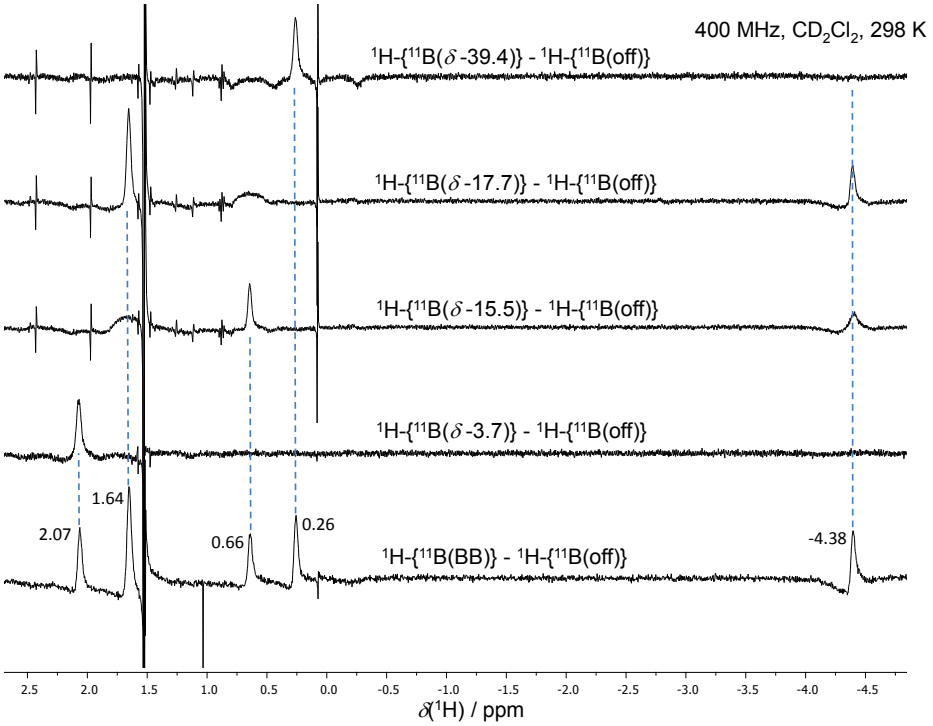

Figure S7 Subtraction of the off-decoupled spectrum, ^{1}H-{^{11}B(off)}, from the Broad Band (BB) decoupled spectrum, ^{1}H-{^{11}B(BB)} (bottom trace); and subtractions of the ^{1}H-{^{11}B(off)} spectrum from the ^{11}B-selectively decoupled spectra, ^{1}H-{^{11}B(δ_B)} for the pyridine adduct, 6,9-$(py)_2$-*arachno*-$B_{10}H_{12}$.

Diffusion coefficients:

The following equation describes the situation for random isotropic diffusion. *I* is the intensity of a peak, *D* is the diffusivity, *G* is the pulse gradient strength, δ is the length of the gradient pulse, and Δ is the diffusion time.

$$I = I_0 \exp[(-D\gamma^2G^2\delta^2(\Delta - \delta/3)]$$

Plotting *I vs*. *G* for a given peak gives a diffusion curve which is fit by TopSpin software to give *D*.

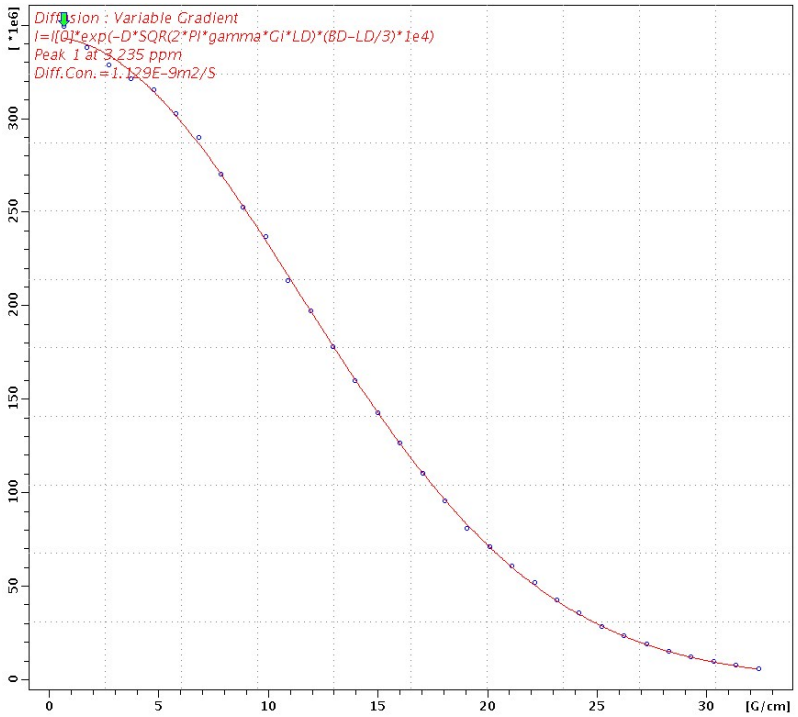

Figure S8. *TopSpin* display after fitting with *SimFit* (T_1/T_2 Analysis). The fitting curve for the peak at +3.24 ppm of salt **1** in CD_2Cl_2 is shown. The plot is ideal, and the fit is, therefore, reliable. This peak corresponds to the $[PSH]^+$ cataion.

