

# Reaction of Hydrogen Halides with Tetrahydroborate Anion and Hexahydro-*closo*-hexaborate Dianion

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## Supplementary Materials

**Table S1.** M06-computed geometric parameters (distances  $r_{(X-Y)}$  in Å, angles in °) of dihydrogen-bonded (DHB) complexes (INTn<sup>DHB</sup>) of  $[BH_{(4-x)}X_x]^-$  ( $x = 0-3$ ) with HX ( $X = F, Cl, Br$ ), their formation energy ( $\Delta G_f^{\circ MeCN}$  and  $\Delta H_f^{\circ MeCN}$  in kcal/mol), electron densities in (+3;-1) critical point of H...H bond ( $\rho_c$  in au), Laplacian of electron density at critical point ( $\nabla^2\rho_c$  in au), bond ellipticity ( $\epsilon$ ), energy of H...H interaction ( $E_{H...H} = 0.5 \cdot V(r)[1, 2]$  in kcal/mol) and donation energy ( $E^2$  in kcal/mol) from  $\sigma(B-H)$  to  $\sigma^*(H-X)$  estimated from 2<sup>nd</sup>-order perturbative analysis of donor acceptor interactions within natural-bond orbital (NBO) analysis. **S3**

**Table S2.** M06-computed geometric parameters (distances  $r_{(X-Y)}$  in Å, angles in °) of H<sub>2</sub> complexes of  $X^-[(H_2)BH_{(4-x)}X_x]^-$  ( $n = 1-2$ ,  $X = Cl, Br$ ) (INTn<sup>H2</sup>), their formation energy ( $\Delta G_f^{\circ MeCN}$  and  $\Delta H_f^{\circ MeCN}$  in kcal/mol), donation energy ( $E_2$  in kcal/mol) from  $\sigma(B-H/X)$  to  $\sigma^*(H-H-B)$  ( $E_1$ ), from  $\sigma(H-H-B)$  to  $\sigma^*(B-H/X)$  ( $E_2$ ) and from  $p(X)$  to  $\sigma^*(H-H-B)$  ( $E_3$ ) estimated from 2<sup>nd</sup>-order perturbative analysis of donor acceptor interactions within natural-bond orbital (NBO) analysis, QTAIM energy of H<sub>2</sub>...H, H...H and B...H interactions ( $E_{X...Y} = 0.5 \cdot V(r)[1, 2]$  in kcal/mol). **S3**

**Table S3.** Hydride affinity (HA<sub>298K</sub> in kcal/mol) of  $[BH_{(4-x)}X_x]^-$  ( $x = 0-3$ ) ( $X = F, Cl, Br$ ). Hybridization of boron orbitals in B-H moieties, QTAIM delocalization indices (DI) of BH bond in  $[BH_{(4-x)}X_x]^-$  ( $X = F, Cl, Br$ ). Hydride (HDA<sub>MeCN</sub> in kcal/mol) and proton (PDA<sub>MeCN</sub> in kcal/mol) donor abilities for Li[BH<sub>(4-x)</sub>X<sub>x</sub>] in MeCN. **S4**

**Table S4.** QTAIM delocalization indices (DI) and Wiberg bond indices (WBI) for H...H contacts, their differences for XH and HB bond and hybridization of boron orbitals in BH moieties of M06-computed geometries of DHB complexes for  $[BH_{(4-x)}X_x]^-$  ( $x = 0-3$ ) with HX ( $X = F, Cl, Br$ ) (INTn<sup>DHB</sup>). **S4**

**Figure S1.** M06-calculated energy profile ( $\Delta G^{\circ MeCN}$  in kcal/mol) of the reaction of BH<sub>4</sub><sup>-</sup> with HF in MeCN. **S5**

**Figure S2.** wB97XD-calculated energy profile ( $\Delta G^{\circ MeCN}$  in kcal/mol) of the reaction of BH<sub>4</sub><sup>-</sup> with HF in MeCN. **S5**

**Figure S3.** wB97XD-calculated energy profile ( $\Delta G^{\circ MeCN}$  in kcal/mol) of the reaction of BH<sub>4</sub><sup>-</sup> with HCl in MeCN. **S6**

**Figure S4.** M06-calculated energy profile ( $\Delta G^{\circ MeCN}$  in kcal/mol) of the reaction of BH<sub>4</sub><sup>-</sup> with HBr in MeCN. **S7**

**Figure S5.** wB97XD-calculated energy profile ( $\Delta G^{\circ MeCN}$  in kcal/mol) of the reaction of BH<sub>4</sub><sup>-</sup> with HBr in MeCN. **S7**

**Table S5.** Free Gibbs activation energy in acetonitrile ( $\Delta G^{\circ MeCN \ddagger}$  in kcal/mol) of the transition state of H<sub>2</sub> elimination (TSn<sup>ELIM<sub>HX</sub></sup>) and concerted transition state of proton-hydride transfer/H<sub>2</sub> elimination (TSn<sup>CONC<sub>HX</sub></sup>) for reaction of BH<sub>4</sub><sup>-</sup> with HX ( $X = F, Cl, Br$ ) and their M06-optimized geometric parameters. **S8**

**Table S6.** Free Gibbs activation energy in acetonitrile ( $\Delta G^{\circ MeCN \ddagger}$  in kcal/mol) of the transition state of H<sub>2</sub> elimination (TSn<sup>ELIM<sub>HX</sub></sup>) and concerted transition state of proton-hydride transfer/H<sub>2</sub> elimination (TSn<sup>CONC<sub>HX</sub></sup>) for reaction of BH<sub>4</sub><sup>-</sup> with HX ( $X = F, Cl, Br$ ) and their wB97XD-optimized geometric parameters. **S8**

**Table S7.** Free Gibbs activation energy in dichloromethane ( $\Delta G^{\circ}_{\text{DCM}}^{\ddagger}$  in kcal/mol)[5] of the concerted transition state of proton-hydride transfer/ $\text{H}_2$  elimination ( $\text{TS}^{\text{CONC}}_{\text{ROH}}$ ) for reaction of  $\text{BH}_4^-$  with HOR [ $\text{ROH} = \text{MeOH}$ ,  $\text{CF}_3\text{CH}_2\text{OH}$  (TFE),  $(\text{CF}_3)_2\text{CHOH}$  (HFIP)] and their M06-optimized geometric parameters. S10

**Table S8.** Hydride ( $\text{HDA}_{\text{MeCN}}$  in kcal/mol) and proton ( $\text{PDA}_{\text{MeCN}}$  in kcal/mol) donor abilities for  $[\text{B}_6\text{H}_{(6-x)}\text{Cl}_x]^{2-}$  ( $x = 0-5$ ) in MeCN. S10

**Table S9.** M06-computed geometric (distances  $r_{(X-Y)}$  in Å, angles in degrees) parameters of hydrogen-bonded complexes of  $[\text{B}_6\text{H}_{(6-x)}\text{Cl}_x]^{2-}$  ( $x = 0-5$ ) with HCl ( $\text{INTn}^{\text{HB}}$ ), their formation energy ( $\Delta G_f^{\circ}_{\text{MeCN}}$  and  $\Delta H_f^{\circ}_{\text{MeCN}}$  in kcal/mol), electron densities at the  $\text{H}\cdots\text{B}(\text{B}2)$  bond (+3;-1) critical point ( $q_c$  in au), Laplacian of electron density at critical point ( $\nabla^2 q_c$  in au), bond ellipticity ( $\epsilon$ ) and energy of  $\text{H}\cdots\text{B}(\text{B}2)$  interaction ( $E_{\text{H}\cdots\text{B}(\text{B}2)} = 0.5 \cdot V(r)$  [1, 2] in kcal/mol) and donation energy ( $E^2_{\text{HB}}$  in kcal/mol) from  $\sigma(\text{B}-\text{B})$  to  $\sigma^*(\text{H}-\text{Cl})$  estimated from 2nd-order perturbative analysis of donor acceptor interactions within natural-bond orbital (NBO) analysis. S11

**Table S10.** M06-computed geometric (distances  $r_{(X-Y)}$  in Å, angles in degrees) parameters of hydrogen bonded complexes of  $\text{Cl}^- \cdot [\text{facHB}_6\text{H}_{(6-x)}\text{Cl}_x]^-$  ( $x = 0-5$ ) with HCl, their formation energy ( $\Delta G_f^{\circ}_{\text{MeCN}}$  and  $\Delta H_f^{\circ}_{\text{MeCN}}$  in kcal/mol), electron densities at the  $\text{H}\cdots\text{B}(\text{B}2)$  bond (+3;-1) critical point ( $q_c$  in au), Laplacian of electron density at critical point ( $\nabla^2 q_c$  in au), bond ellipticity ( $\epsilon$ ) and energy of  $\text{H}\cdots\text{B}(\text{B}2)$  interaction ( $E_{\text{H}\cdots\text{B}(\text{B}2)} = 0.5 \cdot V(r)$  [1, 2] in kcal/mol). S11

**Table S11.** M06-computed geometric parameters (distances  $r_{(X-Y)}$  in Å, angles in °) of  $\text{H}_2$  complexes of  $\text{Cl}^- \cdot (\text{H}_2)\text{B}_6\text{H}_{(5-x)}\text{Cl}_x]^-$  ( $x = 0-5$ ) ( $\text{INTn}^{\text{H}_2}$ ), their formation energy ( $\Delta G_f^{\circ}_{\text{MeCN}}$  and  $\Delta H_f^{\circ}_{\text{MeCN}}$  in kcal/mol), electron densities in (+3;-1) donation energy ( $E^2$  in kcal/mol) from  $\sigma(\text{B}-\text{H}/\text{Cl})$  to  $\sigma^*(\text{H}-\text{H}-\text{B})$  ( $E^2_1$ ), from  $\sigma(\text{H}-\text{H}-\text{B})$  to  $\sigma^*(\text{B}-\text{H}/\text{Cl})$  ( $E^2_2$ ) and from  $p(\text{Cl})$  to  $\sigma^*(\text{H}-\text{H}-\text{B})$  ( $E^2_3$ ) estimated from 2<sup>nd</sup>-order perturbative analysis of donor acceptor interactions within natural-bond orbital (NBO) analysis. S12

