

Reduction of Dinitrogen via 2,3'-Bipyridine-Mediated Tetraboration

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Abstract

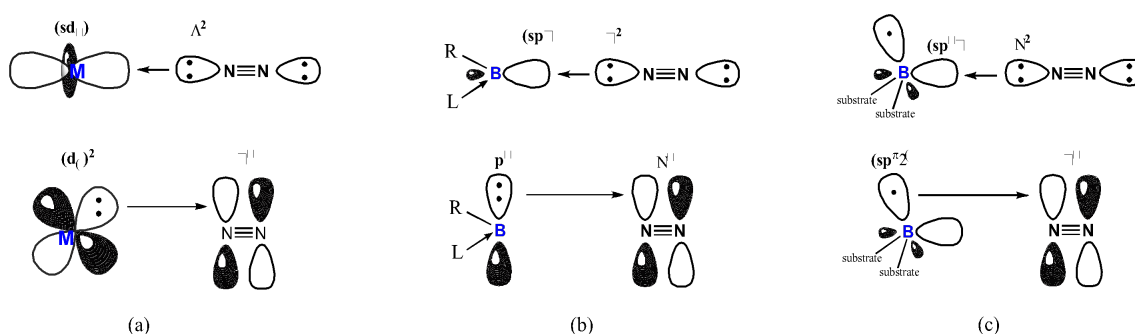
A new molecular system for nitrogen reduction, involving a 2,3'-bipyridine-anchored, end-on-bridging dinitrogen complex of the Me₂B–BMe₂ intermediate (**4**), has been explored by theoretical methods. The 2,3'-bipyridine-mediated cleavage of the B_{sp³}–B_{sp³} bond in **4** may lead to transient electron-rich sp³-hybridized boron species and subsequent activation of the strong N≡N triple bond of the complexed N₂. Through a boryl transfer sequence, a catalytic cycle may be achieved for the reductive addition of diboranes to a dinitrogen molecule with an energy span of 23 kcal/mol. In addition, the reaction is exothermic by 80.5 kcal/mol, providing a substantive chemical driving force.

Introduction

Due to the non-polarity and extremely high bond energy of the $\text{N}\equiv\text{N}$ triple bond (ca. 225 kcal/mol),¹ molecular nitrogen (N_2) (making up appropriately 78% of air) is unusually stable. Nitrogen-fixation, reducing molecular nitrogen to ammonia, is achieved naturally by nitrogenases *via* multiple proton-electron transfers.²⁻⁴ The industrial Haber–Bosch process, utilized for the conversion of N_2 and H_2 to NH_3 , supports half of all global food production. However, this process is conducted under harsh reaction conditions (350–550 °C and 150–350 atm) and consumes about 2% of the annual world-wide energy production.^{5, 6} In the context of energy and climate change challenges, developing energy-efficient and environmentally benign strategies for N_2 reduction reaction (NRR), such as electrocatalytic N_2 reduction, is highly desirable and being actively investigated.⁷⁻⁹ However, to date all electrochemical NRRs suffer from low yield rates ($\text{TON} < 100$) and poor selectivity, due to the competitive $2\text{H}^+/2\text{e}^-$ hydrogen evolution reaction.^{10, 11} In order to improve the efficiency of NRR, many other methods, including biological and biomimetic approaches,¹² heterogeneous thermocatalytic processes,¹³ photocatalytic processes,¹⁴⁻¹⁶ and plasma-mediated N_2 fixation¹⁷ have been explored. Although considerable progress has been made, it is important for scientists to develop more efficient methods for NRR.^{18, 19}

Transition metal-based N_2 fixation and activation involves not only σ -donation of the lone pair of electrons of N_2 into empty d orbitals, but also π -back-donation of filled d

orbitals of the metal center into the unoccupied π^* orbital of N_2 (*i.e.*, Dewar-Chatt-Duncanson bonding model) (Scheme 1a).^{20, 23} The π -back-donation weakens the N–N bond and thus plays a key role in N_2 activation. A series of Mo and Fe molecular catalysts for NRR, through the addition of $6\text{H}^+/6\text{e}^-$ into a weakened dinitrogen ligand, have been documented.^{24–27} The Chatt-type (distal) and alternating pathways have been proposed for mechanistic outlines.^{28–30} In contrast to electron-rich transition metals, high-oxidation-state uranium(V) is electron-poor (with only one 5f valence electron) and thus not a good candidate for N_2 binding. However, recently Liddle and coworkers achieved a rare end-on uranium(V)-dinitrogen complex by utilizing both cooperative heterobimetallic uranium-lithium effects and electron-rich ancillary ligands that result in back-donation of the uranium(V) ion into π^* orbital of N_2 .³¹