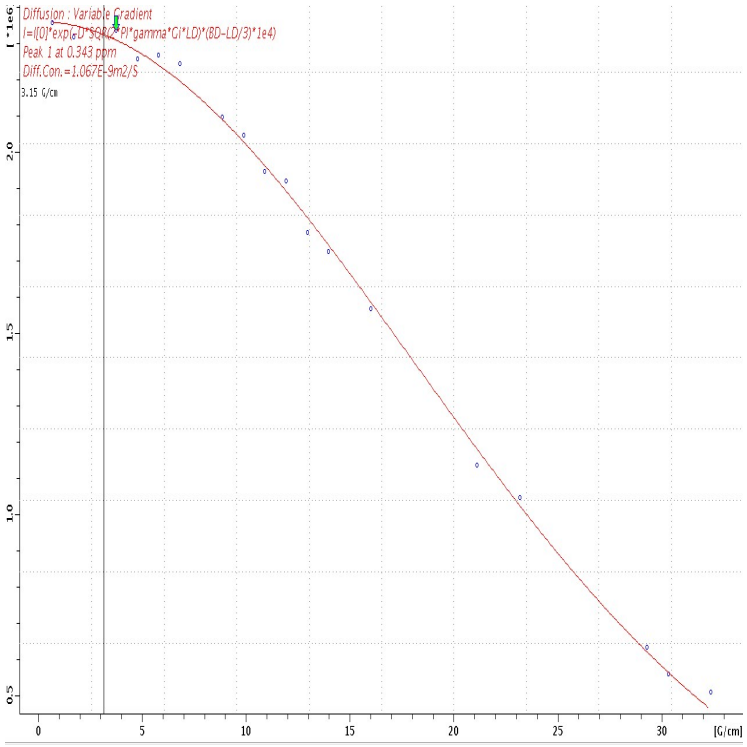

Figure S9. *TopSpin* display after fitting with *SimFit* (T_1/T_2 Analysis). The fitting curve for the peak at +0.34 ppm of salt **1** in CD_2Cl_2 is shown. The plot is not ideal, and the fit is not as reliable as the others. This peak corresponds to the $[B_{10}H_{13}]^-$ anion.

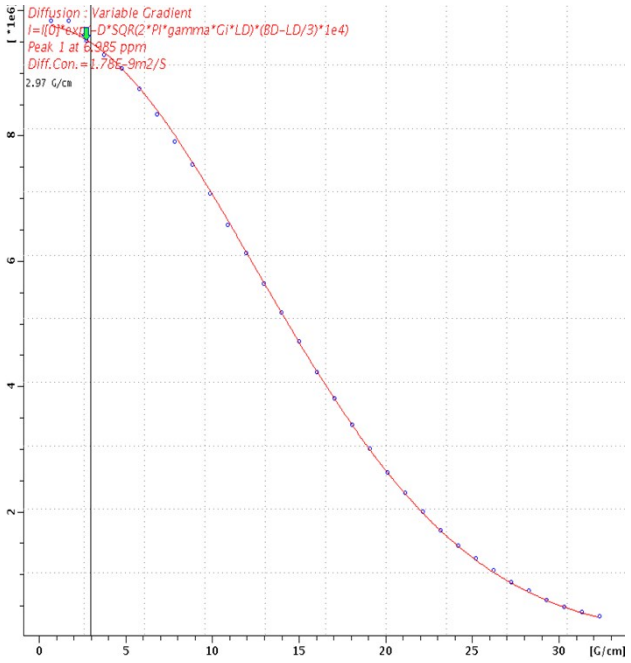

Figure S10. *TopSpin* display after fitting with *SimFit* (T_1/T_2 Analysis). The fitting curve for the peak at +6.98 ppm of pure PS in CD_2Cl_2 is shown. The plot is ideal, and the fit is, therefore, reliable.

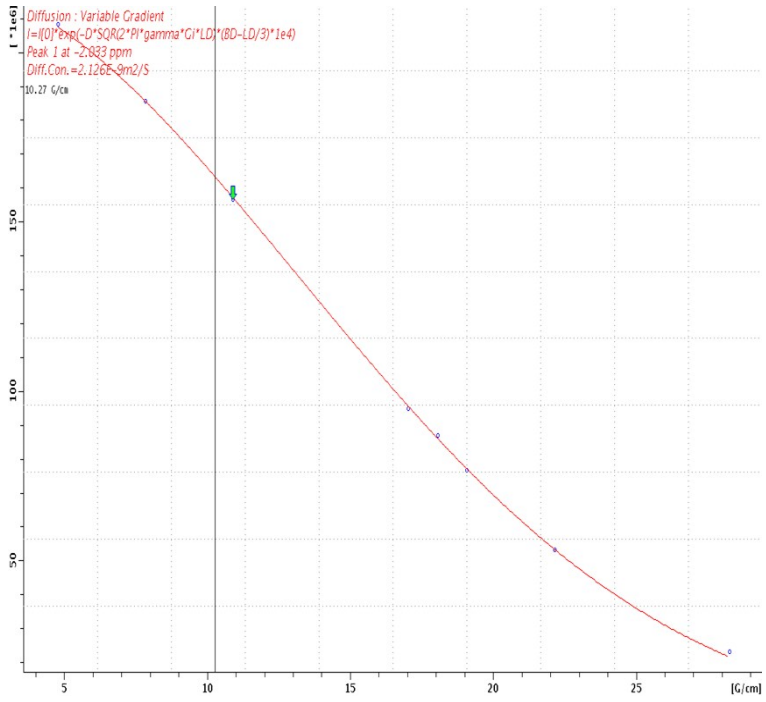

Figure S11. *TopSpin* display after fitting with *SimFit* (T_1/T_2 Analysis). The fitting curve for the peak at -2.03 ppm of pure decaborane, $B_{10}H_{14}$, in CD_2Cl_2 is shown.