**Figure S6.** M06-optimized geometries of the protonated forms  $[\text{facHB}_6\text{H}_{(6-x)}\text{Cl}_x]^-$  ( $x = 0-4$ ) and their free Gibbs formation energies ( $\Delta G_f^{\circ}_{\text{MeCN}}$  in kcal/mol). S13

**Figure S7.** wB97XD-calculated energy profile of halogenation of  $[\text{B}_6\text{H}_{(6-x)}\text{Cl}_x]^{2-}$  ( $x = 0-5$ ) by HCl for the pathway:  $[\text{B}_6\text{H}_6]^{2-} \rightarrow 1-[\text{B}_6\text{H}_5\text{Cl}]^{2-} \rightarrow 1,2-[\text{B}_6\text{H}_4\text{Cl}_2]^{2-}$  (*cis*)  $\rightarrow 1,2,3-[\text{B}_6\text{H}_3\text{Cl}_3]^{2-}$  (*fac*)  $\rightarrow 1,2,3,4-[\text{B}_6\text{H}_2\text{Cl}_4]^{2-}$  (*cis*)  $\rightarrow 1,2,3,4,6-[\text{B}_6\text{HCl}_5]^{2-}$ . S14

**Table S12.** Activation barriers ( $\Delta G^{\circ}_{\text{MeCN}}^{\ddagger}$ , in kcal/mol) for TSs for the reaction of  $[\text{B}_6\text{xH}_6]^{2-}$  with HCl ( $\text{pK}_a^{\text{MeCN}} = 10.3$ ) in MeCN computed at the wB97XD/6-311++G(d,p) theory level. S15

**References** S16

**Table S1.** M06-computed geometric parameters (distances  $r_{(X-Y)}$  in Å, angles in °) of dihydrogen-bonded (DHB) complexes ( $\text{INT}^{\text{DHB}}$ ) of  $[\text{BH}_{(4-x)}\text{X}_x]^-$  ( $x = 0-3$ ) with  $\text{HX}$  ( $X = \text{F}, \text{Cl}, \text{Br}$ ), their formation energy ( $\Delta G_f^\circ_{\text{MeCN}}$  and  $\Delta H_f^\circ_{\text{MeCN}}$  in kcal/mol), electron densities in (+3;-1) critical point of  $\text{H}\cdots\text{H}$  bond ( $\rho_c$  in au), Laplacian of electron density at critical point ( $\nabla^2\rho_c$  in au), bond ellipticity ( $\epsilon$ ), energy of  $\text{H}\cdots\text{H}$  interaction ( $E_{\text{H}\cdots\text{H}} = 0.5 \cdot V(r)$  [1, 2] in kcal/mol) and donation energy ( $E^2$  in kcal/mol) from  $\sigma(\text{B-H})$  to  $\sigma^*(\text{H-X})$  estimated from 2<sup>nd</sup>-order perturbative analysis of donor acceptor interactions within natural-bond orbital (NBO) analysis.

DHB complex	$r_{(\text{H}_X\cdots\text{H}_B)}$	$r_{(\text{XH})}$	$\Delta r_{(\text{XH})}$	$\angle_{\text{XH}\cdots\text{H}}$	$r_{(\text{HB})}$	$\Delta r_{(\text{HB})}$	$\angle_{\text{H}\cdots\text{HB}}$	$\Delta G_f^\circ_{\text{MeCN}}$	$\Delta H_f^\circ_{\text{MeCN}}$	$\rho_c$	$\nabla^2\rho_c$	$\epsilon$	$E_{\text{H}\cdots\text{H}}$	$E^2$
$\text{H}_3\text{BH}\cdots\text{HF}$	1.499	0.951	0.027	159	1.235	-0.002	100	2.7	-4.9	0.036	0.072	0.25	-8.0	16.1
	1.974			131	1.223	-0.014	79							2.8
$\text{FH}_2\text{BH}\cdots\text{HF}$	1.440	0.950	0.026	172	1.243	0.005	105	2.6	-4.3	0.039	0.074	0.13	-9.2	19.2
$\text{F}_2\text{HBH}\cdots\text{HF}$	1.425	0.948	0.024	179	1.245	0.008	111	4.5	-3.7	0.039	0.082	0.08	-9.2	18.6
$\text{F}_3\text{BH}\cdots\text{HF}$	1.469	0.942	0.018	179	1.236	-0.001	113	5.1	-2.5	0.034	0.075	0.08	-7.6	15.7
$\text{H}_3\text{BH}\cdots\text{HCl}$	1.580	1.324	0.031	172	1.236	-0.001	103	3.4	-4.2	0.031	0.064	0.13	-5.6	15.5
$\text{ClH}_2\text{BH}\cdots\text{HCl}$	1.641	1.315	0.021	171	1.220	-0.017	106	3.8	-3.7	0.026	0.061	0.16	-4.4	10.6
$\text{Cl}_2\text{HBH}\cdots\text{HCl}$	1.656	1.308	0.014	174	1.209	-0.028	117	4.4	-3.4	0.023	0.058	0.10	-3.7	7.3
$\text{Cl}_3\text{BH}\cdots\text{HCl}$	1.715	1.305	0.011	178	1.201	-0.037	118	5.1	-2.5	0.020	0.052	0.09	-3.0	5.0
$\text{H}_3\text{BH}\cdots\text{HBr}$	1.726	1.452	0.024	169	1.234	-0.004	103	3.6	-3.7	0.023	0.053	0.15	-3.5	9.5
$\text{BrH}_2\text{BH}\cdots\text{HBr}$	1.797	1.444	0.017	165	1.217	-0.020	104	3.9	-3.6	0.020	0.048	0.19	-2.9	6.2
$\text{Br}_2\text{HBH}\cdots\text{HBr}$	1.840	1.439	0.011	160	1.204	-0.033	113	4.4	-3.0	0.017	0.043	0.13	-2.4	3.6
$\text{Br}_3\text{BH}\cdots\text{HBr}$	1.850	1.437	0.009	163	1.196	-0.041	115	4.2	-3.0	0.016	0.041	0.02	-2.2	3.0

**Table S2.** M06-computed geometric parameters (distances  $r_{(X-Y)}$  in Å, angles in °) of  $\eta^2\text{-H}_2$  complexes of  $\text{X}^-[(\text{H}_2)\text{BH}_{(4-x)}\text{X}_x]^-$  ( $x = 1-2$ ,  $X = \text{Cl}, \text{Br}$ ) ( $\text{INTn}^{\text{H}_2}$ ), their formation energy ( $\Delta G_f^\circ_{\text{MeCN}}$  and  $\Delta H_f^\circ_{\text{MeCN}}$  in kcal/mol), donation energy ( $E_2$  in kcal/mol) from  $\sigma(\text{B-H/X})$  to  $\sigma^*(\text{H-H-B})$  ( $E^1_1$ ), from  $\sigma(\text{H-H-B})$  to  $\sigma^*(\text{B-H/X})$  ( $E^2_2$ ) and from  $p(X)$  to  $\sigma^*(\text{H-H-B})$  ( $E^2_3$ ) estimated from 2<sup>nd</sup>-order perturbative analysis of donor acceptor interactions within natural-bond orbital (NBO) analysis, QTAIM energy of  $\text{H}_2\cdots\text{H}$ ,  $\text{H}\cdots\text{H}$  and  $\text{B}\cdots\text{H}$  interactions ( $E_{X\cdots Y} = 0.5 \cdot V(r)$  [1, 2] in kcal/mol).

$\eta^2\text{-H}_2$ complex	$r_{(\text{H}\cdots\text{H})}$	$r_{(\text{B}\cdots\text{H}_1)}$	$\Delta r_{(\text{B}\cdots\text{H}_1)}$	$r_{(\text{B}\cdots\text{H}_2)}$	$r_{(\text{B}\cdots\text{H}_2)}$	$\Delta r_{(\text{B}\cdots\text{H}_2)}$	$r_{(\text{H}_2\cdots\text{X})}$	$\Delta r_{(\text{H}_2\cdots\text{X})}$	$\Delta G_f^\circ_{\text{MeCN}}$	$\Delta H_f^\circ_{\text{MeCN}}$	$E^1_1$	$E^2_2$	$E^2_3$	$E_{\text{H}_2\cdots\text{X}}$	$E_{\text{H}\cdots\text{H}}$	$E_{\text{B}\cdots\text{H}}$
$\text{Cl}^-(\text{H}_2)\text{BH}_3$	0.841	1.351	0.124	1.327	1.432	0.205	2.272	0.978	3.8	-3.7	13.3	3.7	15.7	-3.9	-63.8	-64.9
											2.9	1.1	1.2			
											2.3	1.3				
$\text{Br}^-(\text{H}_2)\text{BH}_3$	0.846	1.343	0.116	1.340	1.464	0.237	2.302	1.008	8.0	0.2	12.0	4.2	23.7	-4.6	-63.1	-64.4
											2.1	1.4	2.1			
											2.0	1.4				
$\text{Cl}^-(\text{H}_2)\text{BH}_2\text{Cl}$	0.853	1.342	0.115	1.363	1.508	0.281	2.042	0.748	11.7	3.0	8.8	11.5	38.1	-8.0	-61.7	-63.3
											7.9	5.1	3.3			
											4.6	3.3	1.5			

**Table S3.** Hydride affinity ( $HA_{298K}$  in kcal/mol) of  $[BH_{(4-x)}X_x]^-$  ( $x = 0-3$ ) ( $X = F, Cl, Br$ ). Hybridization of boron orbitals in B–H moieties, QTAIM delocalization indices (DI) of BH bond in  $[BH_{(4-x)}X_x]^-$  ( $X = F, Cl, Br$ ). Hydride ( $HDA_{MeCN}$  in kcal/mol) and proton ( $PDA_{MeCN}$  in kcal/mol) donor abilities for  $Li[BH_{(4-x)}X_x]$  in MeCN.