Scheme 1. Schematic representations of the end-on bonding modes in transition metal N_2 complexes (a),²⁰ dicoordinate borylene N_2 complexes (b),²¹ and single sp^3 -hybridized boron atom (decorated on $g\text{-C}_3\text{N}_4$) N_2 complexes (c).²²

Considering their low cost and wide abundance, main group elements have been employed to mimic transition metals in small molecule activation and even potential

catalytic applications.³² Dinitrogen complexation with main group radicals has been probed by electron paramagnetic resonance (EPR) technique.³³ Indeed, Braunschweig and coworkers²¹ discovered that carbene-complexed dicoordinate borylene, as a transient electron-rich B(I) species, may mimic transition metals to reduce dinitrogen *via* $p \rightarrow \pi_{NN}^*$ backbonding interactions (Scheme 1b). Subsequent to the discovery of borylene-mediated N₂ reduction,²¹ a series of boron-doped two-dimensional materials have been explored as metal-free electro- or photo-catalysts for N₂ reduction by both experimental and theoretical methods.³⁴⁻⁴¹ Notably, a theoretical study proposed that the sp³-hybridized boron atom, decorated on the optically active graphitic-carbon nitride (B/g-C₃N₄), may enable solar-driven N₂ fixation.²² In this case, one vacant and one occupied sp³-hybridized orbital of the boron atom give rise to the bonding interactions with N₂ (Scheme 1c). While diboranes without π -donating function (such as H₂B–BH₂) may weakly coordinate N₂ to provide traditional Lewis adducts,⁴²⁻⁴⁵ diborane(4)-based N₂ reduction reactions have yet to be reported. Inspired by recent silico reaction discoveries,^{46, 47} we demonstrate our theoretical study on 2,3'-bipyridine-mediated N₂ reduction by a diborane(4), namely Me₂B–BMe₂.

Computational Methods

This research was carried out with the DFT ω B97X-D⁴⁸ method using the Gaussian 09 programs.⁴⁹ All the structures were optimized in benzene solvent (with a low dielectric

constant; $\epsilon = 2.2706$) using the SMD (Solution Model based on Density) solvation model. The 6-311++G** basis sets were used in the geometry optimization.^{50, 51} All transition states were confirmed to exhibit only one imaginary frequency via Hessian analyses. Intrinsic reaction coordinate (IRC) calculations were performed to confirm that all transition states connect the two related minima. The wavefunction stability was checked for all the stationary points, and the wavefunctions of all structures, including minima and transition states, are found to be stable. The present transformation involves a multicomponent change; thus, entropy overestimations must be taken into account.⁵²⁻⁵⁴ In this study, translational movement was evaluated using the method presented by Whitesides and coworkers.⁵⁵ Natural bond orbital (NBO) analyses were performed using the NBO 6.0 program.⁵⁶ We have thoroughly examined the conformational space of each intermediate and transition state, and the lowest energy conformers are included in the discussion. The Cartesian coordinates of all optimized structures are presented in the Supporting Information.

Results and Discussions

Pyrazines have been reported to undergo addition of B–B bonded boron reagents. After that, 4,4'-bipyridines-catalyzed diboration of sterically demanding pyrazines has been achieved.⁵⁵ These discoveries suggest that nitrogen-containing bases may not only conduct reductive addition by cleaving the boron-boron bond of diborons, but also readily

release the boryl groups to pyrazine substrates.⁵⁷⁻⁵⁹ Herein, we propose a novel strategy for NRR through an unusual N₂ activation mode (Figure 1). This strategy involves building an interconnected bis(Lewis base)-anchored, end-on-bridging dinitrogen complex of diboranes(4) (Figure 1c), which may subsequently undergo catalytic tetraboration of dinitrogen.