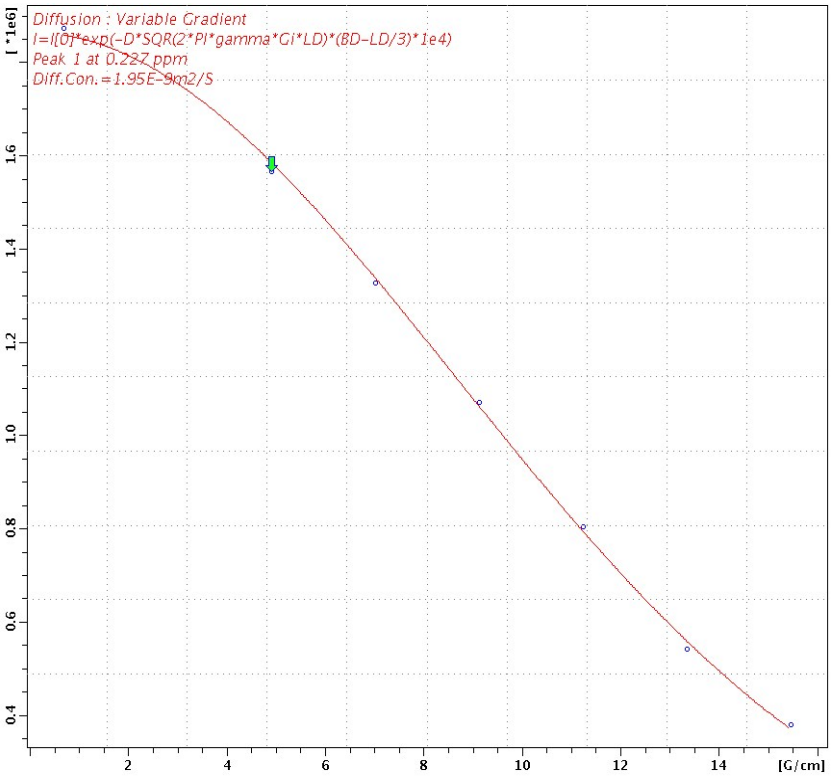

Figure S12. *TopSpin* display after fitting with *SimFit* (T_1/T_2 Analysis). The fitting curve for the peak at +0.23 ppm of salt **1** in CD_3CN is shown. The peak corresponds to the polyhedral anion. The plot is not ideal, and the fit is not as reliable as others in this study.

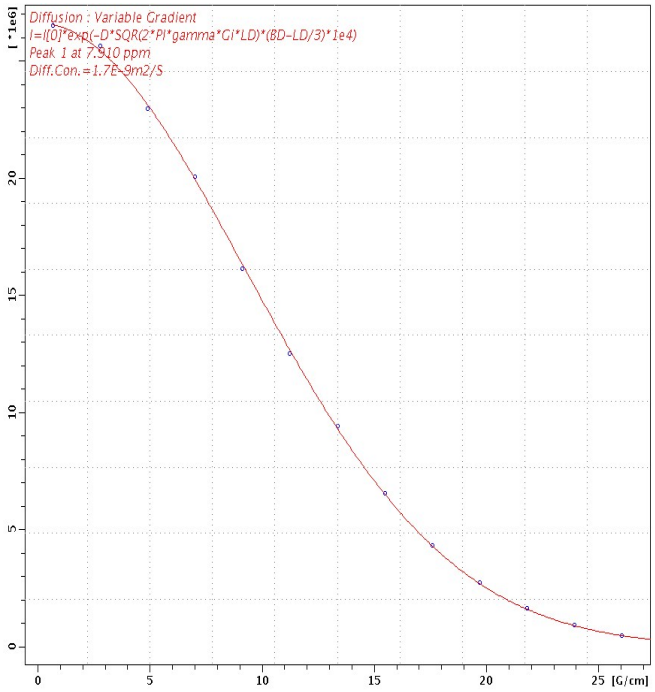

Figure S13. *TopSpin* display after fitting with *SimFit* (T_1/T_2 Analysis). The fitting curve for the peak at +7.91 ppm of salt **1** in CD_3CN is shown. The peak corresponds to PSH^+. The plot is ideal, and the fit is reliable.

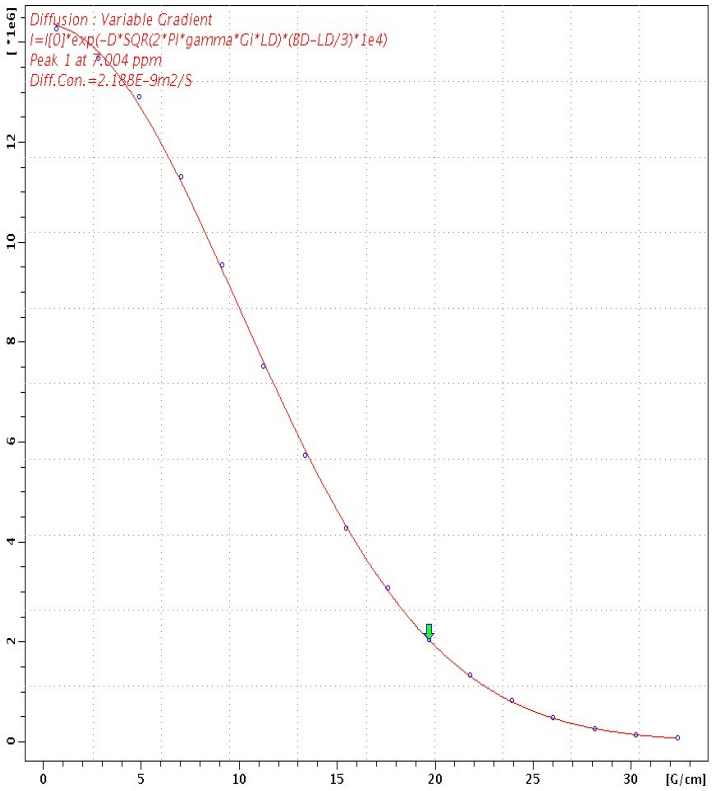

Figure S14. *TopSpin* display after fitting with *SimFit* (T_1/T_2 Analysis). The fitting curve for the peak at +7.00 ppm of PS in CD_3CN is shown. The plot is ideal, and the fit is reliable.