Molecule	$HA_{298K}^a$	Molecule	( $sp^N$ ) B–H	DI (BH)	Molecule	$HDA_{MeCN}^b$	$PDA_{MeCN}$
BH <sub>3</sub>	73.7	BH <sub>4</sub> <sup>−</sup>	3.0	0.537	LiBH <sub>4</sub>	64.86	96.51
FBH <sub>2</sub>	63.2	[BH <sub>3</sub> F] <sup>−</sup>	2.7	0.503	Li[BH <sub>3</sub> F]	54.64	104.37
F <sub>2</sub> BH	60.0	[BH <sub>2</sub> F <sub>2</sub> ] <sup>−</sup>	2.5	0.468	Li[BH <sub>2</sub> F <sub>2</sub> ]	53.12	107.48
F <sub>3</sub> B	70.5	[F <sub>3</sub> BH] <sup>−</sup>	2.1	0.442	Li[BHF <sub>3</sub> ]	61.08	101.22
ClBH <sub>2</sub>	80.9	[BH <sub>3</sub> Cl] <sup>−</sup>	2.6	0.544	Li[BH <sub>3</sub> Cl]	65.34	88.23
Cl <sub>2</sub> BH	88.1	[BH <sub>2</sub> Cl <sub>2</sub> ] <sup>−</sup>	2.4	0.548	Li[BH <sub>2</sub> Cl <sub>2</sub> ]	69.80	93.85
Cl <sub>3</sub> B	95.8	[BHCl <sub>3</sub> ] <sup>−</sup>	2.2	0.552	Li[BHCl <sub>3</sub> ]	73.02	85.49
BrBH <sub>2</sub>	87.3	[BH <sub>3</sub> Br] <sup>−</sup>	2.6	0.553	Li[BH <sub>3</sub> Br]	69.47	88.97
Br <sub>2</sub> BH	97.3	[BH <sub>2</sub> Br <sub>2</sub> ] <sup>−</sup>	2.4	0.571	Li[BH <sub>2</sub> Br <sub>2</sub> ]	74.67	88.81
Br <sub>3</sub> B	104.9	[BHBr <sub>3</sub> ] <sup>−</sup>	2.0	0.592	Li[BHBr <sub>3</sub> ]	77.60	83.47

<sup>a</sup> Calculated values are taken from [3]. <sup>b</sup> Calculated values are taken from [4].

**Table S4.** QTAIM delocalization indices (DI) and Wiberg bond indices (WBI) for  $H\cdots H$  contacts, their differences for  $XH$  and  $HB$  bond and hybridization of boron orbitals in BH moieties of M06-computed geometries of DHB complexes for  $[BH_{(4-x)}X_x]^-$  ( $x = 0-3$ ) with  $HX$  ( $X = F, Cl, Br$ ) ( $INT^{DHB}$ ).

DHB complex	$DI_{(XH\cdots HB)}$	$\Delta DI_{(XH)}$	$\Delta DI_{(HB)}$	$WBI_{(XH\cdots HB)}$	$\Delta WBI_{(XH)}$	$\Delta WBI_{(HB)}$	H–B( $sp^N$ )
H <sub>3</sub> BH $\cdots$ HF	0.082	−0.060	−0.046	0.078	−0.164	−0.098	3.2
	0.022		−0.009	0.009		−0.010	3.0
FH <sub>2</sub> BH $\cdots$ HF	0.095	−0.057	−0.053	0.105	−0.142	−0.133	3.0
F <sub>2</sub> HBH $\cdots$ HF	0.097	−0.052	−0.052	0.057	−0.120	−0.143	2.7
F <sub>3</sub> BH $\cdots$ HF	0.087	−0.045	−0.046	0.102	−0.093	−0.124	2.3
H <sub>3</sub> BH $\cdots$ HCl	0.111	−0.161	−0.047	0.079	−0.161	−0.119	3.2
ClH <sub>2</sub> BH $\cdots$ HCl	0.094	−0.131	−0.038	0.057	−0.110	−0.087	2.8
Cl <sub>2</sub> HBH $\cdots$ HCl	0.084	−0.104	−0.036	0.044	−0.068	−0.071	2.5
Cl <sub>3</sub> BH $\cdots$ HCl	0.074	−0.083	−0.032	0.033	−0.046	−0.051	2.3
H <sub>3</sub> BH $\cdots$ HBr	0.094	−0.145	−0.034	0.049	−0.124	−0.080	3.1
BrH <sub>2</sub> BH $\cdots$ HBr	0.077	−0.122	−0.028	0.032	−0.087	−0.055	2.7
Br <sub>2</sub> HBH $\cdots$ HBr	0.064	−0.100	−0.024	0.021	−0.054	−0.039	2.5
Br <sub>3</sub> BH $\cdots$ HBr	0.063	−0.089	−0.025	0.018	−0.047	−0.033	2.3

Figure S1. M06-calculated energy profile ( $\Delta G^\circ_{\text{MeCN}}$  in kcal/mol) of the reaction of  $\text{BH}_4^-$  with HF in MeCN.

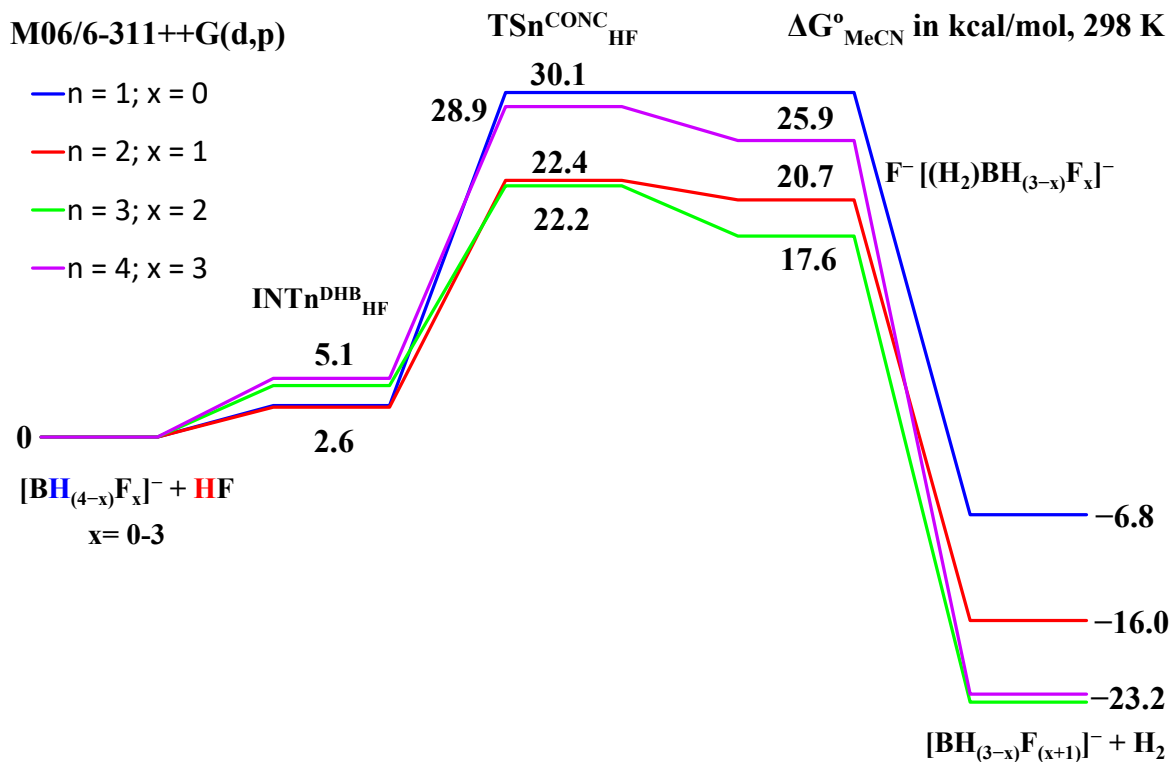


Figure S2. wB97XD-calculated energy profile ( $\Delta G^\circ_{\text{MeCN}}$  in kcal/mol) of the reaction of  $\text{BH}_4^-$  with HF in MeCN.

