Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Consecutive Methane Activation Mediated by Single Metal Boride Cluster Anions NbB_4^-

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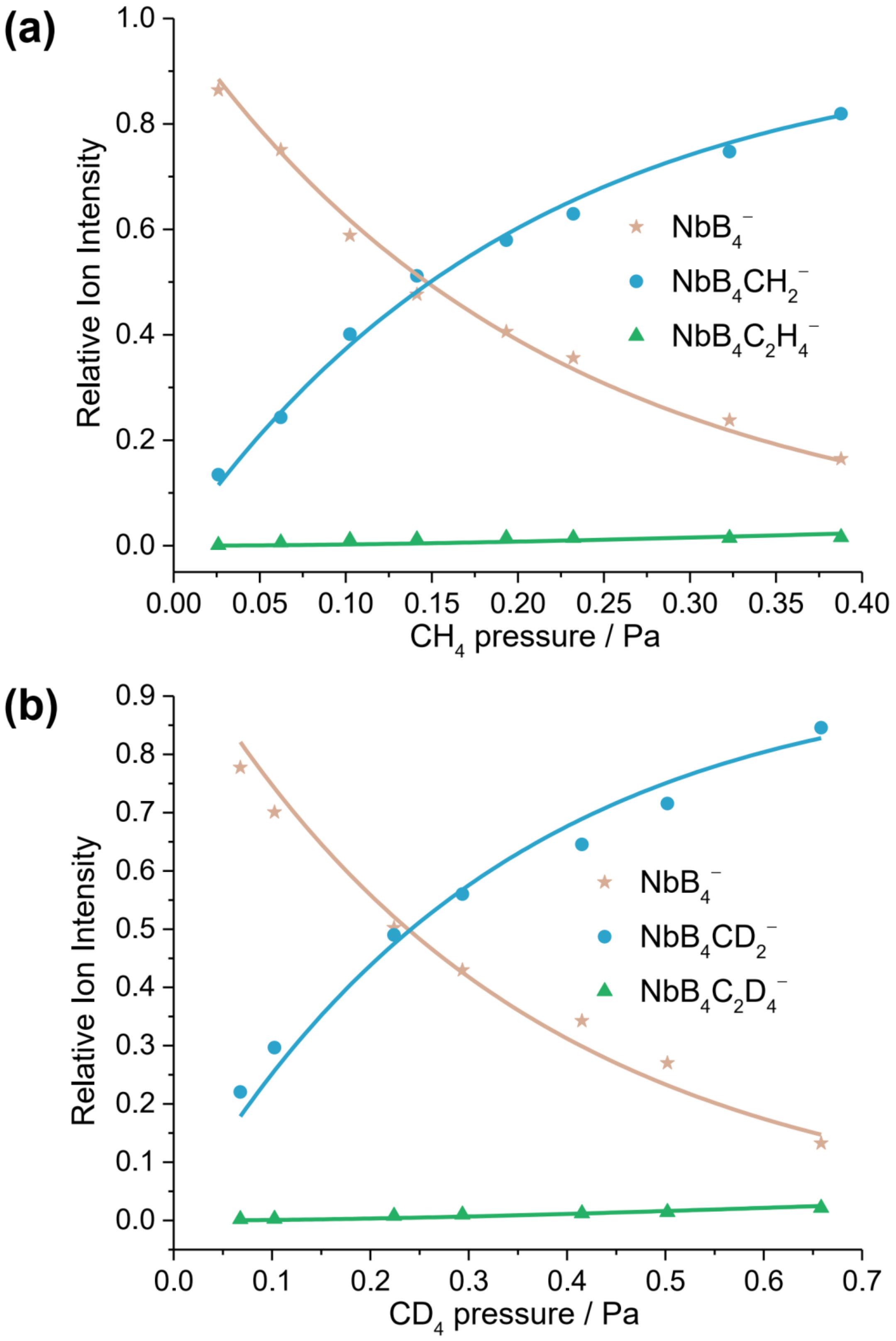

Fig. S1 Variations of relative ion intensities of the reactant and product anions in the reactions of (a) NbB_4^- and CH_4 with respect to the CH_4 pressures for 6.6 ms and (b) NbB_4^- and CD_4 with respect to the CD_4 pressures for 8.6 ms. The solid lines are fitted to the experimental data points by using the equations derived with the approximation of the pseudo-first-order reaction mechanism.