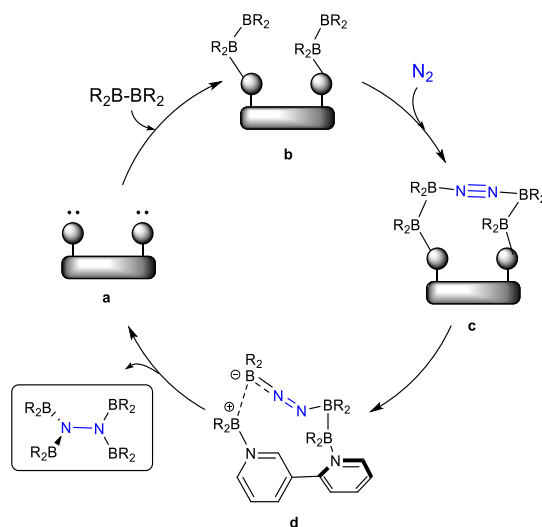


Figure 1. Proposed bis(Lewis base)-catalyzed tetraboration reaction of N₂. Structure (a) stands for the bis(Lewis base) ancillary ligand.

In the present study, 2,3'-bipyridine **1** was selected as the bis(Lewis base) anchor ligand because its N...N distance is suitable to intermediates such as structure **4**, while Me₂B-BMe₂ was chosen as a diborane model (Figure 2). With two anchor sites (i.e., nitrogen atoms), **1** can bind two Me₂B-BMe₂ molecules through classical donor-acceptor bonds to give **2**, which is predicted to be exothermic by 9.1 kcal/mol. Notably, the two terminal boron atoms in **2** are sp² hybridized and thus form a suitable borane pocket for the capture of one dinitrogen molecule. The dinitrogen molecule coordination proceeds in a stepwise manner. Consequently, intermediate **3** with an end-on N₂ ligand is generated

first (Figure 2). Through the transition state **TS3-4**, the N₂ ligand in **3** binds to the other terminal B_{sp2} atom in an end-on fashion, providing the Lewis-base-anchored diborane-(μ-η¹:η¹-N₂) complex **4**. The energy span for the assembly of **4** is 22.6 (= 9.1 + 13.5) kcal/mol. This suggests that the intermediates **4** may exist under mild conditions. Although the classical energy (ΔE) of **TS3-4** is higher than **4** by 1.4 kcal/mol, the Gibbs free energy (ΔG) for **TS3-4** is 0.3 kcal/mol lower than that of **4**. The B1–B2 distance in **4** is 1.883 Å (Figure 3), which is significantly longer than that in free Me₂B–BMe₂ molecule (1.678 Å), suggesting that the synergetic coordination of 2,3'-bipyridine and N₂ would favor cleavage of the B–B bond of Me₂B–BMe₂. The B–B cleavage of Me₂B–BMe₂ across two nitrogen atoms of **1** was also investigated. The generated **9** (Figure S1 in Supporting Information) is less favored than **2**.

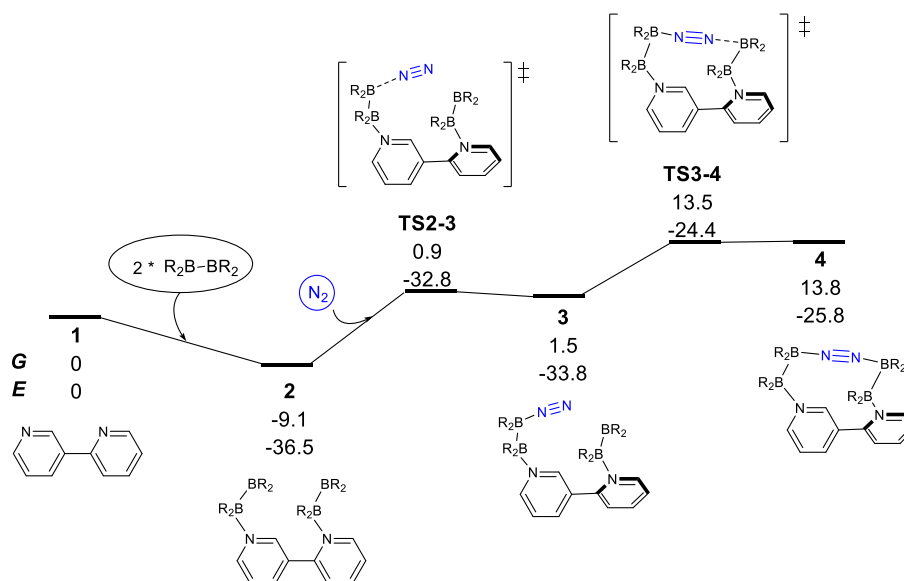


Figure 2. The profile of Gibbs free energies (upper, in kcal/mol at 298.15 K and 1 atm pressure) and classical energies (lower, in kcal/mol) for the assembly of **4** (R = Me). All structures were optimized in benzene.