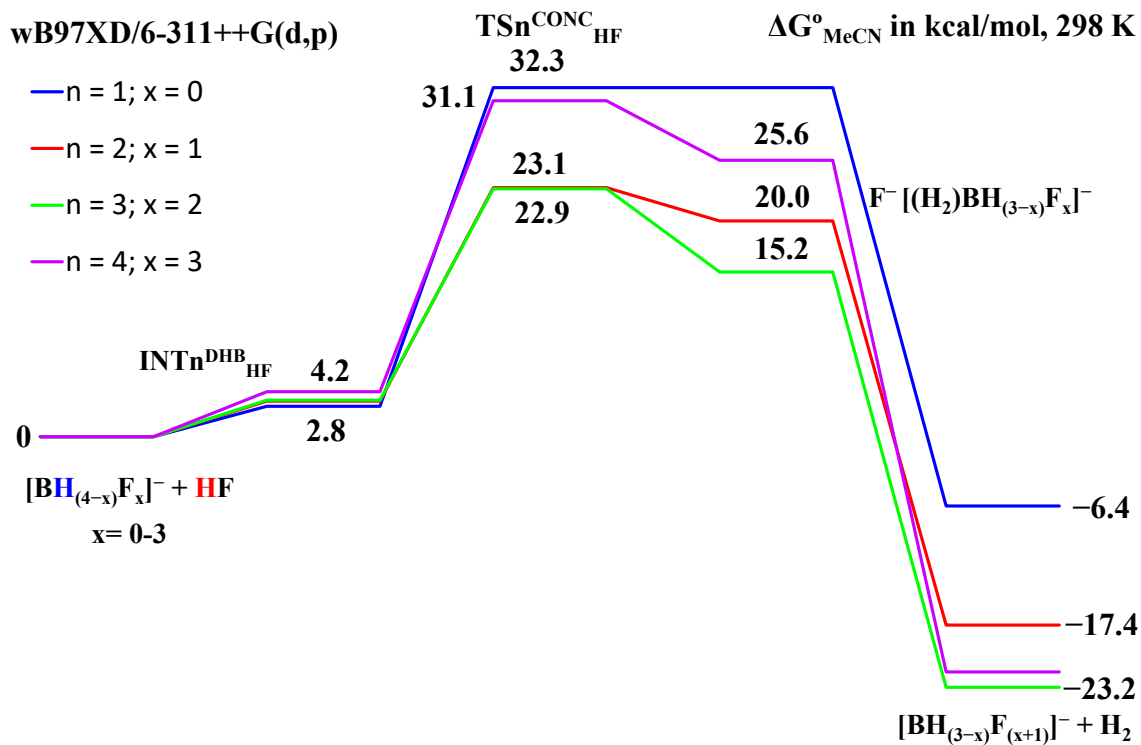


Figure S3. wB97XD-calculated energy profile ( $\Delta G^\circ_{\text{MeCN}}$  in kcal/mol) of the reaction of  $\text{BH}_4^-$  with  $\text{HCl}$  in  $\text{MeCN}$ .

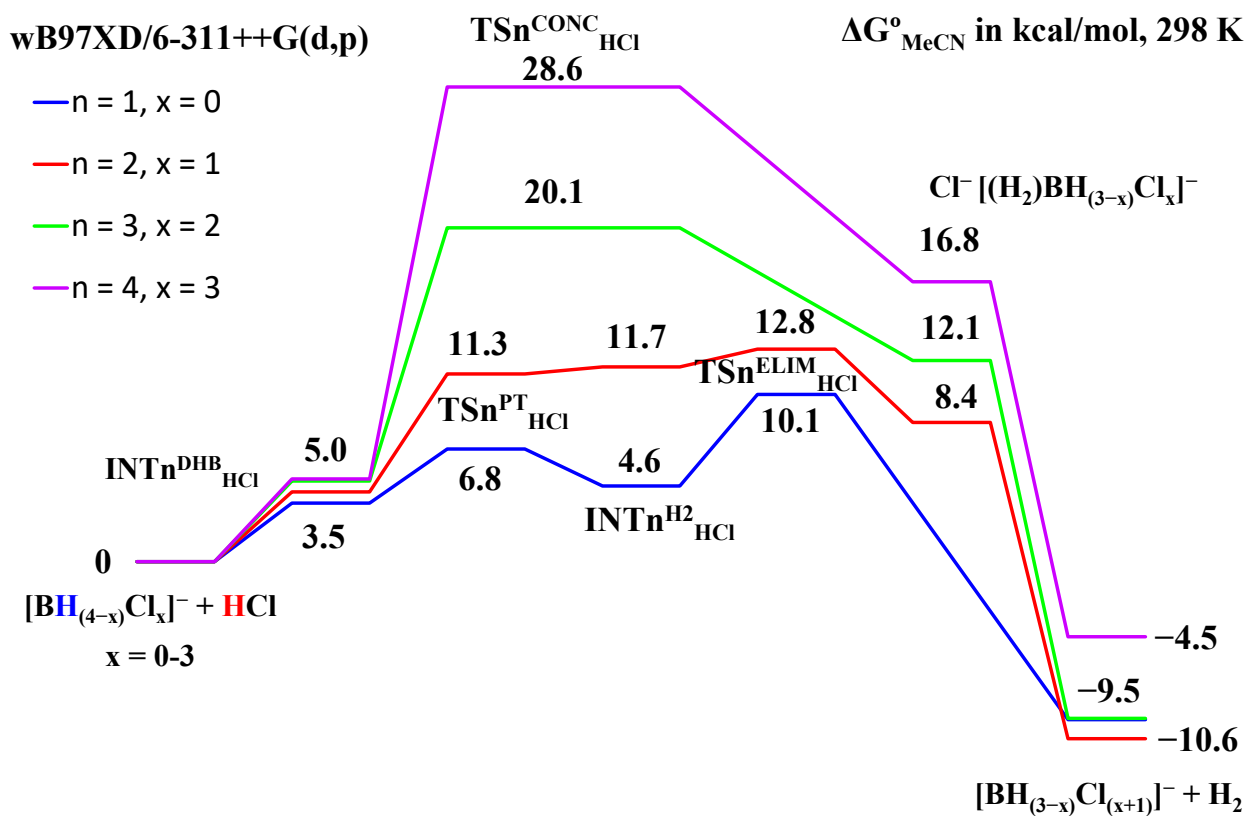


Figure S4. M06-calculated energy profile ( $\Delta G^\circ_{\text{MeCN}}$  in kcal/mol) of the reaction of  $\text{BH}_4^-$  with  $\text{HBr}$  in MeCN.

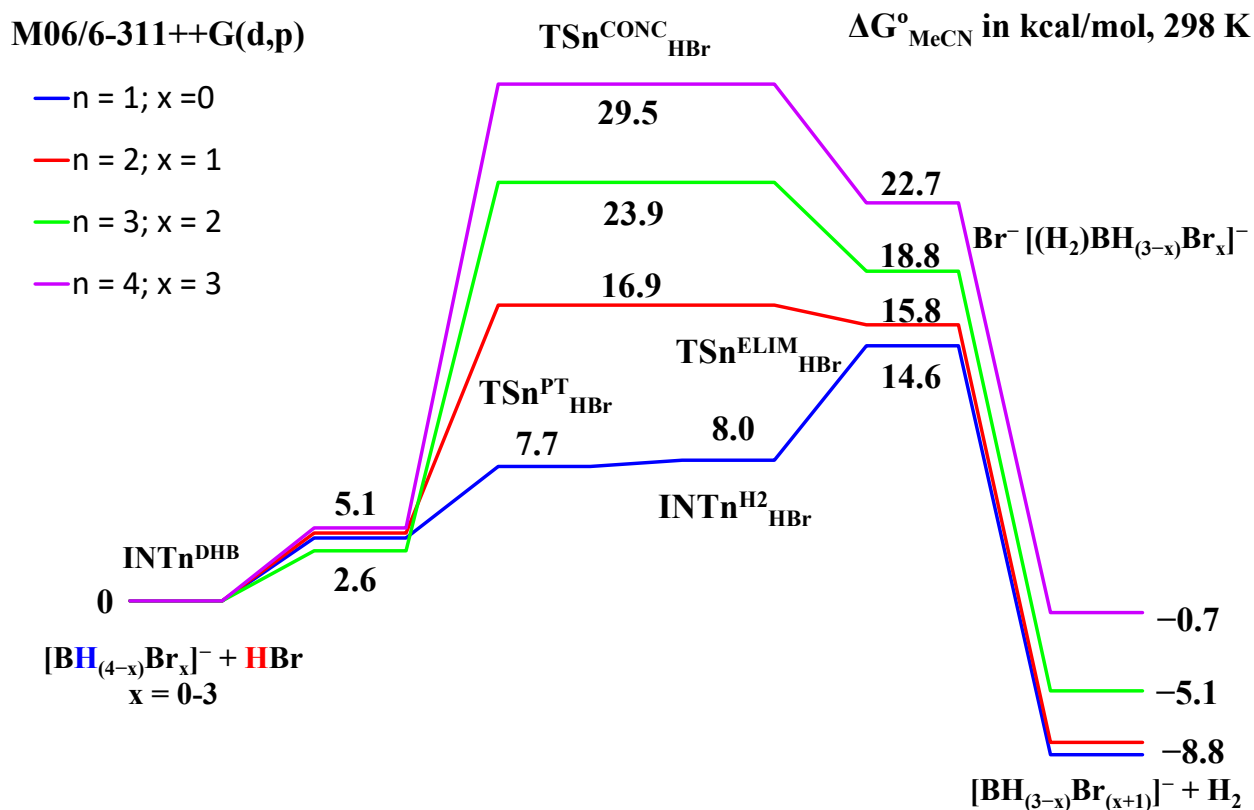
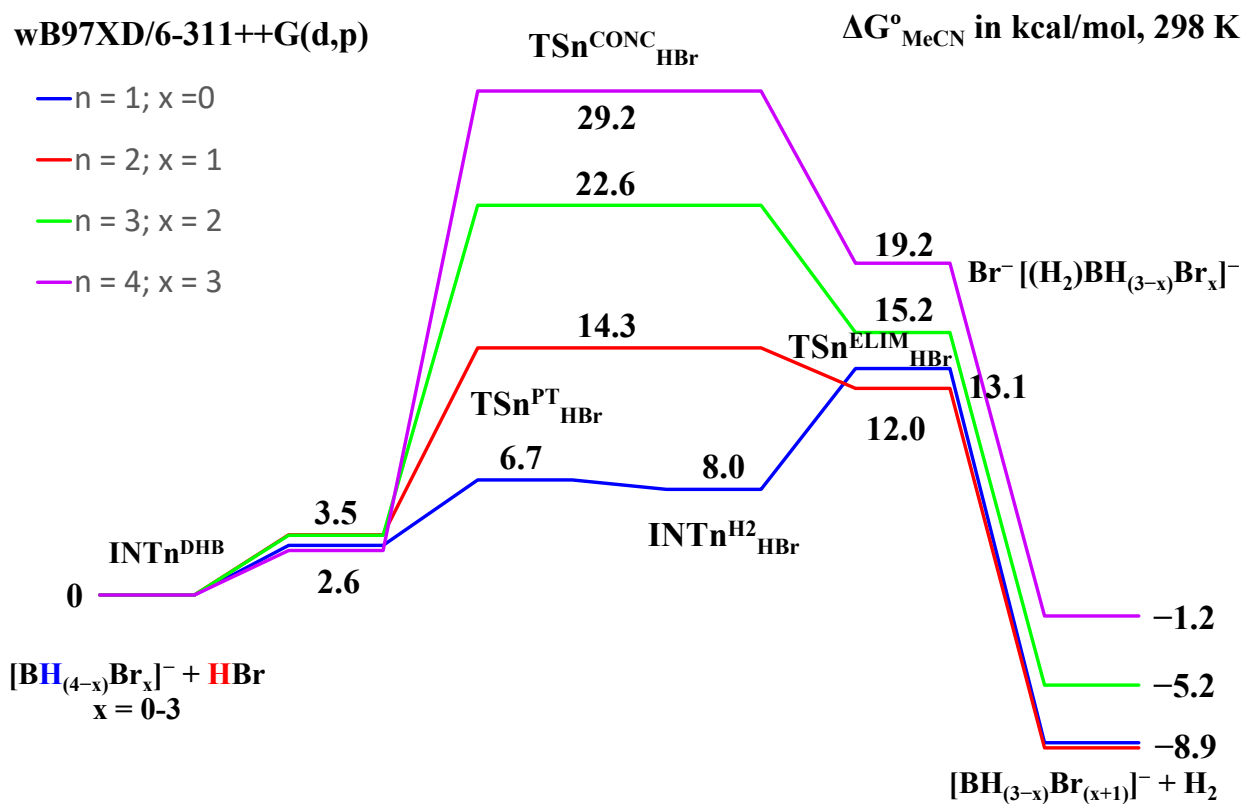