Table S1. DFT-calculated and experimental bond dissociation energies. The values are in unit of eV.

Method	EXP.	Nb–C	B–C	B–H	C–H	Nb–H	H–H	*A.D.*[1]
		5.43 ±0.15	4.64 ±0.30	3.58 ±0.03	3.51 ±0.001	2.29 ±0.09	4.52	
References		1	2	3	4	5	6	
Hybrid Functionals	B1B95	4.85	4.50	3.39	3.31	2.56	4.38	-0.16
	B1LYP	4.86	4.26	3.42	3.38	2.74	4.44	-0.15
	B3LYP	5.09	4.40	3.47	3.44	2.77	4.50	-0.05
	B3P86	5.19	4.68	3.54	3.54	2.74	4.58	0.05
	B3PW91	4.67	4.60	3.39	3.37	2.55	4.37	-0.17
	M05	6.21	4.50	3.44	3.40	2.37	4.42	0.06
	M052X	3.92	4.42	3.46	3.33	2.47	4.40	-0.33
	PBE1PBE	4.92	4.64	3.33	3.33	2.51	4.25	-0.17
	X3LYP	5.08	4.40	3.47	3.43	2.78	4.47	-0.06
	M06	5.98	4.52	3.53	3.39	2.51	4.38	0.06
	M062X	4.52	4.67	3.49	3.34	2.82	4.41	-0.12
	BH&HLYP	4.21	3.99	3.40	3.31	2.69	4.38	-0.33
	BMK	4.47	4.49	3.45	3.35	2.33	4.36	-0.25
Pure Functionals	**M06L**	**5.70**	**4.84**	**3.39**	**3.32**	**2.64**	**4.22**	**0.02**
	BLYP	5.59	4.58	3.44	3.46	2.82	4.31	0.04
	BP86	5.66	4.85	3.51	3.56	2.80	4.56	0.16
	BPBE	5.20	4.84	3.33	3.37	2.54	4.56	-0.02
	BPW91	5.39	4.83	3.35	3.38	2.55	4.31	-0.03
	PBE	5.67	4.97	3.37	3.42	2.61	4.27	0.06
	TPSS	5.32	4.64	3.50	3.53	2.84	4.62	0.08

[1]: $A.D. = \frac{\sum(x_i - x_{\mathrm{exp}})}{n}$, x_{i} is the DFT calculated bond dissociation energy and x_{exp} is the experimental value.

The Rice-Ramsperger-Kassel-Marcus theory (RRKM)[7] was used to calculate the rate constant of traversing transition states from intermediates. For these calculations, the energy (E) of the reaction intermediate and the energy barrier ($E^{‡}$) for each step were needed. The reaction intermediate possesses the vibrational energies (E_{vib}) of $^{1}NbB_4^{-}$, $^{3}NbB_4CH_2^{-}$ and CH_4, the center of mass kinetic energy (E_{k}), and the binding energy (E_{b}) which is the energy difference between the separated reactants ($^{1}NbB_4^{-}/CH_4$ and $^{3}NbB_4CH_2^{-}/CH_4$) and the reaction complexes. The values of E_{vib} and E_{b} were taken from the DFT calculations and $E_{\mathrm{k}} = \mu v^2/2$, in which μ is the reduced mass (14.3 and 14.5, respectively), and v is the velocity (≈ 733 m/s and 672 m/s, respectively). The densities and the numbers of states required for RRKM calculations were obtained by the direct count method[8,9] with the DFT calculated vibrational frequencies under the approximation of harmonic vibrations. According to the DFT calculated energies, the rates of internal conversion ($k_{\mathrm{conversion}}$) for processes of ^{1}**I9**→^{1}**TS9** in Reaction 1 and ^{1}**I19**→^{1}**TS19** in Reaction 2 are 4.5×10^{6} s^{-1} and 8.1×10^{6} s^{-1}, respectively.