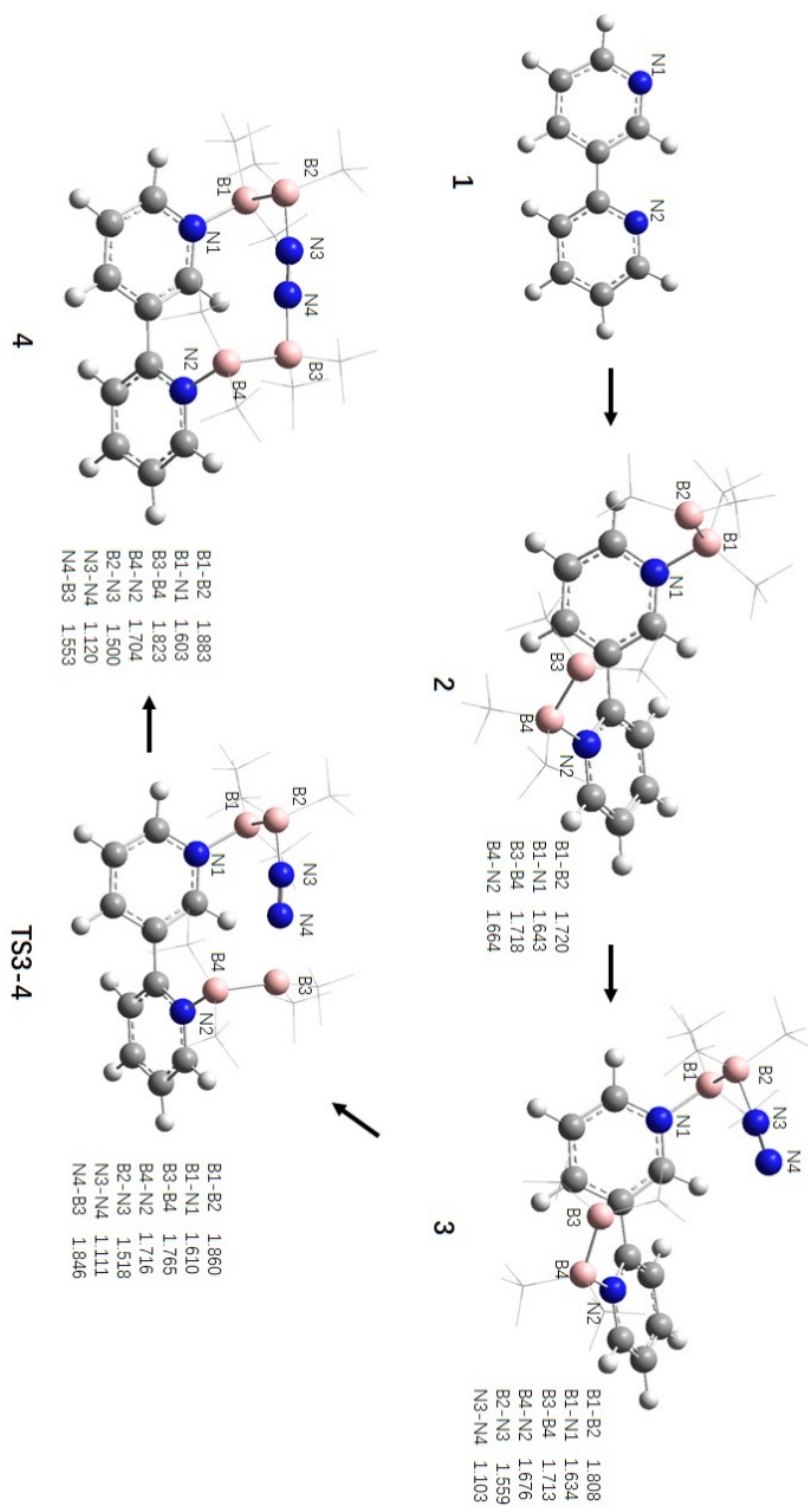


Figure 3. Structures involved in the assembly of **4**. The internuclear separations are given in Å. The methyl groups on the boron atoms are drawn in wireframe for simplicity. All structures were optimized in benzene.