Figure S5. wB97XD-calculated energy profile ( $\Delta G^\circ_{\text{MeCN}}$  in kcal/mol) of the reaction of  $\text{BH}_4^-$  with  $\text{HBr}$  in MeCN.



**Table S5.** Free Gibbs activation energy in MeCN ( $\Delta G^{\circ}_{\text{MeCN}}{}^{\ddagger(\text{span})}$  in kcal/mol) of the transition state of H<sub>2</sub> elimination (**TSn<sup>ELIM</sup><sub>HX</sub>**) and concerted transition state of proton-hydride transfer/H<sub>2</sub> elimination (**TSn<sup>CONC</sup><sub>HX</sub>**) for reaction of BH<sub>4</sub><sup>−</sup> with HX (X = F, Cl, Br) and their M06-optimized geometric parameters (distances  $r_{(\text{X}-\text{Y})}$  in Å).

<b>M06 TS</b>	$\Delta G^{\circ}_{\text{MeCN}}{}^{\ddagger(\text{span})}$	$r(\text{B}\cdots\text{H}_2)$	$r(\text{H}-\text{H})$	$r(\text{H}\cdots\text{X})$	$r(\text{B}\cdots\text{X})$
TS1 <sup>CONC</sup> <sub>HF</sub>	30.1	2.452	0.760	2.030	2.969
TS2 <sup>CONC</sup> <sub>HF</sub>	22.4	1.940	0.781	1.818	3.335
TS3 <sup>CONC</sup> <sub>HF</sub>	22.0	1.895	0.806	1.595	3.304
TS4 <sup>CONC</sup> <sub>HF</sub>	28.9	1.926	0.799	1.627	3.306
TS1 <sup>ELIM</sup> <sub>HCl</sub>	9.1	2.631	0.755	2.661	3.528
TS2 <sup>ELIM</sup> <sub>HCl</sub>	12.9	1.861	0.773	2.460	3.945
TS3 <sup>CON</sup> <sub>HCl</sub>	19.2	1.825	0.789	2.195	3.913
TS4 <sup>CONC</sup> <sub>HCl</sub>	26.1	1.902	0.796	2.086	3.956
TS1 <sup>ELIM</sup> <sub>HBr</sub>	14.6	2.528	0.758	2.741	3.725
TS2 <sup>CONC</sup> <sub>HBr</sub>	16.9	2.004	0.772	2.563	4.231
TS3 <sup>CONC</sup> <sub>HBr</sub>	23.9	2.008	0.789	2.303	4.282
TS4 <sup>CONC</sup> <sub>HBr</sub>	29.5	1.837	0.795	2.226	4.355

**Table S6.** Free Gibbs activation energy in MeCN ( $\Delta G^{\circ}_{\text{MeCN}}{}^{\ddagger(\text{span})}$  in kcal/mol) of the transition states of H<sub>2</sub> elimination (**TSn<sup>ELIM</sup><sub>HX</sub>**) and concerted transition state of proton-hydride transfer/H<sub>2</sub> elimination (**TSn<sup>CONC</sup><sub>HX</sub>**) for reaction of BH<sub>4</sub><sup>−</sup> with HX (X = F, Cl, Br) and their wB97XD-optimized geometric parameters (distances  $r_{(\text{X}-\text{Y})}$  in Å).

<b>wB97XD TS</b>	$\Delta G^{\circ}_{\text{MeCN}}{}^{\ddagger(\text{span})}$	$r(\text{B}\cdots\text{H}_2)$	$r(\text{H}-\text{H})$	$r(\text{H}\cdots\text{X})$	$r(\text{B}\cdots\text{X})$
TS1 <sup>CONC</sup> <sub>HF</sub>	32.3	2.647	0.756	2.079	3.164
TS2 <sup>CONC</sup> <sub>HF</sub>	23.1	1.993	0.773	1.864	3.500
TS3 <sup>CONC</sup> <sub>HF</sub>	22.9	1.870	0.798	1.611	3.326
TS4 <sup>CONC</sup> <sub>HF</sub>	31.1	1.921	0.789	1.665	3.350
TS1 <sup>ELIM</sup> <sub>HCl</sub>	10.1	2.882	0.749	2.845	3.784
TS2 <sup>ELIM</sup> <sub>HCl</sub>	12.8	1.933	0.763	2.641	4.140
TS3 <sup>CONC</sup> <sub>HCl</sub>	20.1	1.798	0.776	2.327	4.020
TS4 <sup>CONC</sup> <sub>HCl</sub>	28.6	1.859	0.785	2.147	3.960
TS1 <sup>ELIM</sup> <sub>HBr</sub>	13.1	2.684	0.752	2.834	3.935
TS2 <sup>CONC</sup> <sub>HBr</sub>	14.3	2.049	0.763	2.682	4.299
TS3 <sup>CONC</sup> <sub>HBr</sub>	22.6	1.955	0.777	2.391	4.295
TS4 <sup>CONC</sup> <sub>HBr</sub>	29.2	2.042	0.786	2.257	4.355



**Table S7.** Free Gibbs activation energy in dichloromethane ( $\Delta G^{\circ}_{\text{DCM}}^{\ddagger}$  in kcal/mol)[5] of the concerted transition state of proton-hydride transfer/ $\text{H}_2$  elimination ( $\text{TS}^{\text{CONC}}_{\text{ROH}}$ ) for reaction of  $\text{BH}_4^-$  with HOR [ $\text{ROH} = \text{MeOH}$ ,  $\text{CF}_3\text{CH}_2\text{OH}$  (TFE),  $(\text{CF}_3)_2\text{CHOH}$  (HFIP)] and their M06-optimized geometric parameters.

Name of TS	$\Delta G^{\circ}_{\text{DCM}}^{\ddagger}$	$r(\text{B}\cdots\text{H}_2)$	$r(\text{H}\cdots\text{H})$	$r(\text{H}\cdots\text{O})$	$r(\text{B}\cdots\text{O})$
$\text{TS1}^{\text{CONC}}_{\text{MeOH}}$	53.3	2.125	0.828	1.565	2.646
$\text{TS2}^{\text{CONC}}_{\text{MeOH}}$	30.1	2.335	0.810	1.692	3.539
$\text{TS3}^{\text{CONC}}_{\text{MeOH}}$	21.9	2.134	0.883	1.400	3.462
$\text{TS4}^{\text{CONC}}_{\text{MeOH}}$	18.8	2.260	0.930	1.312	3.541
$\text{TS1}^{\text{CONC}}_{\text{TFE}}$	44.5	2.183	0.789	1.788	2.800
$\text{TS2}^{\text{CONC}}_{\text{TFE}}$	26.1	2.012	0.815	1.652	3.240
$\text{TS3}^{\text{CONC}}_{\text{TFE}}$	24.3	1.951	0.863	1.436	3.268
$\text{TS4}^{\text{CONC}}_{\text{TFE}}$	21.6	2.026	0.899	1.349	3.258
$\text{TS1}^{\text{CONC}}_{\text{HFIP}}$	35.1	2.233	0.744	1.924	2.847
$\text{TS2}^{\text{CONC}}_{\text{HFIP}}$	21.3	2.291	0.788	1.799	3.246
$\text{TS3}^{\text{CONC}}_{\text{HFIP}}$	16.7 <sup>a</sup>	1.912	0.859	1.440	3.270

<sup>a</sup> This value was calculated for the model reaction of  $[(\text{CF}_3)_2\text{CHO}][(\text{CF}_3)(\text{CH}_3)\text{CHO}]\text{BH}_2^-$  with  $(\text{CF}_3)_2\text{CHOH}$  (HFIP)

**Table S8.** Hydride ( $\text{HDA}_{\text{MeCN}}$  in kcal/mol) and proton ( $\text{PDA}_{\text{MeCN}}$  in kcal/mol) donor abilities for  $[\text{B}_6\text{H}_{(6-x)}\text{Cl}_x]^{2-}$  ( $x = 0\text{--}5$ ) in MeCN.