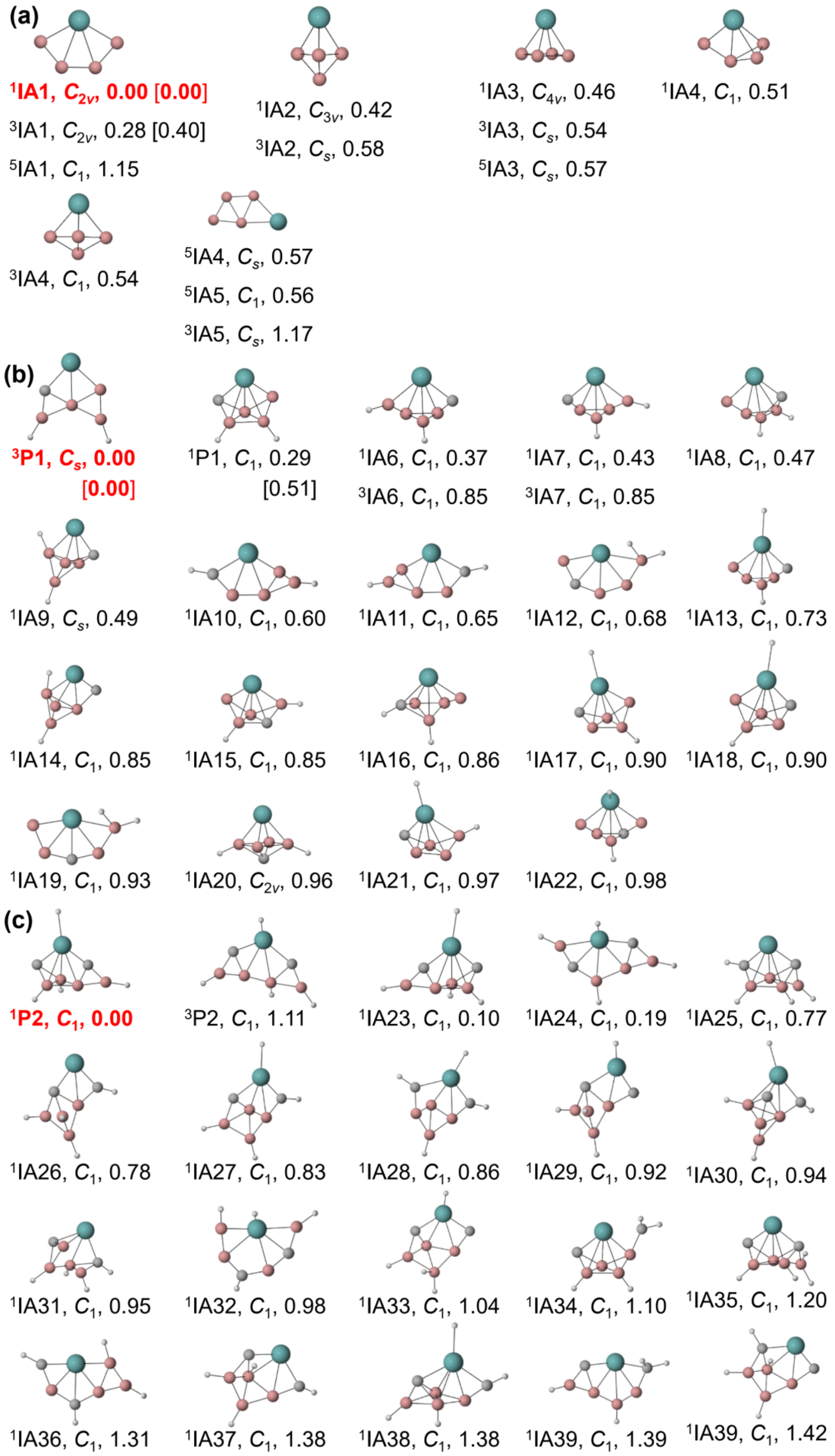

Fig. S2 DFT-calculated structures and relative energies of (a) NbB_4^-, (b) $NbB_4CH_2^-$ and (c) $NbB_4C_2H_4^-$. The zero-point vibration corrected energies (ΔH_{0K} in eV) of each structure are given. The superscripts indicate the spin multiplicities. The high-level CCSD(T) calculated energies for **IA1** and **P1** are given in square brackets.