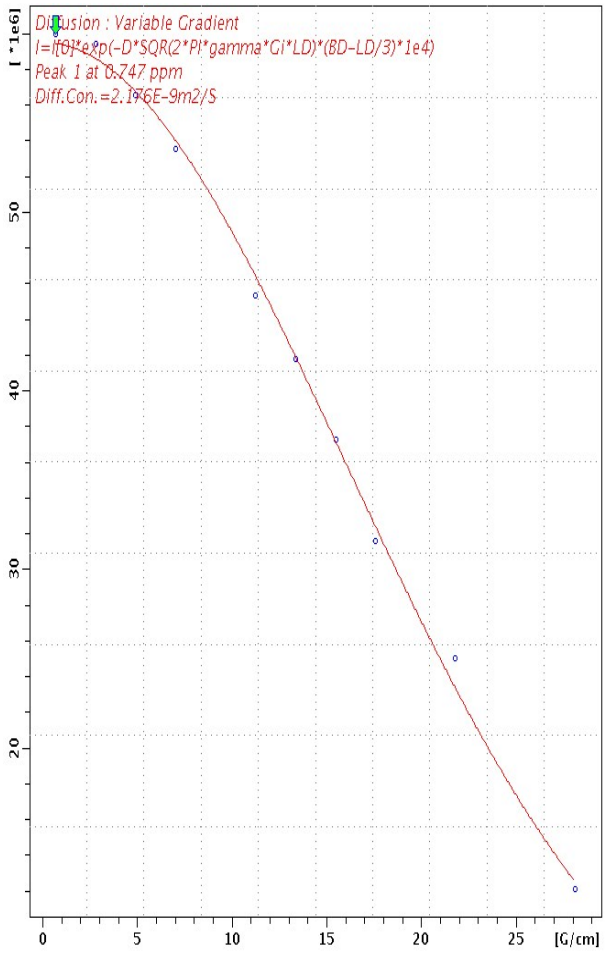

Figure S15. *TopSpin* display after fitting with *SimFit* (T_1/T_2 Analysis). The fitting curve for the peak at +0.75ppm of salt **1** in CD_3CN is shown. This peak corresponds to the polyhedral anion. Plot too short, the fit is not good enough so the value of the diffusion coefficient is not as reliable as the measured for PS in CD_3CN.

Calculation of hydrodynamic radius.

Stokes-Einstein relation:

$$r_H = kT / 6\eta\pi D$$

$k = 1.38064852(79)\times10^{-23}\ JK^{-1}$

T = temperature (K)

η = viscosity of the solvent

Viscosity of dichlomethane = 0.413 cP (25 °C)

Viscosity of dichlomethane = 0.413 cP (25 °C)

Natural Atomic Charges (NBO)

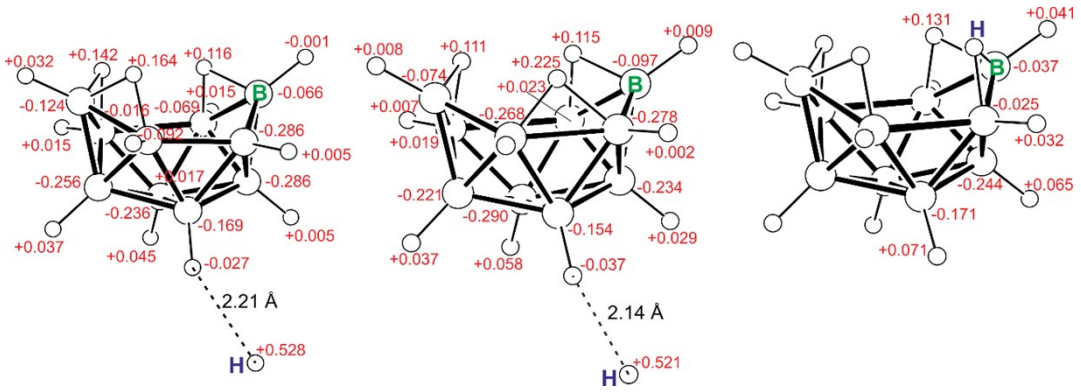

Figure S16. Calculated Natural Atomic Charges in the $[B_{10}H_{13}]^-$ anion of salt **1** and in decaborane. For clarity, it is only shown the proton of the organic cation.

Tables of the optimized geometries (Cartesian coordinates, in Angstroms). Sum of electronic and thermal Free Energies (in Hartrees) in parenthesis.

Table S2. [PSH][$B_{10}H_{13}$] (-910.588615): zero energy reference **1*C*$_1$_a** in Figure 8, main text.

Atom	x	y	z
N	-0.85885600	1.34387000	0.06587200
N	-0.85552100	-1.28686600	0.23732200
H	-0.56801200	-0.25934300	0.19161000
C	-2.28596300	1.28839000	-0.03338800
C	-2.93451600	0.02633100	-0.02301200
C	-2.30222900	-1.23310600	0.09193200
C	-3.00010000	-2.40312600	0.09225900
H	-2.47127900	-3.35191500	0.19017900
C	-4.39144000	-2.39696600	-0.02327700
H	-4.93362000	-3.34250000	-0.02088100
C	-5.05219700	-1.21188900	-0.13128300
H	-6.14045000	-1.18590500	-0.21588900
C	-4.35839500	0.01025700	-0.13427200
C	-5.06586500	1.21902600	-0.24077600
H	-6.15380900	1.17464900	-0.32053100
C	-4.41072900	2.41228800	-0.24364900
H	-4.96311200	3.34900400	-0.32861900
C	-3.01856200	2.43852600	-0.14085300
H	-2.49927800	3.39815100	-0.14942700
C	-0.25647200	1.86869900	-1.13852800
H	-0.56657600	1.26899800	-2.00561200
H	0.83805600	1.81198200	-1.04995500
H	-0.53066200	2.92330200	-1.32880300
C	-0.42049400	2.08037900	1.22857900
H	0.67115300	1.99109200	1.32055100
H	-0.66898700	3.15641700	1.17535700
H	-0.88296200	1.66295900	2.13298000
C	-0.20062000	-2.00502000	-0.85805200
H	-0.53146400	-3.04946900	-0.87295000
H	-0.45487100	-1.52204200	-1.80784800
H	0.88213600	-1.96806800	-0.69800100
C	-0.44719300	-1.81387700	1.54180800
H	0.64196000	-1.72128100	1.62938500
H	-0.93666100	-1.23402400	2.33214400
H	-0.73436600	-2.86795800	1.62477100
B	2.89594100	-0.06249200	0.17734300
H	1.73204100	0.09680100	0.40973000
B	3.48248000	-0.84385400	-1.27101800
H	2.73900300	-1.16843300	-2.15295400
B	3.84290200	0.86137800	-1.01857800
H	3.44837900	1.65731000	-1.81935100
B	3.90269600	1.32438000	0.69467900
H	3.35895800	2.31235700	1.08949300
B	3.64462600	-1.61882600	0.34735700