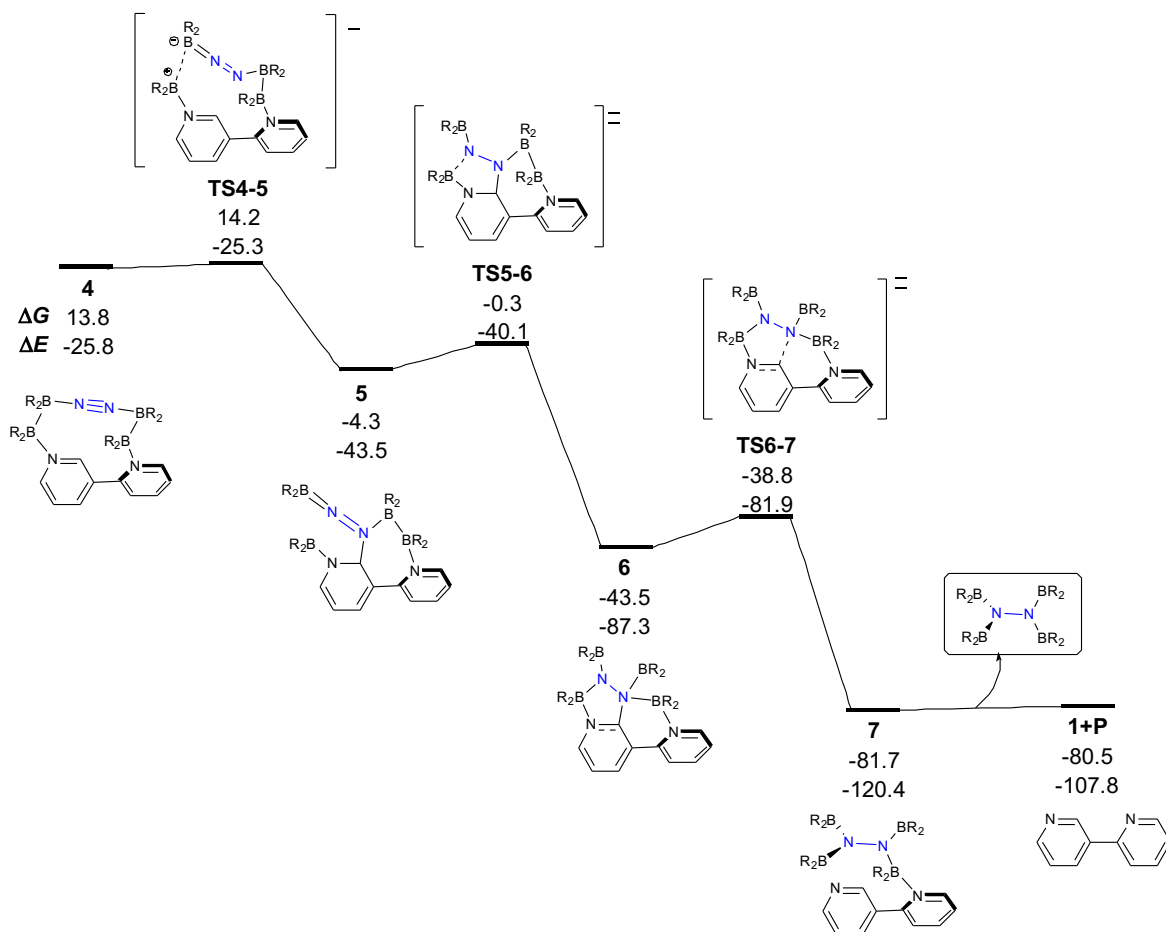


Figure 4. The profile of Gibbs free energies (upper, in kcal/mol at 298.15 K and 1 atm pressure) and classical energies (lower, in kcal/mol) for 2,3'-bipyridine-mediated reductive tetraboration of N_2 ($R = Me$). All structures were optimized in benzene.