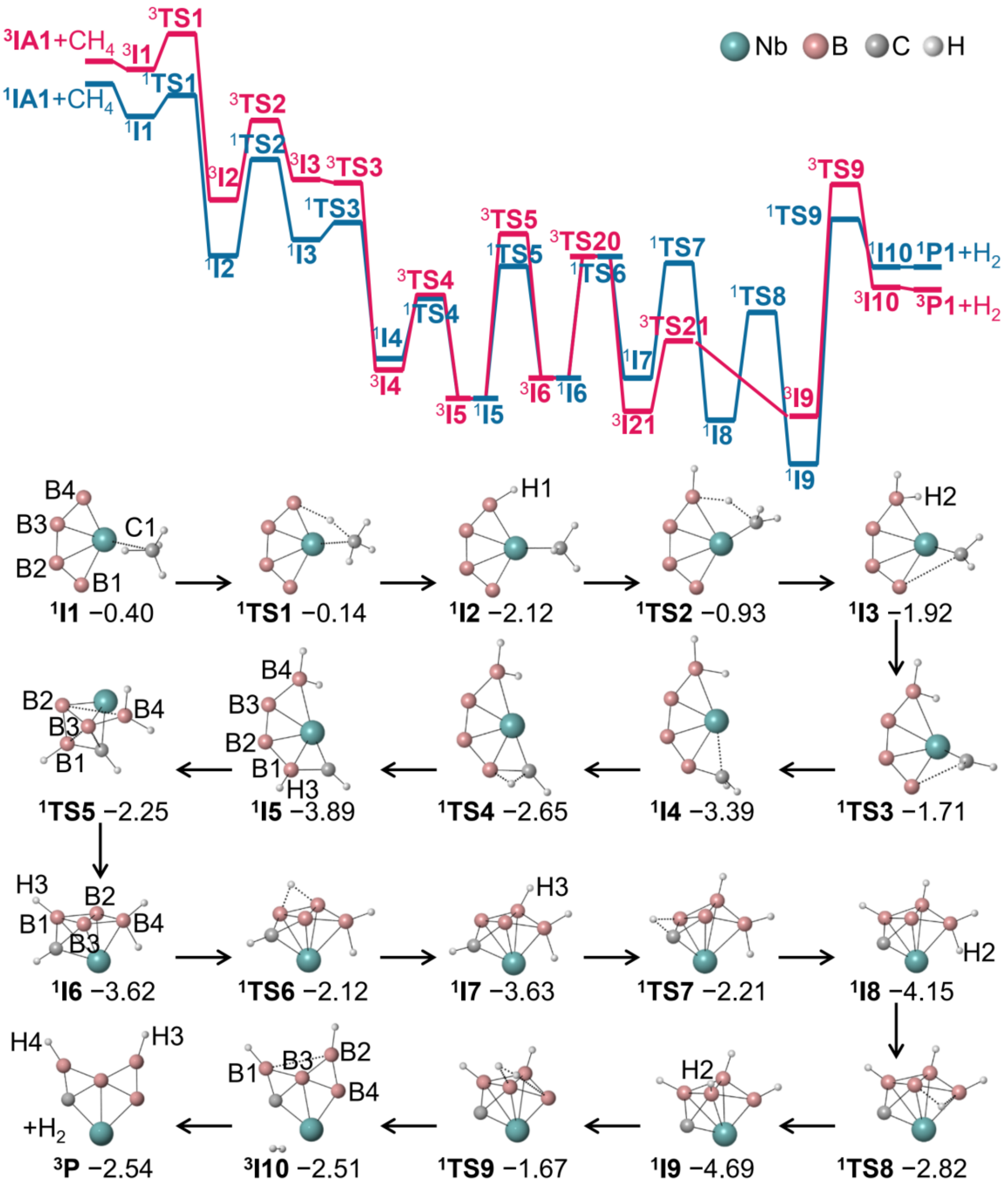

Fig. S3 DFT-calculated potential energy surfaces for the reaction of NbB_4^- with CH_4. The zero-point vibration-corrected energies (ΔH_{0K} in eV) of the reaction intermediates, transition states, and products with respect to the separated reactants are given. The superscripts indicate the spin multiplicities.