H	2.92807100	-2.51766800	0.71193800
B	4.86050100	-1.80958200	-0.77095200
H	5.33140800	-2.79431000	-1.26104200
B	5.12338800	-0.23761400	-1.54829000
H	5.70820300	-0.11478500	-2.58106800
H	5.86578600	-0.92727100	-0.71948000
B	5.36036000	1.32955300	-0.31543900
H	5.95181300	2.29099500	-0.69698300
H	6.25699900	0.66271300	0.40634500
B	5.38966300	0.85906700	1.39476500
H	5.96686300	1.40331700	2.27800700
B	4.01785000	-0.27140400	1.55121400
H	3.64049800	-0.42211900	2.67738400
H	5.34204400	-0.44448300	1.60683200

Table S3. [PSH][$B_{10}H_{13}$] (-910.588534): zero reference energy **1*C*$_1$_b** in Figure 8, main text.

Atom	x	y	z
N	-0.89598100	-1.19787200	0.01022400
N	-1.06689600	1.41523500	0.16731100
H	-0.71544700	0.40267500	0.10920600
C	-2.32474400	-1.24604800	-0.06006300
C	-3.05992600	-0.03337400	-0.02794900
C	-2.51136200	1.26599800	0.07724300
C	-3.28786900	2.38597100	0.10588800
H	-2.82573800	3.37097900	0.18949700
C	-4.67779200	2.28269300	0.02666500
H	-5.28548900	3.18774800	0.05235100
C	-5.25781500	1.05520100	-0.08017300
H	-6.34332300	0.95492400	-0.14213900
C	-4.48246900	-0.11570800	-0.10870000
C	-5.10432200	-1.37105900	-0.21124700
H	-6.19413500	-1.40317100	-0.26745100
C	-4.36638200	-2.51546600	-0.23780800
H	-4.85423500	-3.48795800	-0.31790900
C	-2.97395700	-2.44500900	-0.16239300
H	-2.38795000	-3.36576600	-0.18715600
C	-0.38617300	-1.86860600	1.18475000
H	-0.85906200	-1.45839500	2.08705700
H	0.69827000	-1.70310200	1.25098700
H	-0.56548800	-2.95917500	1.16363300
C	-0.27840100	-1.71768700	-1.18965000
H	0.80653500	-1.55206400	-1.13749500
H	-0.45503800	-2.80067900	-1.32408100
H	-0.67041200	-1.19289500	-2.07121800
C	-0.64403700	1.96678400	1.45670000
H	-1.00180400	2.99694800	1.56059200
H	-1.05738700	1.35068200	2.26237400
H	0.45064600	1.94922900	1.50185200

C	-0.50789200	2.17089800	-0.95495500
H	0.58434900	2.17060800	-0.86719400
H	-0.80338500	1.69129200	-1.89419300
H	-0.87575000	3.20262800	-0.93461300
B	3.67869600	-0.27056000	-1.14450200
H	3.11327100	-0.44788200	-2.18607100
B	3.60065000	-1.39713500	0.19212200
H	3.04798600	-2.45488800	0.08543100
B	5.14855000	-1.12729600	-0.60280300
H	5.70242700	-2.05034600	-1.12059600
B	5.29473900	0.48388400	-1.33509300
H	5.73759600	0.63038400	-2.43231200
B	2.81912700	0.21954400	0.28340300
H	1.63220700	0.36060600	0.15014600
B	3.51414700	-0.42289500	1.64892000
H	3.04914800	-0.68845900	2.72091200
B	5.05839100	-1.14392000	1.16450600
H	5.64721200	-1.92786500	1.84523700
H	4.78480800	-0.08379500	1.88719900
B	6.27029000	0.01593600	0.07086700
H	7.44303200	-0.19313600	0.07668700
H	6.11822900	1.02600700	0.92250800
B	5.64141500	1.65963800	-0.14537000
H	6.27389200	2.65491500	-0.28503500
B	3.93031800	1.41049600	-0.58042700
H	3.42074800	2.35405000	-1.11511700
H	4.52164900	1.91838200	0.50619500

Table S4. [PSH][$B_{10}H_{13}$] (-910.582221): ion pair, **1*C*$_1$_c**, TS +4.0 kcal mol^{-1} above the lowest energy pairs in Figure 8, main text.

Atom	**x**	**y**	**z**
N	-0.89409100	-1.19859800	-0.01368500
N	-1.07042900	1.42659800	-0.10042800
H	-0.70627800	0.42403100	-0.14773000
C	-2.31522500	-1.25522300	-0.12650300
C	-3.05494100	-0.04788100	-0.01497300
C	-2.50696600	1.25313200	0.06148200
C	-3.28167000	2.36545300	0.20055400
H	-2.81728800	3.35112700	0.23873000
C	-4.67101900	2.25286100	0.26948500
H	-5.27673000	3.15039700	0.39178800
C	-5.25339100	1.02695400	0.15432200
H	-6.33984200	0.92164400	0.17362800
C	-4.47818300	-0.13510700	0.00036500
C	-5.10128300	-1.38467900	-0.15288700
H	-6.19227000	-1.42168800	-0.14395300
C	-4.36157600	-2.51581300	-0.31585000
H	-4.85005800	-3.48283200	-0.44553000
C	-2.96626900	-2.44695000	-0.28865200