	Molecule	$\text{HDA}_{\text{MeCN}}$	$\text{PDA}_{\text{MeCN}}$
	$[\text{B}_6\text{H}_6]^{2-}$	71.94	106.58
[1]	$[\text{B}_6\text{ClH}_5]^{2-}$	$\text{BH}_{\text{eq}}$ 76.55 $\text{BH}_{\text{ax}}$ 80.01	$\text{BH}_{\text{eq}}$ 103.11 $\text{BH}_{\text{ax}}$ 102.41
[1,2] ( <i>cis</i> )	$[\text{B}_6\text{Cl}_2\text{H}_4]^{2-}$	$\text{BH}_{\text{cis}}$ 80.97 $\text{BH}_{\text{trans}}$ 84.67	$\text{BH}_{\text{cis}}$ 100.42 $\text{BH}_{\text{trans}}$ 99.70
[1,6] ( <i>trans</i> )	$[\text{B}_6\text{Cl}_2\text{H}_4]^{2-}$	81.06	100.05
[1,2,3] ( <i>fac</i> )	$[\text{B}_6\text{Cl}_3\text{H}_3]^{2-}$	88.60	96.64
[1,6,2] ( <i>mer</i> )	$[\text{B}_6\text{Cl}_3\text{H}_3]^{2-}$	$\text{BH}_{\text{cis}}$ 84.89 $\text{BH}_{\text{trans}}$ 88.63	$\text{BH}_{\text{cis}}$ 97.23 $\text{BH}_{\text{trans}}$ 96.42
[1,2,3,4] ( <i>cis</i> )	$[\text{B}_6\text{Cl}_4\text{H}_2]^{2-}$	92.54	95.67
[1,6,2,4] ( <i>trans</i> )	$[\text{B}_6\text{Cl}_4\text{H}_2]^{2-}$	88.43	91.71
[1,2,3,4,6]	$[\text{B}_6\text{Cl}_5\text{H}]^{2-}$	95.65	89.27

**Table S9.** M06-computed geometric (distances  $r_{(X-Y)}$  in Å, angles in degrees) parameters of hydrogen-bonded complexes of  $[B_6H_{(6-x)}Cl_x]^{2-}$  ( $n = 0-5$ ) with HCl (**INT<sup>HB</sup>**), their energy formation energy ( $\Delta G_f^{\circ MeCN}$  and  $\Delta H_f^{\circ MeCN}$  in kcal/mol), electron densities at the  $H \cdots B(B_2)$  bond (+3;-1) critical point ( $\rho_c$  in au), Laplacian of electron density at critical point ( $\nabla^2 \rho_c$  in au), bond ellipticity ( $\epsilon$ ) and energy of  $H \cdots B(B_2)$  interaction ( $E_{H \cdots B(B_2)} = 0.5 \cdot V(r)$  [1, 2] in kcal/mol) and donation energy ( $E_{HB}^2$  in kcal/mol) from  $\sigma(B-B)$  to  $\sigma^*(H-Cl)$  estimated from 2nd-order perturbative analysis of donor acceptor interactions within natural-bond orbital (NBO) analysis.

N	INT <sup>HB3</sup>	TS <sup>PT</sup>	TS <sup>ISO</sup> fac-apx	TS <sup>ISO</sup> fac-fac*	$r_{(H \cdots B_3)}$	$r_{(XH)}$	$\Delta r_{(XH)}$	$\angle_{XH \cdots B_3}$	$\Delta G_f^{\circ MeCN}$	$\Delta H_f^{\circ MeCN}$	$\rho_c$	$\nabla^2 \rho_c$	$\epsilon$	$E_{H \cdots B(B_2)}$	$E_{HB}^2$
	$[B_6H_6]^{2-} \cdots HCl$	0.7	20.1	17.3	2.006	1.339	0.045	180	1.8	-6.9	0.026	0.046	0.01	-3.7	9.77
[1]	$[B_6ClH_5]^{2-} \cdots HCl$	1.3/2.3	19.8/19.0	14.7/14.2	2.021	1.336	0.042	179	1.9	-6.7	0.026	0.046	0.03	-3.6	9.29
[1,2] ( <i>cis</i> )	$B_6Cl_2H_4]^{2-} \cdots HCl$	2.1/2.2	19.4/17.9	11.6	2.037	1.333	0.039	179	2.1	-6.4	0.025	0.046	0.01	-3.4	9.14
[1,6] ( <i>trans</i> )	$[B_6Cl_2H_4]^{2-} \cdots HCl$	3.6	16.7	14.2	2.112	1.326	0.032	179	2.6	-6.0	0.022	0.044	0.30	-3.0	8.52
[1,2,3] ( <i>fac</i> )	$[B_6Cl_3H_3]^{2-} \cdots HCl$	2.1	17.4	13.3	2.058	1.330	0.036	179	2.2	-6.1	0.024	0.045	0.04	-3.2	8.81
[1,6,2] ( <i>mer</i> )	$[B_6Cl_3H_3]^{2-} \cdots HCl$	3.9/4.2	16.0/15.0	10.6	2.121	1.325	0.031	178	2.6	-5.9	0.022	0.044	0.32	-3.0	8.41
[1,2,3,4] ( <i>cis</i> )	$[B_6Cl_4H_2]^{2-} \cdots HCl$	4.8	13.8	10.4	2.133	1.323	0.029	178	2.7	-5.8	0.021	0.043	0.33	-2.9	8.23
[1,6,2,4] ( <i>trans</i> )	$[B_6Cl_4H_2]^{2-} \cdots HCl$	7.2	–	9.5	2.235	1.316	0.022	179	2.7	-5.5	0.018	0.040	0.55	-2.4	7.56
[1,2,3,4,6]	$[B_6Cl_5H]^{2-} \cdots HCl$	8.0	–	7.9	2.234	1.315	0.021	178	2.7	-5.5	0.018	0.039	0.52	-2.4	7.49

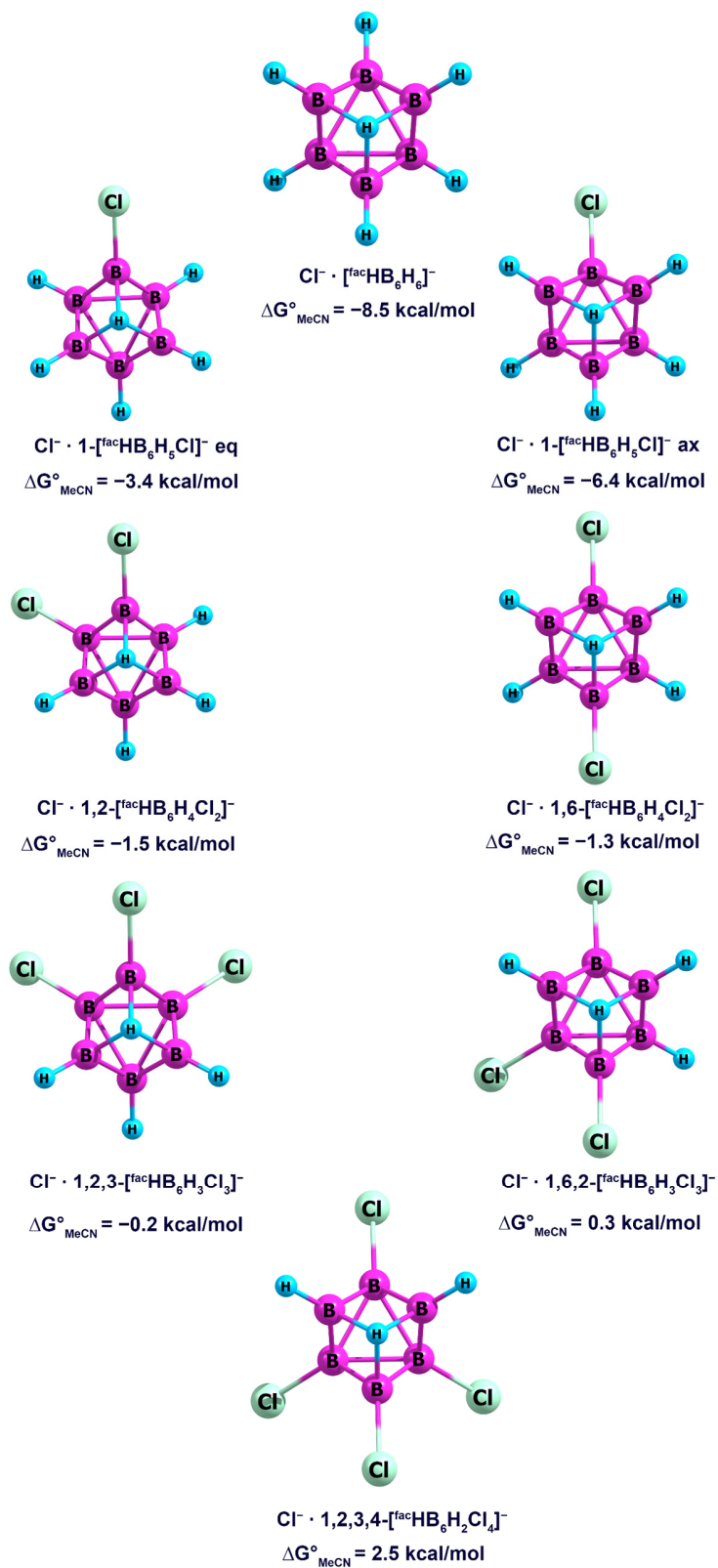
**Table S10.** M06-computed geometric (distances  $r_{(X-Y)}$  in Å, angles in degrees) parameters of hydrogen bonded complexes of  $Cl^- \cdot [^{fac}HB_6H_{(6-x)}Cl_x]^-$  ( $x = 0-5$ ) with HCl, their energy formation energy ( $\Delta G_f^{\circ MeCN}$  and  $\Delta H_f^{\circ MeCN}$  in kcal/mol), electron densities at the  $H \cdots B(B_2)$  bond (+3;-1) critical point ( $\rho_c$  in au), Laplacian of electron density at critical point ( $\nabla^2 \rho_c$  in au), bond ellipticity ( $\epsilon$ ) and energy of  $H \cdots B(B_2)$  interaction ( $E_{H \cdots B(B_2)} = 0.5 \cdot V(r)$  [1, 2] in kcal/mol).