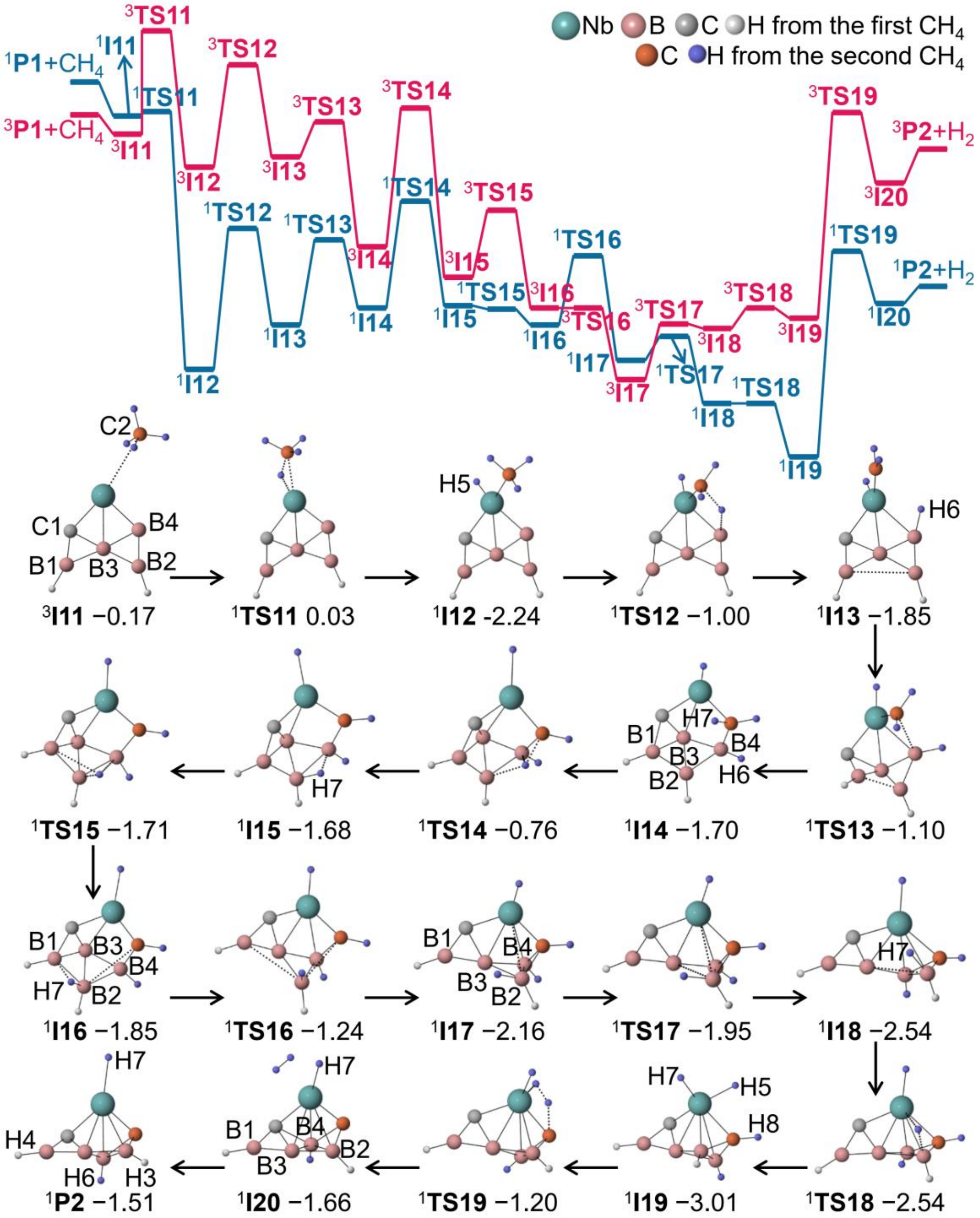

Fig. S4 DFT-calculated potential energy surface for the reaction of $NbB_4CH_2^-$ with CH_4. The zero-point vibration-corrected energies (ΔH_{0K} in eV) of the reaction intermediates, transition