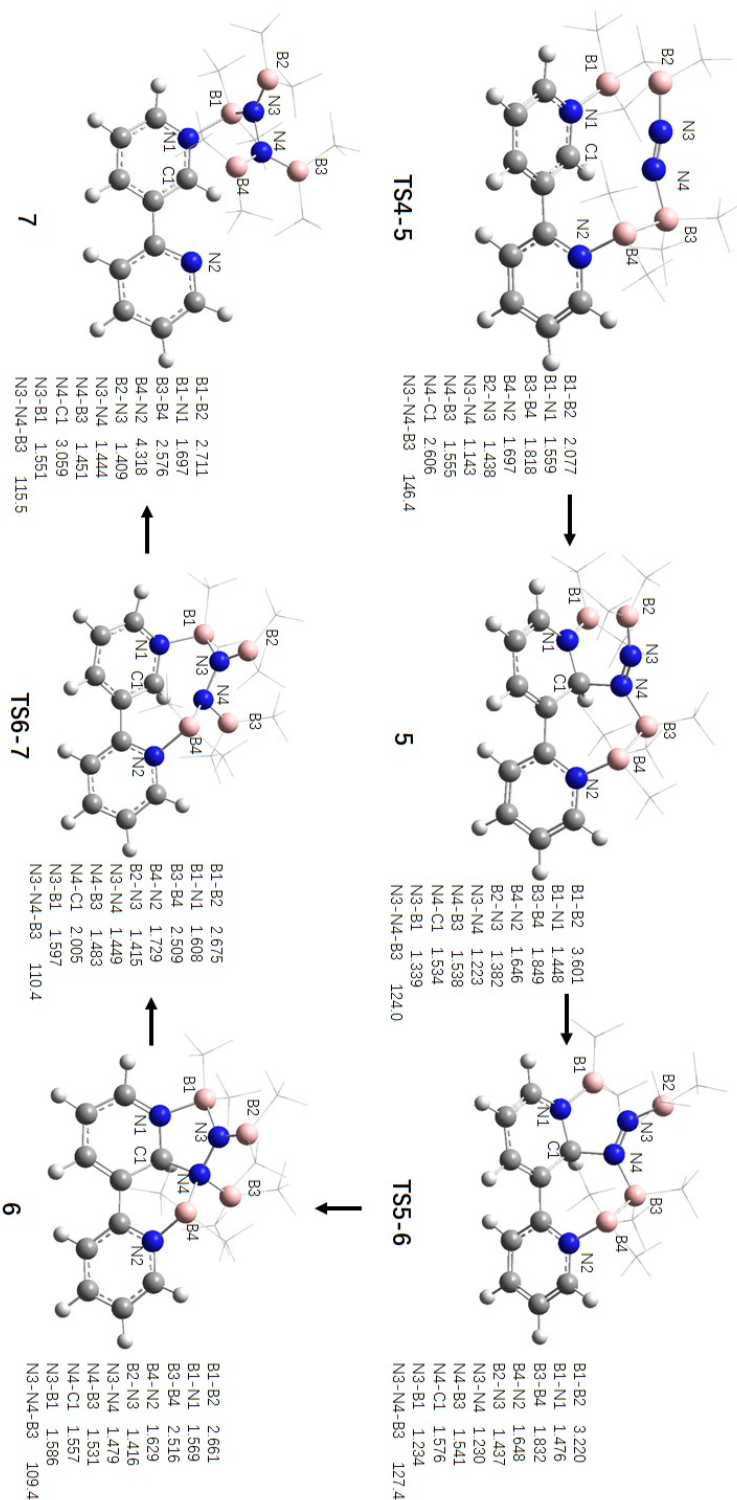


Figure 5. Structures accompanying 2,3'-bipyridine-mediated reductive tetraboration of N_2 . The internuclear separations are given in Å. The methyl groups on the boron atoms are drawn in wireframe for simplicity. All structures were optimized in benzene.

Our results for the $B_{sp^3}-B_{sp^3}$ bond cleavage in **4** are shown in Figure 4. Due to the lability of the $B_{sp^3}-B_{sp^3}$ bond in **4**, its cleavage should be facile with a low energy barrier of 0.4 kcal/mol. The IRC result indicates that **TS4-5** connects with another intermediate **5**, which lies 18.1 kcal/mol lower than **4**. Accompanying the cleavage of the B(1)–B(2) bond, the N(4) atom with a lone pair is bonded to the C(1) atom next to the N(1) atom of the pyridine ring with a single carbon-nitrogen bond length of 1.534 Å (Figure 5). The C-N bond formation in **5** is energetically favorable, because it avoids the high-energy $XN=NX$ structure.⁶⁰ The natural atomic charges for B(1) (+1.02) and N(3) (-0.35) atoms are computed. The N–N bond distance of the complexed N_2 moiety is elongated by ca. 0.1 Å from **4** to **5**, whereas the B(2)–N(3) bond distance is correspondingly decreased from 1.500 Å (for **4**) to 1.382 Å (for **5**). Therefore, we can draw the conclusion that the cleavage of the $B_{sp^3}-B_{sp^3}$ bond in **TS4-5** would lead to the activation of $N\equiv N$ triple bonds, and this finding may be ascribed to the formation of transient sp^3 -hybridized B^- atom that back-donates the electron density to the π^* orbital of N_2 (Figure 6).