H	-2.38622200	-3.36571600	-0.37501400
C	-0.48119800	-1.49867000	1.34319200
H	-1.03295300	-0.86826000	2.05373600
H	0.59229900	-1.29241200	1.45303000
H	-0.66618100	-2.55715600	1.60634700
C	-0.19345700	-2.03664300	-0.95581900
H	0.88242100	-1.82727200	-0.88545300
H	-0.32852100	-3.11632700	-0.76460400
H	-0.52605600	-1.81451900	-1.97772300
C	-0.43213700	2.10137600	1.03186900
H	-0.79138500	3.13352300	1.10727100
H	-0.66269800	1.55807400	1.95437400
H	0.65054600	2.10541600	0.86376000
C	-0.74661400	2.08785700	-1.36770000
H	0.34230300	2.10181200	-1.48601700
H	-1.20307000	1.52646500	-2.19002800
H	-1.13082000	3.11400500	-1.36006400
B	4.01698500	-0.83662900	-0.98597800
H	3.59718900	-1.51738000	-1.87539800
B	3.47190500	-1.15429000	0.65762200
H	2.80837600	-2.12523600	0.88283300
B	5.17986700	-1.27233000	0.30145300
H	5.79258900	-2.29801500	0.36288300
B	5.68479200	-0.23058800	-1.06979900
H	6.46259000	-0.66201000	-1.86344600
B	2.86779900	0.26292600	-0.21829300
H	1.76543700	0.46074300	-0.64533400
B	3.25722300	0.36800300	1.50604000
H	2.40365700	0.70667100	2.27917100
B	4.70431700	-0.41415700	1.73894700
H	5.03904700	-0.90567100	2.78374700
H	3.22727100	1.27844700	0.52408400
B	6.03550400	0.25882100	0.64202100
H	7.14427200	0.30257800	1.08730100
H	5.62040800	1.53177300	0.63946600
B	5.74467100	1.42905500	-0.67069800
H	6.51071800	2.23782400	-1.08173600
B	4.30711500	0.80064800	-1.49691300
H	4.01485100	1.16978300	-2.59226400
H	4.52071100	1.92689800	-0.82439900

Table S5. [PSH][$B_{10}H_{13}$] (-910.58004800): ion pair, **1*C*$_s$_a**, +5.4 kcal mol^{-1} above the lowest energy pair in Figure 8, main text.

Atom	x	y	z
N	-0.81772700	1.31128000	0.06118300
N	-0.86630400	-1.31785900	0.22044700
H	-0.56060000	-0.29403700	0.19204000
C	-2.24614300	1.28682000	-0.02669700
C	-2.92103600	0.03883600	-0.01125600

C	-2.31377600	-1.23408000	0.09314700
C	-3.03709100	-2.38910600	0.09418600
H	-2.52936200	-3.35091100	0.17819600
C	-4.42909100	-2.35233500	-0.00661100
H	-4.99126800	-3.28632200	-0.00277600
C	-5.06567900	-1.15302500	-0.10304300
H	-6.15399600	-1.10355500	-0.17656300
C	-4.34585100	0.05361700	-0.10935200
C	-5.02786000	1.27763000	-0.20754000
H	-6.11724700	1.25686400	-0.27537000
C	-4.34716000	2.45643000	-0.21883900
H	-4.88028600	3.40470800	-0.29875200
C	-2.95376100	2.45246800	-0.13030000
H	-2.41371300	3.40055300	-0.14711000
C	-0.21403100	1.80014200	-1.15799800
H	-0.56095000	1.20539900	-2.01424900
H	0.87857600	1.70155200	-1.08562400
H	-0.45178500	2.86237200	-1.35502900
C	-0.35365600	2.06001800	1.20620900
H	0.73664700	1.95248900	1.28935200
H	-0.58260200	3.13911600	1.13651900
H	-0.81420100	1.66675800	2.12223500
C	-0.23879500	-2.02090500	-0.90059900
H	-0.56699500	-3.06632500	-0.91955100
H	-0.51957000	-1.52771200	-1.83749900
H	0.84831600	-1.98178400	-0.76970700
C	-0.45049400	-1.88042800	1.50769500
H	0.64322900	-1.83620900	1.57098300
H	-0.89407600	-1.29012800	2.31683500
H	-0.78125500	-2.92161900	1.58643000
B	2.89348200	-0.08203000	0.28281500
H	1.72072700	0.01234500	0.48782900
B	3.39128500	-0.48814600	-1.35279000
H	2.53163100	-0.63364500	-2.17456800
B	3.83883400	1.09294100	-0.72625900
H	3.44683900	2.06930900	-1.29896300
B	3.93004700	1.12692200	1.02975300
H	3.40830100	1.98046800	1.68618600
B	3.70655000	-1.64534400	-0.00135500
H	3.05933700	-2.62863000	0.23193400
B	4.74747000	-1.54623000	-1.36827100
H	5.07990600	-2.39400400	-2.13706600
B	5.00602900	0.14274700	-1.64543300
H	5.53481400	0.58616900	-2.61685200
H	5.80787600	-0.78894000	-1.12792200
B	5.39745700	1.30272600	0.07935900
H	6.09710700	2.23645600	-0.16299000
H	6.17594400	0.30700700	0.51250500
B	5.41012400	0.44845200	1.58415200
H	6.11987500	0.73667300	2.49665900
B	4.04430600	-0.59861600	1.54079500
H	3.56867800	-1.06150500	2.53786200

H	4.78694400	-1.45045700	0.79577500

Table S6. [PSH][$B_{10}H_{13}$] (-910.57801): ion pair, **1*C*$_s$_b**, +6.6 kcal mol^{-1} above the lowest energy pair in Figure 8, main text.