states, and products with respect to the separated reactants are given. The superscripts indicate the spin multiplicities.

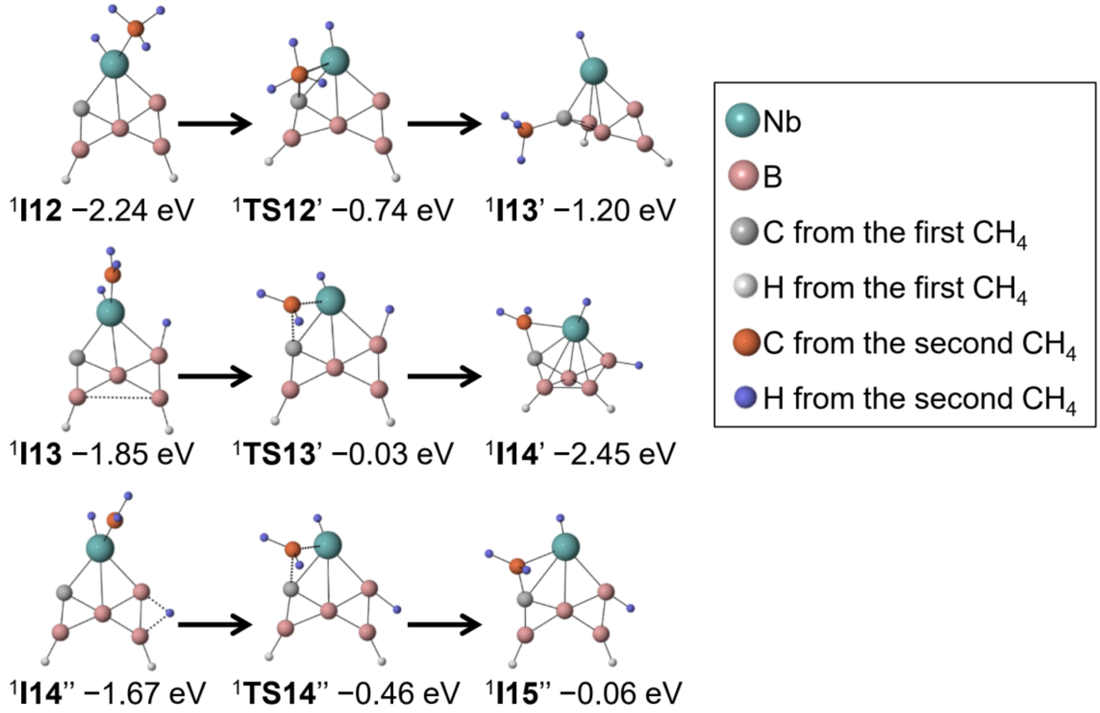

Fig. S5 DFT-calculated pathways for C−C coupling process.

Table S2. Natural charges on all atoms of reactants and products in the reactions of NbB_4^- and $NbB_4CH_2^-$ with CH_4.

	^{1}**IA1** + CH_4	^{3}**P1** + H_2	^{3}**P1** + CH_4	^{1}**P2** + H_2
Nb	0.53	0.38	0.38	0.99
B1	−0.43	0.22	0.22	0.22
B2	−0.34	−0.04	−0.04	−0.19
B3	−0.34	−0.27	−0.27	−0.20
B4	−0.43	−0.40	−0.40	−0.02
C1	−0.79	−0.74	−0.74	−0.68
C2	–	–	−0.79	−0.52
H1	0.20	0.00	–	–
H2	0.20	0.00	–	–
H3	0.20	−0.08	−0.08	−0.01
H4	0.20	−0.06	−0.06	−0.08
H5	–	–	0.20	0.00
H6	–	–	0.20	−0.01
H7	–	–	0.20	−0.49
H8	–	–	0.20	0.00

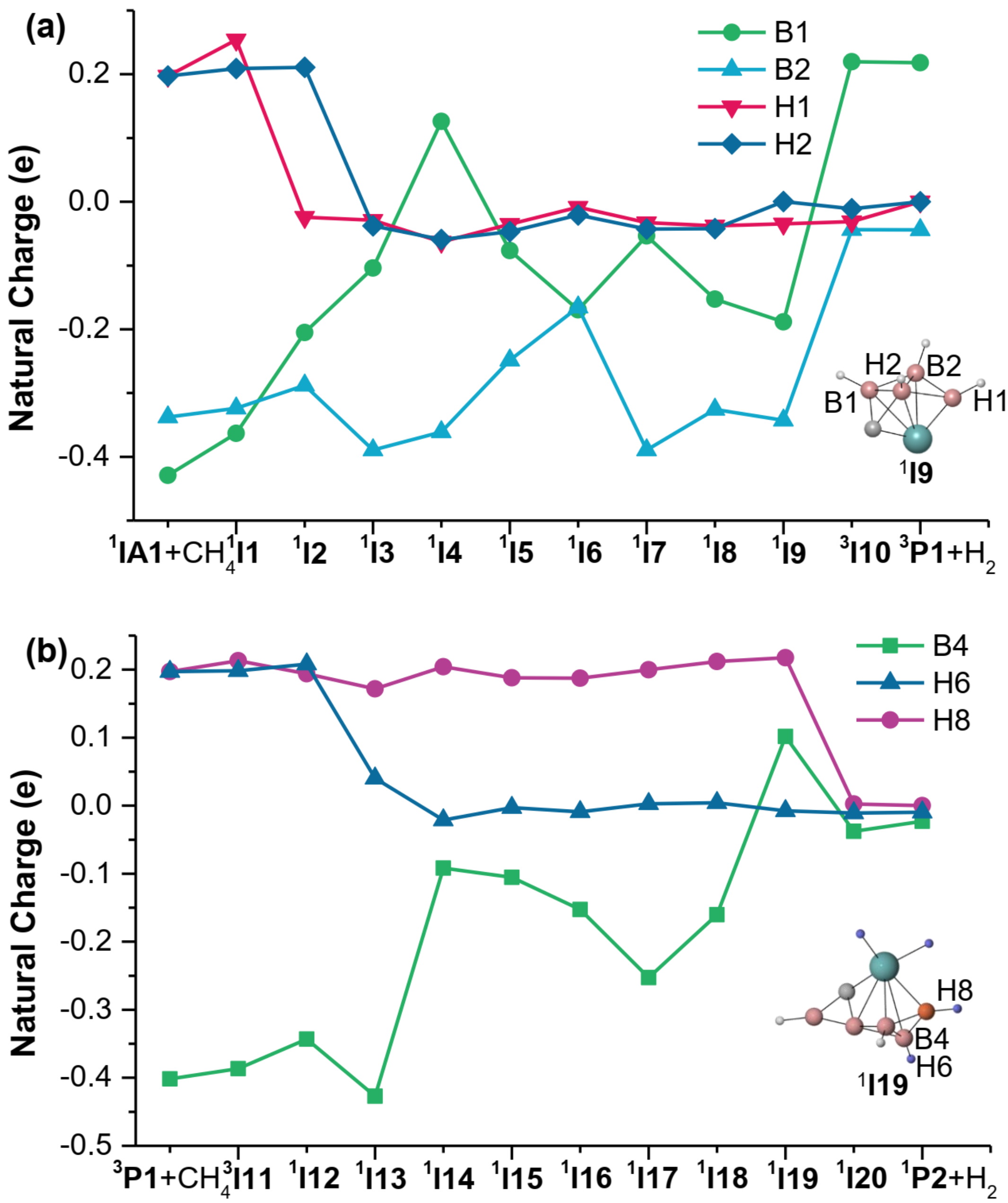