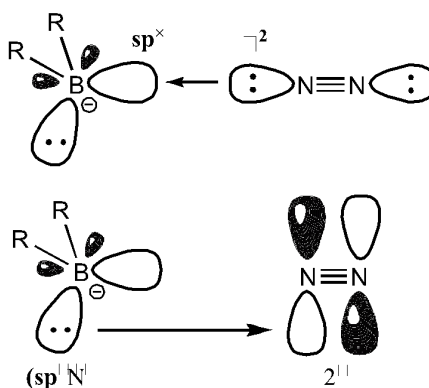


Figure 6. The end-on bonding modes for N_2 with the sp^3 -hybridized B^- atom in the transition state **TS4-5**.

The subsequent boryl transfer steps experienced by **5** finally result in the release of a reduced nitrogen product $(\text{BMe}_2)_2\text{N}-\text{N}(\text{BMe}_2)_2$ through a downhill energy pathway with low barriers (Figure 4). The Lewis basic N(3) atom in **5** approaches the Lewis acidic B(1) atom via the transition state **TS5-6** (with an energy barrier of 4 kcal/mol), giving an intermediate **6**, which is favored in energy with respect to **5** by 39.2 kcal/mol. The transition state **TS6-7** involves both N(4)–C(1) and B(4)–N(2) bond cleavage, and leads to intermediate **7**, an adduct of bipyridine **1** with $(\text{BMe}_2)_2\text{N}-\text{N}(\text{BMe}_2)_2$. The cleavage of the C–N bond is energetically favored in this step because two strong B–N–B conjugation arrangements are obtained in the generated $(\text{BMe}_2)_2\text{N}-\text{N}(\text{BMe}_2)_2$ moiety of intermediate **7**. Thus the step from **6** to **7** is exothermic by 38.2 kcal/mol. The final dissociation of $(\text{BMe}_2)_2\text{N}-\text{N}(\text{BMe}_2)_2$ is expected to regenerate the starting species **1**, thereby affording a complete catalytic cycle (Figure 1). The production of $(\text{BMe}_2)_2\text{N}-\text{N}(\text{BMe}_2)_2$ (as shown in Figure 4) experiences a substantial energy decrease of 80.5 kcal/mol, which provides the important chemical driving force for the catalytic reaction.

The effects of temperature, pressure, and solvent on the Gibbs free energies are included in this study, and these conditions do not change the free energy span significantly (Tables S3 – S5, in SI). Table S3 shows that the free energy span is from 22 kcal/mol at 273 K to 27 kcal/mol at 373 K, with the low temperature slightly in favor of the reaction. When the pressures increased from 1 atm to 2 atm, the energy span changes by only 0.4

kcal/mol (Table S4 in SI), and the three different solvents (benzene, trichloromethane, and dichloromethane) predict a very close energy span within 0.5 kcal/mol (Table S5 in SI).

Conclusions

While the bonding interaction between diborane(4) and N_2 is reportedly weak, the present study suggests that a 2,3'-bipyridine-anchored diborane pocket may be utilized in both capturing an N_2 molecule and in its activation. Our research study unveils an unprecedented N_2 activation mode: the boron–boron bond cleavage of the $\text{Me}_2\text{B-BMe}_2$ moiety in **4** will lead to a transient sp^3 -hybridized B^- atom and donating electron density to the π^* orbital of N_2 . The complete catalytic cycle includes both an assembly process (giving **4**) and a boryl transfer sequence [giving $(\text{BMe}_2)_2\text{N-N}(\text{BMe}_2)_2$ product and regenerating the bipyridine **1**]. The corresponding energy span of 23.3 kcal/mol (= 14.2 + 9.1) indicates that this conversion is kinetically feasible under mild conditions. In addition, this catalyzed reaction is thermodynamically favorable with a reaction free energy of -80 kcal/mol. We hope that the present study will provide strong motivation for further studies on NRR.

ASSOCIATED CONTENT

Supporting Information

The optimized geometries and energies of all stationary points along the reaction pathways, as well as the imaginary vibrational frequencies of transition states. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Notes

The authors declare no competing financial interest.

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TOC Graphic:

