

Supplementary Information for

Anomalous π -backbonding in complexes between $B(SiR_3)_3$ and N_2 : Catalytic activation and breaking of scaling relations

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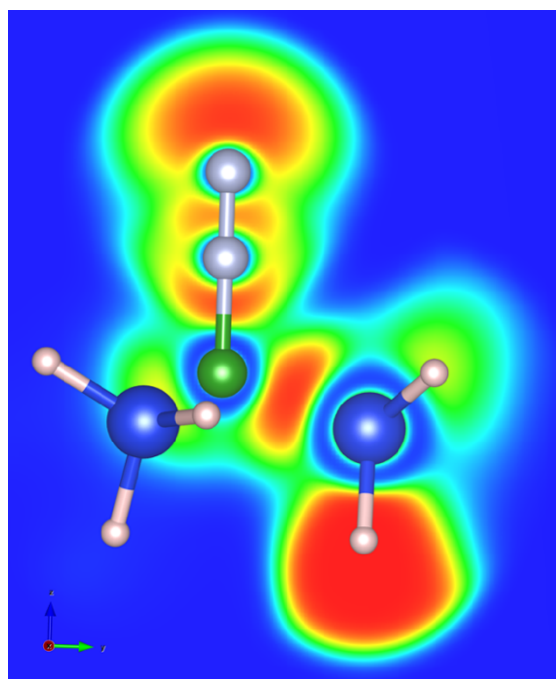


Fig. S1. ELF of $B(SiH_3)_3 \cdot N_2$. It is not clear from the ELF pattern whether there is a covalent B-N bond or a non-covalent interaction with the lower lone pair of N_2 interacting with the electron deficient side of B (empty sp^3) of $B(SiH_3)_3$. Note that VESTA does not draw the B-Si bond because of its length.

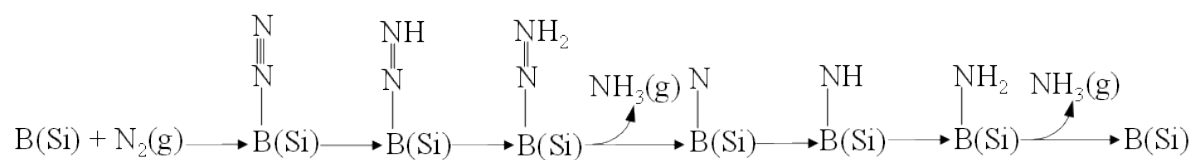


Fig. S2. Schematic depiction of distal pathway for N_2 electro reduction to NH_3 at the reaction site of the B single atom from the B doped Si systems.

