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

Nitrogen Adsorption on $Nb_2C_6H_4^+$ Cations: The Important Role of Benzyne (*Ortho*-C_6H_4)

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Table S1. DFT-calculated and experimental bond dissociation energies.

Method \ Exp		Nb–Nb	Nb–C	Nb–N	N≡N	C–C	C–H	C≡N	H–H	N–H	MSE	RMSE	MAE
		5.22	5.62	6.56	9.76	6.21	3.46	7.76	4.48	3.47			
References		1	2	3	4	4	4	4	5	4			
Hybrid Functionals	**B1B95**	3.67	5.04	5.92	9.44	6.01	3.35	7.42	4.38	3.35	0.43	0.66	0.50
	B1LYP	3.69	4.85	5.99	9.33	5.77	3.43	7.25	4.44	3.49	0.49	0.70	0.54
	B3LYP	4.05	5.09	6.25	9.60	5.98	3.49	7.51	4.50	3.56	0.24	0.49	0.35
	B3P86	3.89	5.02	6.26	9.78	6.24	3.59	7.74	4.57	3.66	0.29	0.53	0.34
	B3PW91	3.43	5.16	5.91	9.43	6.08	3.42	7.49	4.37	3.46	0.51	0.71	0.47
	M05	5.99	6.41	6.92	9.36	6.11	3.45	7.54	4.41	3.41	0.20	0.44	0.35
	M052X	4.48	5.44	6.14	9.46	5.82	3.38	7.24	4.36	3.37	0.16	0.40	0.36
	PBE0	3.32	4.87	5.85	9.42	6.10	3.38	7.48	4.25	3.43	0.62	0.79	0.56
	X3LYP	4.03	5.09	6.23	9.58	5.97	3.48	7.49	4.47	3.55	0.25	0.50	0.36
	M06	5.92	6.10	6.53	9.27	6.04	3.43	7.48	4.38	3.33	0.14	0.37	0.30
	M062X	4.39	5.64	6.25	9.44	5.91	3.38	7.38	4.40	3.34	0.14	0.38	0.30
	BHANDHLYP	2.42	4.11	5.12	8.63	5.08	3.36	6.55	4.42	3.34	2.03	1.43	1.19
	BMK	3.74	5.11	6.49	9.49	5.77	3.40	7.40	4.37	3.45	0.35	0.60	0.42
Pure Functionals	**M06L**	**5.39**	**6.05**	**6.70**	**9.41**	**6.34**	**3.37**	**7.76**	**4.21**	**3.33**	**0.06**	**0.24**	**0.22**
	BLYP	5.19	5.66	6.94	10.09	6.35	3.50	8.04	4.47	3.63	0.04	0.22	0.18
	BPW91	4.42	5.43	6.55	9.95	6.50	3.43	8.05	4.31	3.53	0.11	0.34	0.25
	BP86	5.00	5.70	6.92	10.25	6.61	3.61	8.25	4.56	3.74	0.12	0.34	0.32
	BPBE	4.43	5.44	6.55	9.95	6.51	3.41	8.05	4.29	3.52	0.11	0.34	0.25
	PBE	4.88	5.72	6.85	10.24	6.72	3.47	8.31	4.27	3.59	0.13	0.36	0.32
	TPSS	4.47	5.35	6.45	9.53	6.20	3.57	7.66	4.62	3.65	0.10	0.31	0.24

MSE, RMSE and MAE represents mean square error, root mean square error and mean absolute error, respectively. Unit: eV