N	HB3 complex	TS <sup>PT</sup> <sub>2nd</sub>	TS <sup>PT</sup> <sub>2nd(rev)</sub>	$r_{(H \cdots B_3)}$	$r_{(XH)}$	$\Delta r_{(XH)}$	$\angle_{XH \cdots B_3}$	$\Delta G_f^{\circ MeCN}$	$\Delta H_f^{\circ MeCN}$	$\rho_c$	$\nabla^2 \rho_c$	$\epsilon$	$E_{H \cdots B(B_2)}$
	$Cl^- \cdot [^{fac}HB_6H_6]^- \cdots HCl$	9.5	3.8	2.122	1.314	0.390	180	3.9	-4.1	0.020	0.044	0.01	-2.7
[1] ( <i>cis</i> )	$Cl^- \cdot [^{fac}HB_6ClH_5]^- \cdots HCl$	11.1	2.8	2.143	1.312	0.388	178	7.0	-1.2	0.019	0.043	0.03	-2.6
[1] ( <i>trans</i> )	$Cl^- \cdot [^{fac}HB_6ClH_5]^- \cdots HCl$	13.3	2.3	2.219	1.308	0.384	179	4.2	-3.8	0.017	0.040	0.29	-2.3
[1,2] ( <i>fac</i> )	$Cl^- \cdot [^{fac}HB_6Cl_2H_4]^{2-} \cdots HCl$	15.0	1.4	2.228	1.307	0.383	177	6.7	-3.6	0.017	0.039	0.34	-2.2
[1,2] ( <i>mer</i> )	$Cl^- \cdot [^{fac}HB_6Cl_2H_4]^{2-} \cdots HCl$	14.6	1.1	2.235	1.307	0.383	176	6.9	-3.5	0.017	0.040	0.33	-2.2
[1,6] ( <i>mer</i> )	$Cl^- \cdot [^{fac}HB_6Cl_2H_4]^{2-} \cdots HCl$	15.3	1.4	2.229	1.307	0.383	179	3.9	-3.6	0.017	0.039	0.25	-2.2
[1,2,3] ( <i>cis</i> )	$Cl^- \cdot [^{fac}HB_6Cl_3H_3]^{2-} \cdots HCl$	18.9	0.0	2.362	1.303	0.379	174	6.7	-3.1	0.014	0.035	1.08	-1.9
[1,6,2] ( <i>trans</i> )	$Cl^- \cdot [^{fac}HB_6Cl_3H_3]^{2-} \cdots HCl$	19.0	0.2	2.343	1.302	0.378	178	4.3	-3.2	0.014	0.034	0.57	-1.8
[1,2,3,4] ( <i>cis</i> )	$Cl^- \cdot [^{fac}HB_6Cl_4H_2]^{2-} \cdots HCl$	22.8	0.3	2.589	1.297	0.373	177	5.3	-2.6	0.008	0.022	0.10	-1.1
[1,6,2,4] ( <i>trans</i> )	$Cl^- \cdot [^{fac}HB_6Cl_4H_2]^{2-} \cdots HCl$	23.2	0.4	2.351	1.301	0.377	179	1.3	-6.2	0.014	0.034	0.55	-2.2
[1,2,3,4,6]	$Cl^- \cdot [^{fac}HB_6Cl_5H]^{2-} \cdots HCl$	23.0	0.0	2.745	1.296	0.372	175	5.3	-2.5	0.006	0.016	0.38	-0.8

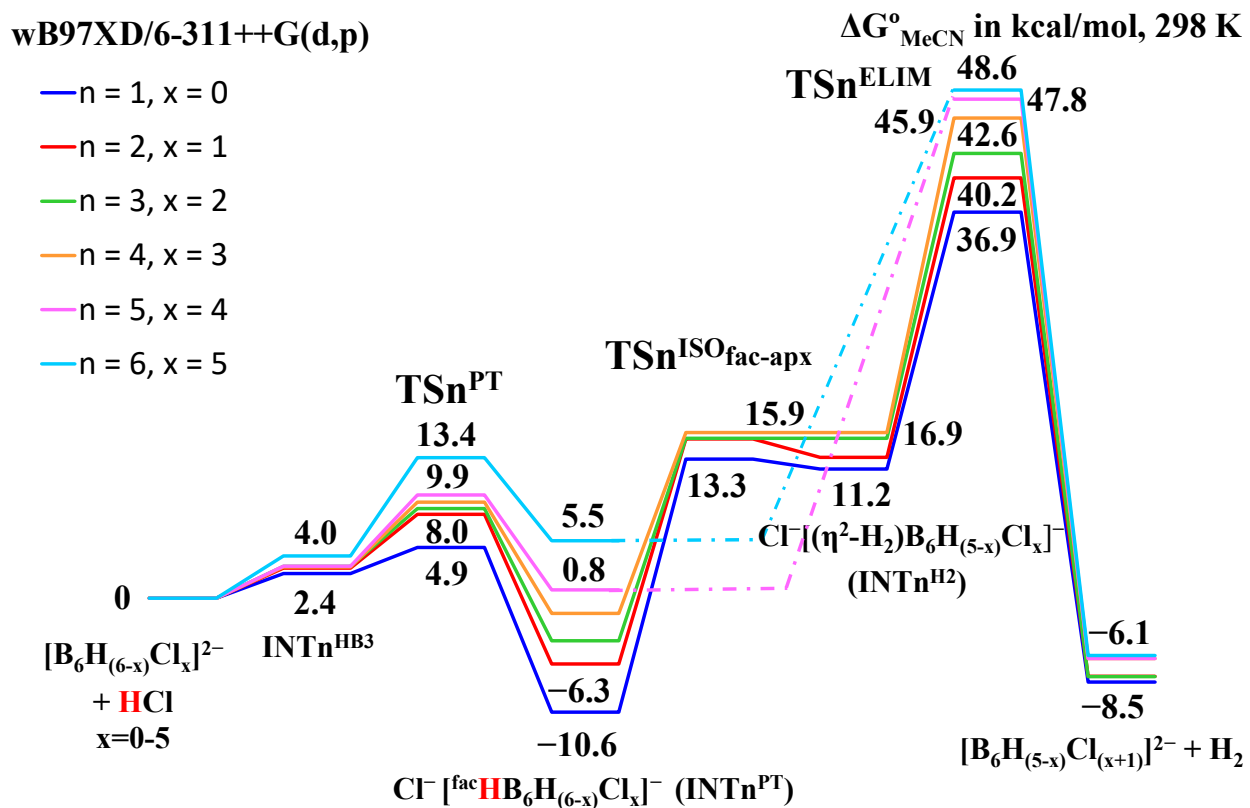
**Table S6.** M06-computed geometric parameters (distances  $r_{(X-Y)}$  in Å, angles in °) of H<sub>2</sub> complexes of Cl<sup>-</sup>[(H<sub>2</sub>)B<sub>6</sub>H<sub>(5-x)</sub>Cl<sub>x</sub>]<sup>-</sup> ( $x = 0-5$ ) (**INT<sup>H2</sup>**), their energy formation energy ( $\Delta G_f^{\circ MeCN}$  and  $\Delta H_f^{\circ MeCN}$  in kcal/mol), electron densities in (+3;-1) donation energy ( $E^2$  in kcal/mol) from  $\sigma(B-H/Cl)$  to  $\sigma^*(H-H-B)$  ( $E_1$ ), from  $\sigma(H-H-B)$  to  $\sigma^*(B-H/Cl)$  ( $E_2$ ) and from  $p(Cl)$  to  $\sigma^*(H-H-B)$  ( $E_3$ ) estimated from 2<sup>nd</sup>-order perturbative analysis of donor acceptor interactions within natural-bond orbital (NBO) analysis.