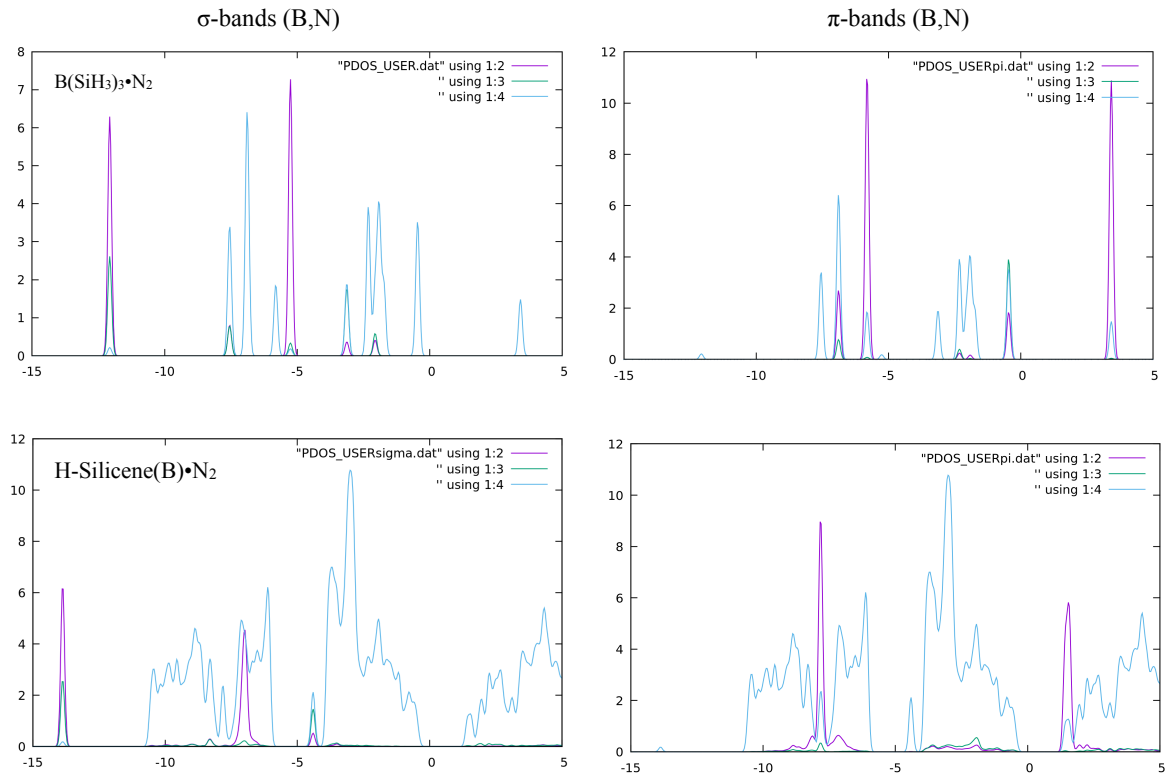


Fig. S3. Partial density of states (PDOS) for $\text{B}(\text{SiH}_3)_3 \cdot \text{N}_2$ (top) and N_2 adsorbed on B-doped and hydrogen terminated silicene (bottom). The PDOS analysis is divided into bands/orbitals of σ -symmetry (left) and π -symmetry (right) with respect to the N-N bond, i.e. $\text{N}(s, p_z)$ and $\text{B}(s, p_z)$ components for σ -symmetry and $\text{N}(p_x, p_y)$ and $\text{B}(p_x, p_y)$ components for π -symmetry. For Si all components (s, p, d) are included for both plots. 1:2, 1:3, and 1:4 refers to N, B, and Si elements respectively. The energies of the bands in eV are shifted such that the Fermi level corresponds to 0 (zero) energy. Corresponding plots with the energy shifted so that the LUMO energy is zero are found as Fig. 4 of the main article.

Table S1. Alpha-angle (Deg), bond length and complexation enthalpy for complexes with N₂, CO and NH₃

Lewis Acid	alpha N ₂ Deg	R _{B-N} Å	ΔH _{N2}	alpha CO Deg	R _{B-C} Å	ΔH _{CO} kcal/mol	alpha NH ₃	R _{B-N} Å	ΔH _{NH3} kcal/mol
B(SiH ₃) ₃	109.2	1.477	-15.9	109.2	1.463	-45.4	108.6	1.635	-35.2
B(Si(CH ₃) ₃) ₃	106.2	1.465	-19.5	105.6	1.451	-50.6	107.3	1.646	-32.8
B(Si(SiH ₃) ₃) ₃	105.6	1.493	-10.1	104.7	1.475	-38.3	107.6	1.626	-36.1
B(Si(OH) ₃) ₃	110.3	1.479	-24.9	110.0	1.464	-54.7	107.2	1.631	-54.4
B(SiF ₃) ₃	108.9	1.505	-23.9	105.5	1.486	-52.0	106.5	1.635	-56.6
B(GeH ₃) ₃	108.4	1.474	-16.4	107.9	1.464	-46.5	107.8	1.632	-35.8
B(Ge(CH ₃) ₃) ₃	107.0	1.460	-21.0	106.5	1.452	-52.4	107.8	1.639	-34.4
B(CH ₃) ₃	-	-	-	105.5	1.607	-1.9	106	1.601	-13.9
B(CF ₃) ₃	104.3	1.622	-14.7	103.4	1.665	-30.1	105.3	1.623	-61.2
B(CN) ₃	101.5	1.779	0.2	102.7	1.687	-13.6	105	1.614	-45.9
BCl ₃	-	-	-	104.8	1.590	4.0	104.4	1.679	-25.5
BH ₃	102.3	1.594	-5.0	103.7	1.539	-25.3	110.8	1.651	-27.5
Al(SiH ₃) ₃	94.0	2.252	-5.2	95.5	2.118	-13.0	99.1	2.072	-28.9
Al(CF ₃) ₃	94.4	2.157	-13.0	95.0	2.206	-19.0	99.2	1.991	-50.3
AlCl ₃	96.1	2.223	-5.8	97.1	2.221	-11.1	100.9	1.989	-38.3

Table S2. Atomic charges of B(SiH₃)₃•N₂ and the system of N₂ bonded to boron doped H-silicene.

System	Method	H	Si	B	N ₍₁₎	N ₍₂₎	Δq ^a
B(SiH ₃) ₃ •N ₂	Bader/VASP ^b	-0.61	2.30	-0.87	-0.80	0.32	-0.48
H-Silicene(B)•N ₂	Bader/VASP ^b	-0.58	0.92 ^c	-0.38	-0.74	0.26	-0.48
B(SiH ₃) ₃ •N ₂	Bader ^c	-0.62	2.29	-0.79	-0.52	0.07	-0.45
B(SiH ₃) ₃ •N ₂	APT ^d	-0.23	0.84	-0.67	0.59	-0.41	0.18
B(SiH ₃) ₃ •N ₂	MK ^e	-0.14	0.57	-0.64	0.42	-0.21	0.21
B(SiH ₃) ₃ •N ₂	MBS ^f	-0.09	0.33	-0.20	0.04	-0.01	0.03
B(SiH ₃) ₃ •N ₂	NBO ^g	-0.11	0.60	-0.91	-0.01	0.08	0.07
B(SiH ₃) ₃ •N ₂	Hirshfeld ^h	-0.06	0.21	-0.16	0.11	0.00	0.11

^aCharge transfer to N₂, i.e. $q(N_{(1)}) + q(N_{(2)})$. ^bBader charge¹ computed from the charge density obtained by VASP using a plane wave basis.² ^cSi bonded to B. ^eBader charge computed from the charge density obtained at the PBE/6-31+G(2d,p) level using analytical integration in G16. Following charge methods use the same charge density/wavefunction.^dAtomic polar tensor charges.³ ^eElectrostatic potential derived charges using Merz-Kollman scheme.⁴ ^fMinimum basis set localization population analysis.⁵ ^gNBO charges.⁶ ^hHirshfeld charges.⁷

Visualization

Visualization of results were done using Molden,⁸ Vesta,⁹ LUMO and ChimeraX¹⁰ for molecular structures, difference plots, molecular orbitals and surface properties, respectively. Magic Plot and Gnuplot was used for PDOS plots.

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