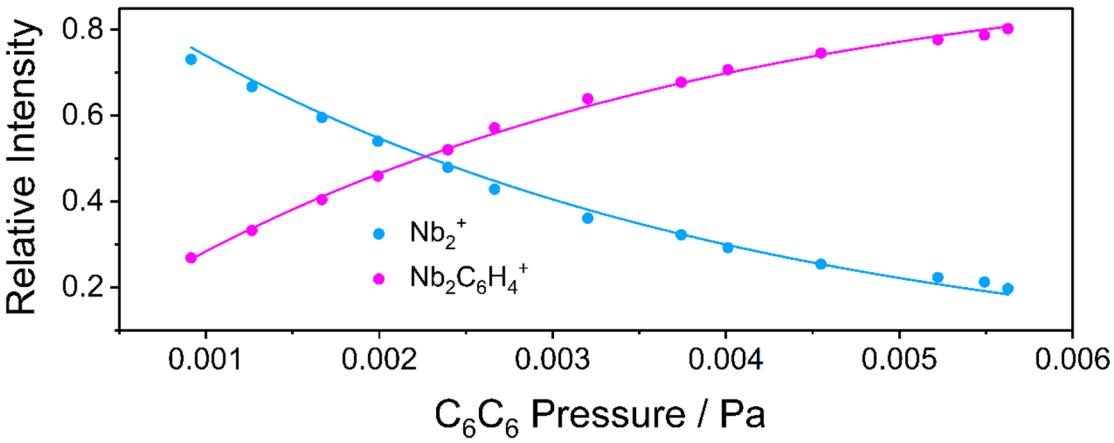

Fig. S1 Variations of the relative intensities of the reactant and product cations in the reactions of Nb_2^+ with C_6H_6 relative to the C_6H_6 pressures for 5 ms. The solid lines are fitted to the experimental data points by using the equations derived from the approximation of the pseudo-first-order reaction mode.

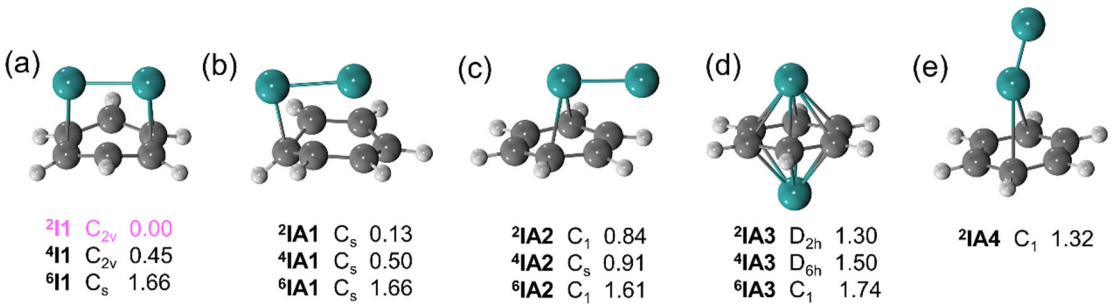

Fig. S2 DFT-calculated structures and relative energies of Nb_2^+ cluster on C_6H_6. The lowest-energy isomers of $Nb_2C_6H_6^+$ are marked with a magenta color. The point group of each structure is also given, and the superscripts indicate the spin multiplicities. The zero-point vibration corrected energies (ΔH_{0K} in eV) of each structure are given.

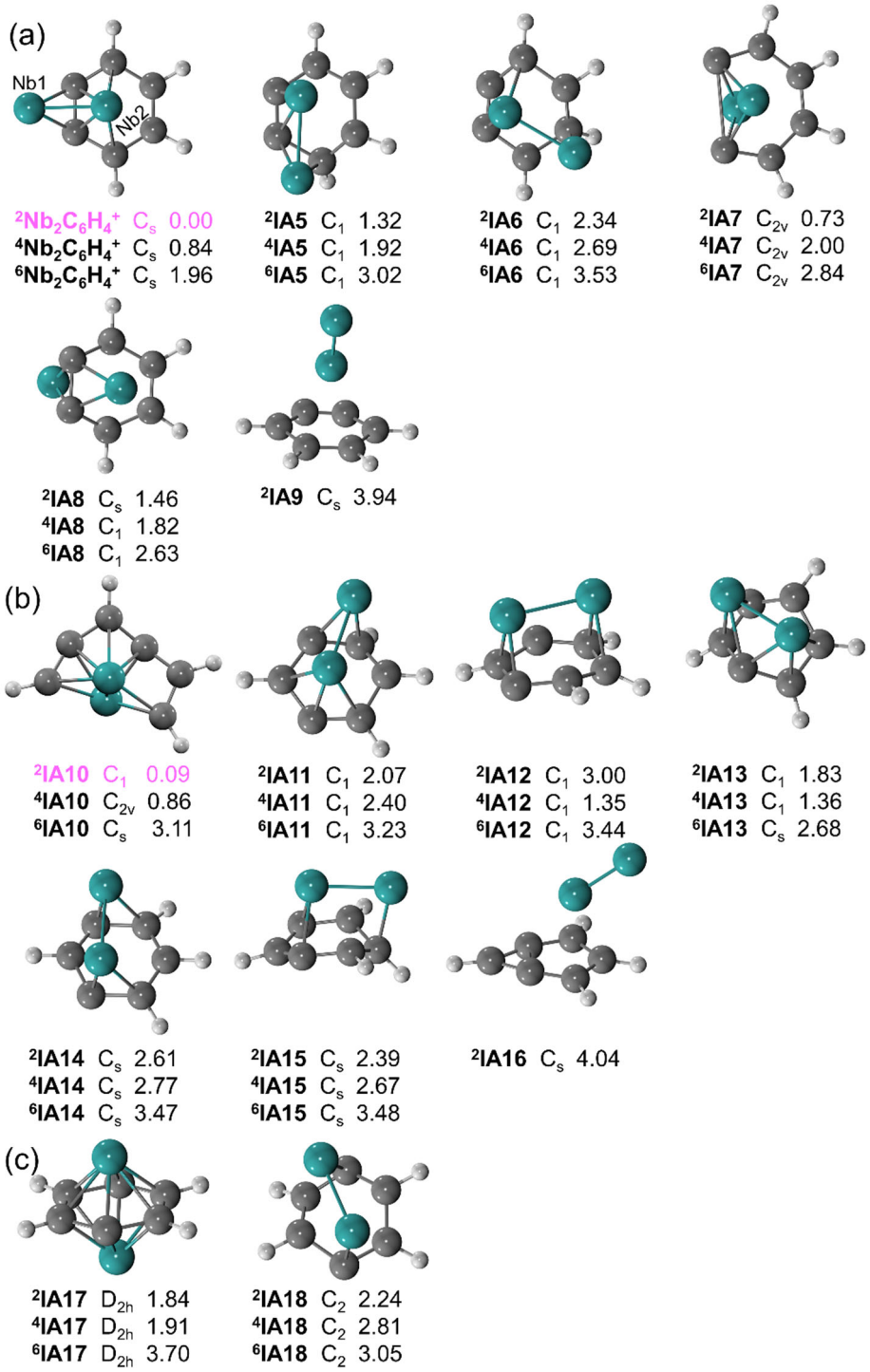

Fig. S3 DFT-calculated structures and relative energies of $Nb_2C_6H_4^+$. The two lowest-energy isomers of $Nb_2C_6H_4^+$ are marked with a magenta color. C_6H_4 is designed with three types: (a) *ortho*-, (b) *meta*-, and (c) *para*-sites, respectively. Various adsorption modes of Nb_2^+ are considered in each C_6H_4 type. The point group of each structure is

given, and the superscripts indicate the spin multiplicities. The zero-point vibration corrected energies (ΔH_{0K} in eV) of each structure are given.

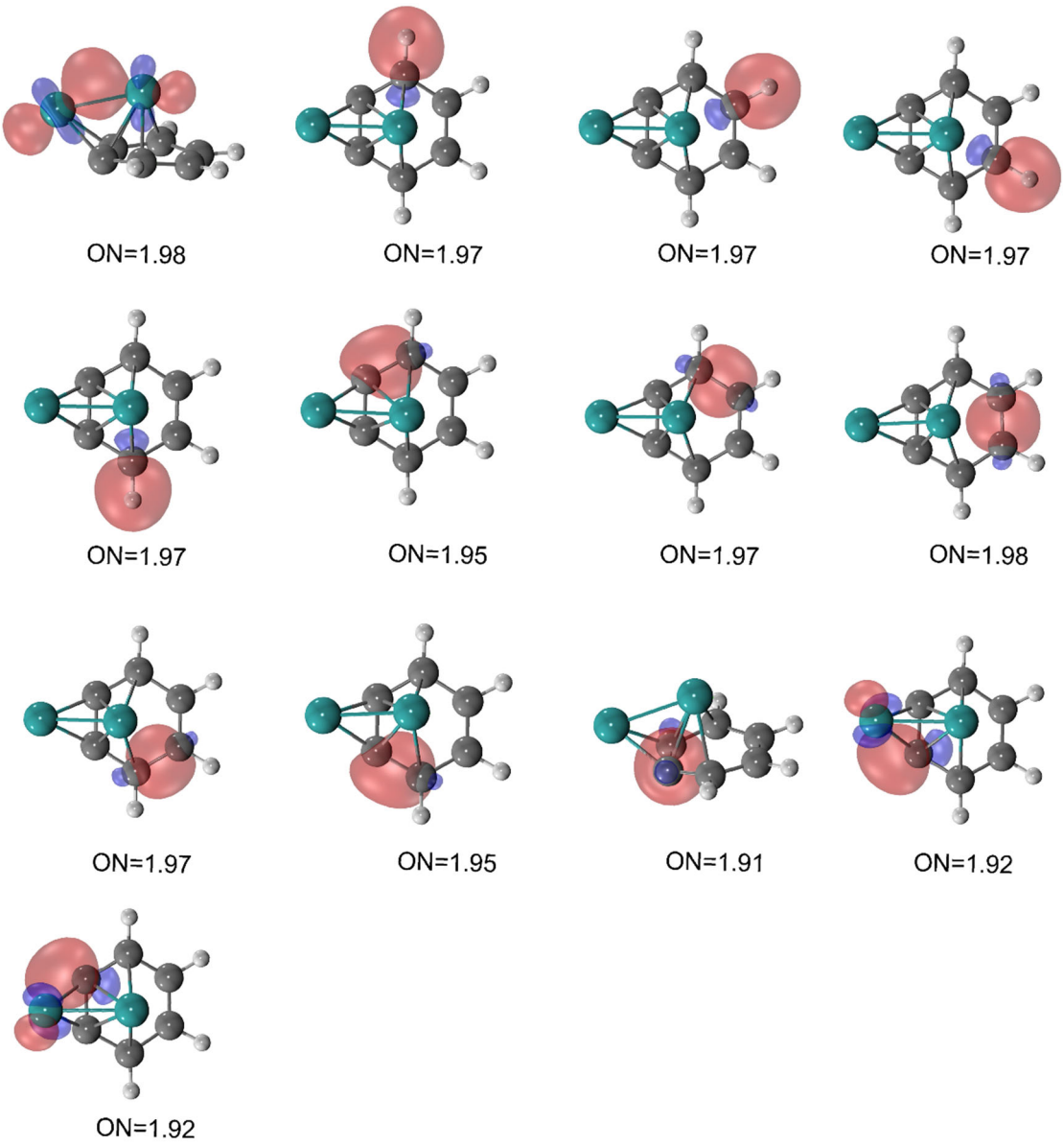

Fig. S4 Adaptive natural density partitioning (AdNDP) bonding analysis for two-center two electron (2c–2e) bonds in $Nb_2C_6H_4^+$ cluster. ON stands for the occupation number. The red and blue colors represent the positive value and negative value, respectively.

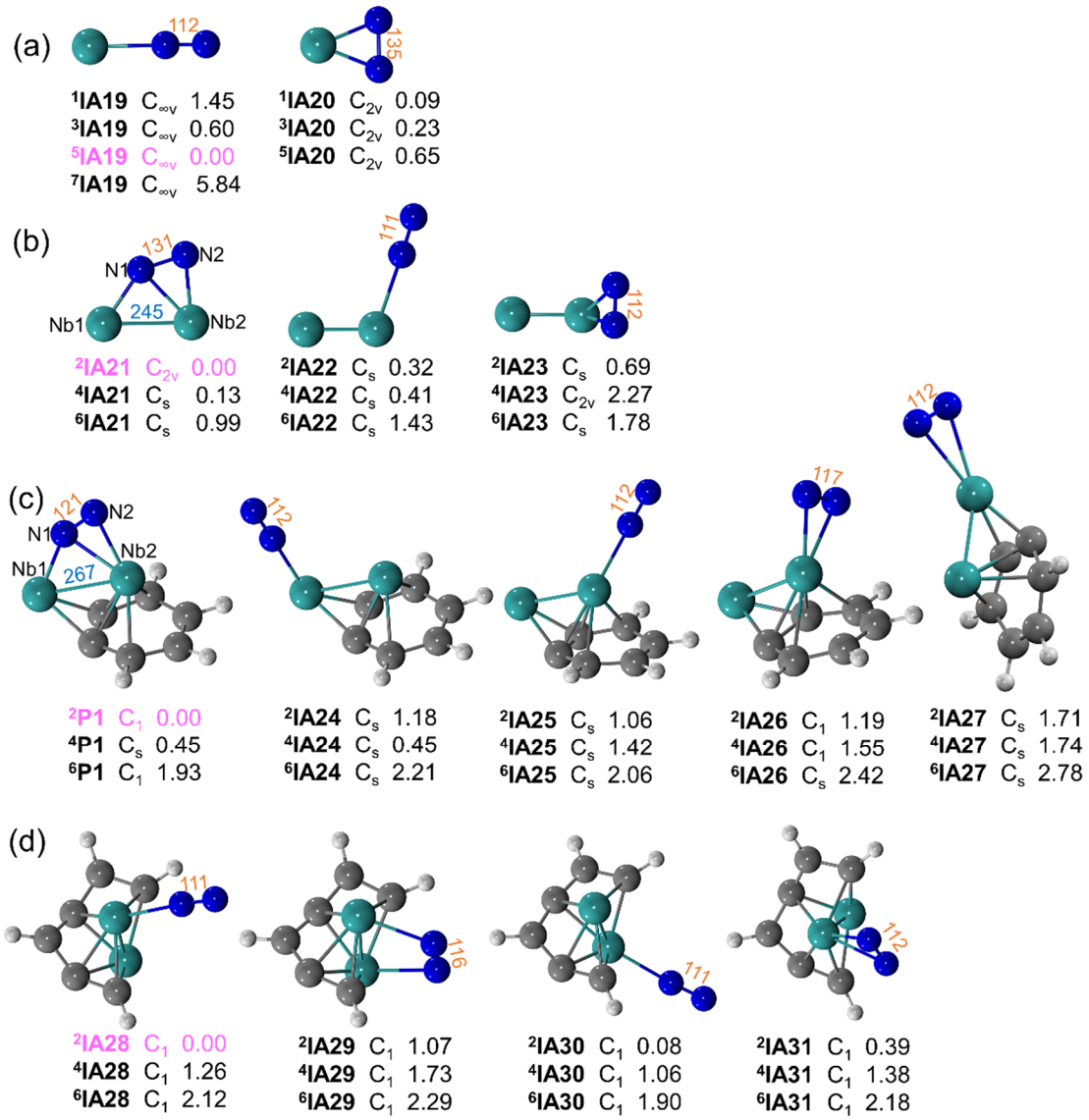

Fig. S5 DFT-calculated structures and relative energies of (a) NbN_2^+, (b) $Nb_2N_2^+$, and (c) (d) $Nb_2C_6H_4N_2^+$. The lowest-energy structure in each type is marked with a magenta color. Two isomers of $Nb_2C_6H_4N_2^+$ is considered in (c) and (d). Note that there is a significantly larger N_2 adsorption energy (1.20 eV) in **P1** compared to **IA28**. The point group and N_2 bond length are given in each structure, the superscripts indicate the spin multiplicities. The zero-point vibration corrected energies (ΔH_{0K} in eV) of each structure are given.

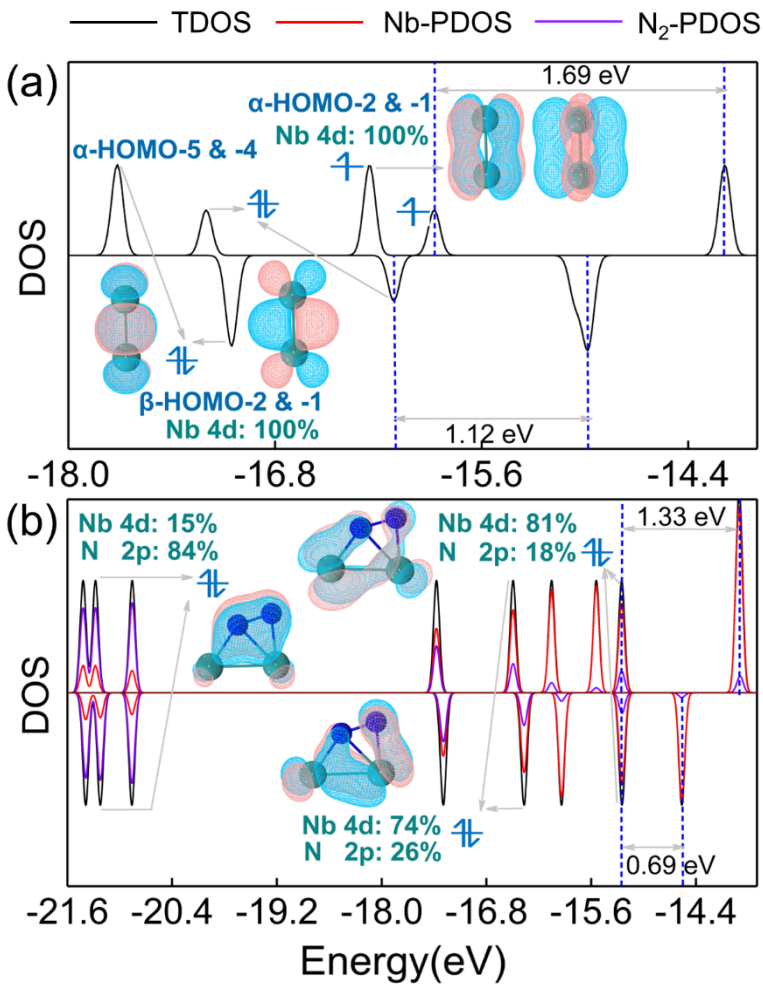

Fig. S6 Total density of states (TDOS, black line) for (a) Nb_2^+ and (b) $Nb_2N_2^+$. Projected density of states (PDOS) of Nb (red line) and N_2 (purple line) are also given. In each panel, the HOMO position is indicated by the blue dotted line. The HOMO–LUMO energy gaps are also given. The orbital insets are shown to illustrate the bond interactions between the Nb_2^+ cluster and N_2. The corresponding orbital contribution for Nb and N are also presented.

References

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