N	H <sub>2</sub> -complex	$r(H\cdots H)$	$r(B\cdots H1)$	$\Delta r(B\cdots H1)$	$r(B\cdots H_2)$	$r(B\cdots H2)$	$\Delta r(B\cdots H2)$	$r(H2\cdots X)$	$\Delta r(H2\cdots X)$	$\Delta G_f^{\circ MeCN}$	$\Delta H_f^{\circ MeCN}$	$E_1$	$E_2$	$E_3$	$E_{H2\cdots X}$	$E_{H\cdots H}$	$E_{B\cdots H}$
1	Cl <sup>-</sup> [(H <sub>2</sub> )B <sub>6</sub> H <sub>5</sub> ] <sup>-</sup>	0.910	1.269	0.069	1.222	1.338	0.138	2.206	0.912	11.2	3.1	15.7/6.6/5.9/4.8 4.5/4.3/3.7 3.1/2.1	2.0 1.9	19.5 1.9	-4.7	-56.9	-82.2
[1,2 ( <i>cis</i> )	Cl <sup>-</sup> [(H <sub>2</sub> )B <sub>6</sub> H <sub>4</sub> Cl] <sup>-</sup>	0.914	1.267	0.069	1.221	1.340	0.142	2.186	0.892	12.8	4.8	10.8/8.1/7.9/5.5 4.3/3.4/1.3/1.2 1.1/1.0/0.9	2.4/2.3 2.0/0.5	20.6 2.0	-4.9	-56.1	-82.4
1,6 ( <i>trans</i> )	Cl <sup>-</sup> [(H <sub>2</sub> )B <sub>6</sub> H <sub>4</sub> Cl] <sup>-</sup>	0.921	1.260	0.063	1.210	1.328	0.131	2.203	0.909	11.9	3.7	16.8/5.5/5.1 4.5/4.1/3.4 2.9/2.0/1.6	8.6/5.6 4.2/3.8 1.0	20.2 1.9	-4.7	-56.9	-82.2
1,2,3 ( <i>fac</i> )	Cl <sup>-</sup> [(H <sub>2</sub> )B <sub>6</sub> H <sub>3</sub> Cl <sub>2</sub> ] <sup>-</sup>	0.918	1.263	0.067	1.224	1.351	0.155	2.128	0.834	14.7	6.2	17.8/16.5/14.3/9.9/ 4.7/4.5/1.9/1.7 1.4/0.7/0.6	4.8/3.0/2.9	26.7 3.1	-5.9	-55.3	-82.6
1,2,6 ( <i>mer</i> )	Cl <sup>-</sup> [(H <sub>2</sub> )B <sub>6</sub> H <sub>3</sub> Cl <sub>2</sub> ] <sup>-</sup>	0.926	1.259	0.064	1.209	1.330	0.135	2.180	0.886	13.8	5.3	18.5/11.1/6.4 6.0/3.9/0.4/0.3	5.2/1.6/0.5	21.8 2.1	-5.0	-55.0	-84.6
1,6,2 ( <i>mer</i> )	Cl <sup>-</sup> [(H <sub>2</sub> )B <sub>6</sub> H <sub>3</sub> Cl <sub>2</sub> ] <sup>-</sup>	0.919	1.263	0.067	1.222	1.347	0.151	2.142	0.848	14.7	6.2	13.8/7.2/4.9 4.4/3.9/3.8 3.7/2.6/1.9/ 1.7/1.3	3.5/2.4 2.1/1.8	25.1 2.5	-5.7	-55.4	-82.7
1,2,3,4 ( <i>cis</i> )	Cl <sup>-</sup> [(H <sub>2</sub> )B <sub>6</sub> H <sub>2</sub> Cl <sub>3</sub> ] <sup>-</sup>	0.928	1.256	0.063	1.214	1.342	0.149	2.122	0.828	15.5	7.1	30.8/8.1/ 6.3/5.6/4.6 4.1/3.8/3/7	5.3/3.1/1.1	26.5 2.6	-6.0	-54.3	-84.6
1,6,2,3 ( <i>cis</i> )	Cl <sup>-</sup> [(H <sub>2</sub> )B <sub>6</sub> H <sub>2</sub> Cl <sub>3</sub> ] <sup>-</sup>	0.923	1.259	0.065	1.228	1.362	0.168	2.073	0.779	15.3	6.9	15.6/7.0/6.1 5.2/5.0/2.0/1.4	4.1/3.7/1.6	33.2 3.3	-7.1	-54.3	-83.0
1,6,2,4 ( <i>trans</i> )	Cl <sup>-</sup> [(H <sub>2</sub> )B <sub>6</sub> H <sub>2</sub> Cl <sub>3</sub> ] <sup>-</sup>	0.931	1.256	0.062	1.211	1.337	0.143	2.140	0.846	16.2	7.6	18.1/6.2/5.5/3.9 1.3/1.0	3.2/1.7/1.6 1.3/1.0	24.9 2.5	-5.7	-54.2	-84.8
1,2,3,4,6	Cl <sup>-</sup> [(H <sub>2</sub> )B <sub>6</sub> HCl <sub>4</sub> ] <sup>-</sup>	0.935	1.252	0.060	1.218	1.355	0.163	2.064	0.770	16.9	8.4	22.1/21.0/20.1 19.4/17.1/12.6 10.1/9.7/8.3/7.5	–	40.2 30.1 5.35	-7.3	-53.1	-84.8

**Figure S6.** M06-optimized geometries of the protonated forms  $[\text{facHB}_6\text{H}_{(6-x)}\text{Cl}_x]^-$  ( $x = 0-4$ ) and their free Gibbs formation energies ( $\Delta G_f^{\circ\text{MeCN}}$  in kcal/mol).



**Figure S7.** wB97XD-calculated energy profile of halogenation of  $[\text{B}_6\text{H}_{(6-x)}\text{Cl}_x]^{2-}$  ( $x = 0-5$ ) by HCl for the pathway:  $[\text{B}_6\text{H}_6]^{2-} \rightarrow 1-[\text{B}_6\text{H}_5\text{Cl}]^{2-} \rightarrow 1,2-[\text{B}_6\text{H}_4\text{Cl}_2]^{2-}$  (*cis*)  $\rightarrow 1,2,3-[\text{B}_6\text{H}_3\text{Cl}_3]^{2-}$  (*fac*)  $\rightarrow 1,2,3,4-[\text{B}_6\text{H}_2\text{Cl}_4]^{2-}$  (*cis*)  $\rightarrow 1,2,3,4,6-[\text{B}_6\text{HCl}_5]^{2-}$ .



**Table S12.** Activation barriers ( $\Delta G^{\circ}_{\text{MeCN}}^{\ddagger}$ , in kcal/mol) for TSs for the reaction of  $[\text{B}_6\text{H}_6]^{2-}$  with  $\text{HCl}$  ( $\text{pK}_a^{\text{MeCN}} = 10.3$ )[42] in MeCN computed at the wB97XD/6-311++G(d,p) theory level.

<b>n</b>	<b>N of position</b>	$\Delta G^{\circ}_{\text{MeCN}}^{\ddagger}$ ( <b>TSn<sup>PT</sup></b> ), <sup>a</sup>	$\Delta G^{\circ}_{\text{MeCN}}^{\ddagger}$ ( <b>TSn<sup>ISOfac-apx</sup></b> ), <sup>b</sup>	$\Delta G^{\circ}_{\text{MeCN}}^{\ddagger}$ ( <b>TSn<sup>ELIM</sup></b> ), <sup>c</sup>	$\Delta G^{\circ}_{\text{MeCN}}^{\ddagger}$ (span), <sup>d</sup>
1	<b>1</b>	2.5	24.2	24.6	47.8
2	1,2 ( <i>cis</i> )	3.1	21.9	29.5	46.5
	1,6 ( <i>trans</i> )	5.1	21.5	26.7	51.2
3	1,2,3 ( <i>fac</i> )	5.5	19.4	27.2	46.6
	1,2,6 ( <i>mer</i> )	5.5	19.1	30.1	48.3
	1,6,2 ( <i>mer</i> )	6.4	19.7	28.0	47.7
4	1,2,3,4 ( <i>cis</i> )	6.2	17.3	30.1	47.4
	1,6,2,3 ( <i>cis</i> )	6.0	16.9	30.5	47.4
	1,6,2,4 ( <i>trans</i> )	6.0	41.8*		46.4
5	1,2,3,4,6	6.8	44.7*		47.8
	1,6,2,4,3	9.2	42.3*		46.0
6	1,2,3,4,6,5	9.4	44.6*		48.6

<sup>a</sup> Calculated as  $\Delta G^{\circ}_{\text{MeCN}}^{\ddagger}(\text{TSn}^{\text{PT}}) = G^{\circ}_{\text{MeCN}}(\text{TSn}^{\text{PT}}) - G^{\circ}_{\text{MeCN}}(\text{INTn}^{\text{HB3}})$ ; <sup>b</sup> Calculated as  $\Delta G^{\circ}_{\text{MeCN}}^{\ddagger}(\text{TSn}^{\text{ISOfac-apx}}) = G^{\circ}_{\text{MeCN}}(\text{TSn}^{\text{ISOfac-apx}}) - G^{\circ}_{\text{MeCN}}(\text{INTn}^{\text{PT}})$ ; <sup>c</sup> Calculated as  $\Delta G^{\circ}_{\text{MeCN}}^{\ddagger}(\text{TSn}^{\text{ELIM}}) = G^{\circ}_{\text{MeCN}}(\text{TSn}^{\text{ELIM}}) - G^{\circ}_{\text{MeCN}}(\text{INTn}^{\text{H2}})$ ; <sup>d</sup> Calculated as  $\Delta G^{\circ}_{\text{MeCN}}^{\ddagger}(\text{span}) = G^{\circ}_{\text{MeCN}}(\text{TSn}^{\text{ELIM}}) - G^{\circ}_{\text{MeCN}}(\text{INTn}^{\text{H2}})$  for  $n=1-4$  and as  $\Delta G^{\circ}_{\text{MeCN}}^{\ddagger}(\text{span}) = G^{\circ}_{\text{MeCN}}(\text{TSn}^{\text{ELIM}}) - G^{\circ}_{\text{MeCN}}([\text{B}_6\text{H}_{(6-x)}\text{Cl}_x]^{2-}) - G^{\circ}_{\text{MeCN}}(\text{HCl})$  for  $n=5-6$ ; \* **TSn<sup>CONC</sup>** for 5<sup>th</sup> and 6<sup>th</sup> halogenation steps.

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