Atom	x	y	z
N	0.81126400	-1.29953200	0.07294900
N	0.87681600	1.32488300	0.23449800
H	0.56632200	0.30076900	0.20088000
C	2.23890200	-1.28480000	-0.03137500
C	2.92208600	-0.04177000	-0.01542900
C	2.32348700	1.23399900	0.10089000
C	3.05388900	2.38457700	0.10430800
H	2.55263800	3.34903800	0.19735300
C	4.44493300	2.33943700	-0.00690300
H	5.01328600	3.26972200	-0.00103900
C	5.07301800	1.13680200	-0.11798900
H	6.16030300	1.08113900	-0.20191200
C	4.34571600	-0.06520700	-0.12664200
C	5.01801700	-1.29304100	-0.24146500
H	6.10677500	-1.27936200	-0.32018900
C	4.32900900	-2.46709100	-0.25496300
H	4.85500200	-3.41812900	-0.34833300
C	2.93673200	-2.45467900	-0.15106800
H	2.39032500	-3.39926700	-0.16856200
C	0.19057000	-1.79190800	-1.13649000
H	0.52149200	-1.19623900	-1.99847200
H	-0.90073500	-1.69908300	-1.04598000
H	0.42883200	-2.85315600	-1.33661300
C	0.35701800	-2.04112900	1.22679100
H	-0.73298500	-1.93517300	1.31632500
H	0.58732600	-3.12014600	1.16227700
H	0.82429300	-1.64169700	2.13674400
C	0.24966000	2.04087000	-0.87802500
H	0.58455600	3.08419000	-0.89060200
H	0.52122700	1.55332700	-1.82049100
H	-0.83716600	2.00799800	-0.74372700
C	0.46957500	1.88005700	1.52721600
H	-0.62418600	1.84340200	1.59381800
H	0.91122200	1.28032700	2.33046300
H	0.80767400	2.91834100	1.61340500
B	-2.93810400	0.03813400	0.26418400
H	-1.77284400	0.02975900	0.54138900
B	-3.42591700	0.65614600	-1.30486100
H	-2.64129400	0.85116000	-2.18852500
B	-3.82673800	-1.01515000	-0.92129100
H	-3.31123800	-1.86903100	-1.58075800
B	-3.93675500	-1.29577100	0.81408900
H	-3.47262000	-2.31330100	1.23928300
B	-3.62628200	1.65466200	0.12735400

H	-3.03200400	2.61088500	0.52918400
B	-4.78689000	1.70030500	-1.15598400
H	-5.08926500	2.69804800	-1.73298500
B	-5.10956800	0.05807900	-1.55086600
H	-5.59186900	-0.25756500	-2.59924600
H	-4.92849700	1.93506000	0.14419300
B	-5.43721900	-1.20714400	-0.17773600
H	-6.07958900	-2.14484600	-0.55010600
H	-5.27645200	0.59445100	1.60132500
B	-5.41729000	-0.71984900	1.47386200
H	-6.08035900	-1.09647700	2.38917600
B	-3.99376900	0.24369100	1.66152200
H	-3.55918600	0.60344100	2.71272600
H	-5.94055600	0.01273700	-0.47763200

Table S7. [PSH][$B_{10}H_{13}$] (-910.572406): ion pair, **1*C*$_s$_c**, TS +10.2 kcal mol^{-1} above the lowest energy pair in Figure 8, main text.

Atom	x	y	z
N	-0.90463400	-1.20688700	-0.02751700
N	-1.07235100	1.42079700	-0.10717100
H	-0.71228100	0.41660400	-0.15410700
C	-2.32800500	-1.25589200	-0.13060600
C	-3.06211100	-0.04559700	-0.01668600
C	-2.50932800	1.25348600	0.05543900
C	-3.27910100	2.36914900	0.19474100
H	-2.81060200	3.35296000	0.22977500
C	-4.66858100	2.26232400	0.26900500
H	-5.27018600	3.16267900	0.39096000
C	-5.25594200	1.03822600	0.16076600
H	-6.34268100	0.93708200	0.18563300
C	-4.48576600	-0.12722200	0.00692100
C	-5.11457900	-1.37501800	-0.13686300
H	-6.20564200	-1.40763800	-0.12084100
C	-4.38042100	-2.50976600	-0.29972300
H	-4.87344700	-3.47537900	-0.42190300
C	-2.98474600	-2.44569800	-0.28322700
H	-2.40833600	-3.36674200	-0.37123300
C	-0.48396200	-1.53765800	1.31929300
H	-1.01347600	-0.90618700	2.04564500
H	0.59501000	-1.35673700	1.41991600
H	-0.68887700	-2.59574700	1.56895400
C	-0.21603000	-2.03075900	-0.99115500
H	0.86262800	-1.83530900	-0.91846900
H	-0.36386900	-3.11297500	-0.82568300
H	-0.54684400	-1.78019900	-2.00715600
C	-0.43196600	2.09097700	1.02645400
H	-0.78811900	3.12403400	1.10453600
H	-0.66411400	1.54654900	1.94793200
H	0.65048300	2.09309100	0.85769400

C	-0.74706200	2.08297800	-1.37360200
H	0.34170200	2.09636900	-1.49226300
H	-1.20427700	1.52311900	-2.19656100
H	-1.13013700	3.10951700	-1.36484700
B	4.01696200	-0.76664900	-1.00973600
H	3.56737100	-1.41200000	-1.91285600
B	3.50904000	-1.13523700	0.63264300
H	2.91967300	-2.13801000	0.91357000
B	5.22303700	-1.26181800	0.25995400
H	5.71517900	-2.34816700	0.32338200
B	5.69136000	-0.23915200	-1.09558700
H	6.46757700	-0.68189500	-1.88757000
B	2.83243100	0.25750800	-0.19903200
H	1.75729600	0.45675500	-0.68492600
B	3.13924400	0.30450500	1.50464000
H	2.29179200	0.54105200	2.31389900
B	4.72011100	-0.33459200	1.70651300
H	5.10443500	-0.75651900	2.75792800
H	3.11966700	1.28235200	0.60878600
B	6.13649500	0.23435300	0.58420800
H	7.21383800	0.09916100	1.08439800
H	5.21414800	0.87846600	1.32742400
B	5.84413100	1.41156800	-0.63721600
H	6.54859100	2.28610000	-1.03512900
B	4.40010800	0.90380400	-1.44601300
H	4.00342600	1.38234000	-2.46384700
H	4.60998100	1.89926200	-0.58664300

Cartesian coordinates (in Angstroms) corresponding to the Transition States calculated for the H-tautomerisms of *nido*-$[B_{10}H_{13}]^-$. Energies (in Hartrees) in parenthesis.

Table S8. [PSH][$B_{10}H_{13}$] (-910.577951): TS +6.7 kcal mol^{-1} above the lowest energy pair in Figure 5, main text.

Atom	x	y	z
N	-0.79091700	1.28238200	0.12232200
N	-0.89089200	-1.34961000	0.23152000
H	-0.56168000	-0.33260100	0.23038700
C	-2.21816200	1.28679600	0.01442500
C	-2.91677700	0.05221800	-0.00202900
C	-2.33443700	-1.23343500	0.08656300
C	-3.07900800	-2.37465500	0.05409500
H	-2.58988600	-3.34718300	0.12337000
C	-4.46825100	-2.31007200	-0.06663600
H	-5.04762700	-3.23333900	-0.09105500
C	-5.08120000	-1.09735200	-0.15015800
H	-6.16709100	-1.02606200	-0.24061200
C	-4.33922100	0.09529500	-0.12285800
C	-4.99620700	1.33377900	-0.20996200
H	-6.08456100	1.33499200	-0.29504600

C	-4.29298900	2.49939700	-0.19100500
H	-4.80696700	3.45888200	-0.26254900
C	-2.90149200	2.46742900	-0.08143500
H	-2.34393200	3.40570700	-0.07601600
C	-0.16305800	1.78343500	-1.07972100
H	-0.50198300	1.20647200	-1.95125600
H	0.92607100	1.67284800	-0.98981200
H	-0.38712300	2.85102300	-1.26318400
C	-0.32775500	2.00558400	1.28393400
H	0.76134600	1.88750500	1.36895900
H	-0.54722400	3.08758500	1.23360300
H	-0.79533000	1.59944000	2.19070500
C	-0.26288100	-2.04137000	-0.89676400
H	-0.60787900	-3.08061200	-0.93823400
H	-0.52582100	-1.52666600	-1.82722200
H	0.82329000	-2.02231300	-0.75349000
C	-0.50727800	-1.95290500	1.51030000
H	0.58599600	-1.94763300	1.58476400
H	-0.94009700	-1.36604600	2.32759700
H	-0.87326200	-2.98385400	1.56305500
B	2.92747700	-0.15607900	0.37203500
H	1.78964100	-0.11474200	0.74244800
B	3.24822600	-0.32551400	-1.34360400
H	2.31778800	-0.32995500	-2.10178400
B	3.75384000	1.16062200	-0.54942100
H	3.30222000	2.20471300	-0.92310200
B	4.05147900	0.96864100	1.18233500
H	3.61327700	1.72720300	1.99354100
B	3.71490600	-1.64669300	-0.18483300
H	3.09999300	-2.66468300	-0.00103500
B	4.61799800	-1.37189500	-1.58117600
H	4.86538000	-2.09025500	-2.50326400
B	4.82227900	0.36002900	-1.70107700
H	5.22556700	0.93507800	-2.66494600
H	5.68287300	-0.60661000	-1.40011100
B	5.39030700	1.28786500	0.07939300
H	6.05743200	2.26394500	-0.06772500
H	6.23439300	0.28952900	0.29783200
B	5.56596000	0.23046000	1.45017600
H	6.38165900	0.30266400	2.31154000
B	4.16810500	-0.79755900	1.44650800
H	3.85673000	-1.37855300	2.44184300
H	5.05887200	-1.34012600	0.71973400

Table S9. [PSH][$B_{10}H_{13}$] (-910.566276): TS +14.0 kcal mol^{-1} above the lowest energy pair in Figure 6, main text.

Atom	x	y	z
N	0.75287300	1.24831800	-0.00380700
N	0.90667800	-1.37934700	-0.21769500

H	0.54996000	-0.37535900	-0.21657200
C	2.18077000	1.29147800	-0.02368500
C	2.90565100	0.07017300	-0.01362200
C	2.34695600	-1.22788400	-0.06899500
C	3.11313900	-2.35479500	-0.03275700
H	2.64115300	-3.33679300	-0.08117100
C	4.50238300	-2.26234600	0.05825100
H	5.10005500	-3.17367600	0.09104700
C	5.09425900	-1.03648600	0.09094200
H	6.18080400	-0.94277600	0.14461600
C	4.32957300	0.14115100	0.05292900
C	4.96677600	1.39395900	0.06960100
H	6.05723500	1.41694900	0.11422900
C	4.24090500	2.54476900	0.02872600
H	4.73838600	3.51522700	0.03903700
C	2.84589600	2.48631200	-0.00984900
H	2.27366900	3.41500600	-0.01179100
C	0.25322200	1.50766300	1.33057000
H	0.72858600	0.82931600	2.05236700
H	-0.83254300	1.33824200	1.35320700
H	0.45318000	2.54742300	1.65171400
C	0.13224100	2.13929700	-0.95411800
H	-0.94885200	1.94527800	-0.96945400
H	0.27079500	3.20617300	-0.70317500
H	0.53277300	1.95977400	-1.96017900
C	0.29004500	-2.09398500	0.90329000
H	0.64877000	-3.12875600	0.92890300
H	0.54839900	-1.58798000	1.83964200
H	-0.79671500	-2.08759500	0.76267500
C	0.54768300	-1.98762700	-1.50184200
H	-0.54479200	-2.02091900	-1.57816000
H	0.95949100	-1.37784600	-2.31304500
H	0.95079300	-3.00424300	-1.56003700
B	-2.91923400	-0.20774800	-0.38389700
H	-1.79855900	-0.23638400	-0.81015400
B	-3.30939900	-0.38967900	1.32175000
H	-2.46141600	-0.49641100	2.16125700
B	-3.67413000	1.15503900	0.54977000
H	-3.14627700	2.18791400	0.85307400
B	-3.97309800	0.97659000	-1.20598800
H	-3.51011700	1.75942000	-1.97716600
B	-3.65393500	-1.68083700	0.20094800
H	-3.11735900	-2.73815700	0.02038400
B	-4.75102800	-1.32313100	1.51338400
H	-4.92316800	-2.06097900	2.44468900
B	-4.82105800	0.41876700	1.64482600
H	-5.21508600	1.02147200	2.60035600
H	-5.62891400	-1.26308500	0.69162400
B	-5.29691100	1.33669300	-0.07213000
H	-5.89953300	2.36297800	-0.01589900
H	-6.18292000	0.41070500	-0.28922600
B	-5.51964700	0.30008800	-1.47704900

H	-6.31721300	0.44769900	-2.34232700
B	-4.12338700	-0.77071000	-1.51675800
H	-3.84539000	-1.31423600	-2.54087300
H	-5.36991600	-1.04661800	-1.27999100