Fig. S6 Natural charges of the Nb and H atoms of the reactions (a) NbB_4^- + CH_4 and (b) $NbB_4CH_2^-$ + CH_4 along with the reaction coordinates.

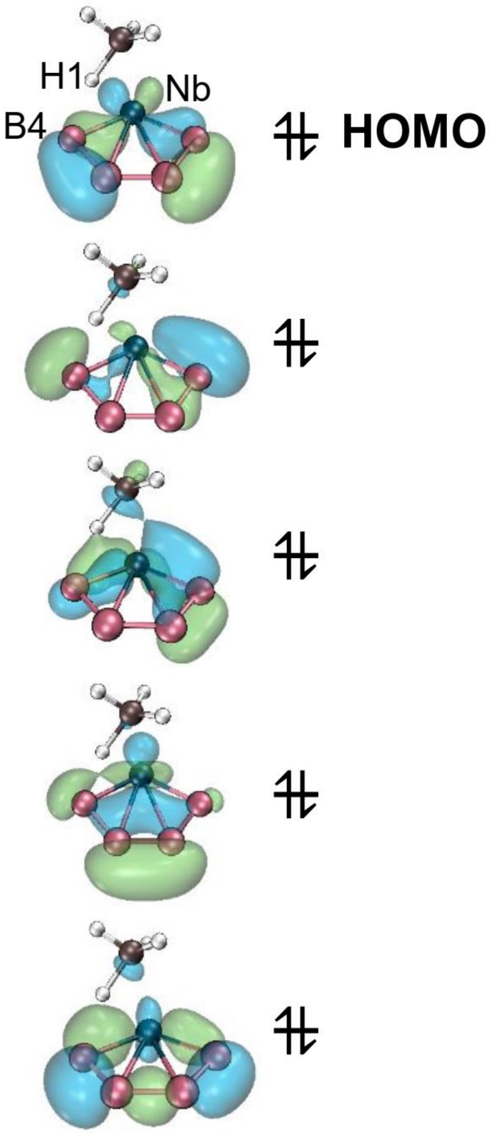

Fig. S7 Schematic molecular orbital diagrams for ^{1}**TS1**. Only representative orbitals are shown for the transition state.

In the process of activating the first methane, the significant stabilizing interactions of the ^{1}**TS1** reflect the reaction barriers (25.1 kJ mol^{-1}) well below the corresponding deformation energies (117.3 kJ mol^{-1}). The detailed molecular orbitals are shown in **Figure S7**. These two assignments point to the PCET process.[10,11]

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