



HAL
open science

Ammonia Synthesis at Room Temperature and Atmospheric Pressure from N₂

Soukaina Bennaamane, Barbara Rialland, Lhoussain Khrouz, Marie Fustier-Boutignon, Christophe Bucher, Eric Clot, Nicolas Mézailles

► **To cite this version:**

Soukaina Bennaamane, Barbara Rialland, Lhoussain Khrouz, Marie Fustier-Boutignon, Christophe Bucher, et al.. Ammonia Synthesis at Room Temperature and Atmospheric Pressure from N₂: A Boron-Radical Approach. *Angewandte Chemie International Edition*, 2022, 10.1002/anie.202209102 . hal-03839021

HAL Id: hal-03839021

<https://hal.science/hal-03839021>

Submitted on 4 Nov 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Ammonia Synthesis at Room Temperature and Atmospheric Pressure from N₂ : A Boron-Radical Approach

Soukaina Bennaamane,^[a] Barbara Rialland,^[a] Lhoussain Khrouz,^[b] Marie Fustier-Boutignon,^[a] Christophe Bucher,^[b] Eric Clot,^[c] Nicolas Mézailles*^[a]

Dedication : In memory of Pascal Le Floch.

[a] Dr. S. Bennaamane, B. Rialland, Dr. M. Fustier-Boutignon, Dr. N. Mézailles
Laboratoire Hétérochimie Fondamentale et Appliquée
Université Paul Sabatier, CNRS
118 Route de Narbonne, 31062 Toulouse (France)
E-mail: nicolas.mezailles1@univ-tlse3.fr

[b] L. Khrouz, Dr. C. Bucher
Univ Lyon, ENS Lyon, CNRS, Université Lyon 1, Laboratoire de Chimie, UMR 5182, 46 allée d'Italie, 69364 Lyon (France)

[c] Dr. E. Clot
ICGM, Univ. Montpellier, CNRS, ENSCM, Montpellier (France)

Supporting information for this article is given via a link at the end of the document.

Abstract: Ammonia, NH₃, is an essential molecule, being part of fertilizers. It is currently synthesized via the Haber-Bosch process, from the very stable dinitrogen molecule, N₂ and dihydrogen, H₂. This process requires high temperatures and pressures, thereby generating ca 1.6% of the global CO₂ emissions. Alternative strategies are needed to realize the functionalization of N₂ to NH₃ under mild conditions. Here, we show that boron-centered radicals provide a means of activating N₂ at room temperature and atmospheric pressure whilst allowing a radical process to occur, leading to the production of borylamines. Subsequent hydrolysis released NH₄⁺, the acidic form of NH₃. EPR spectroscopy supported the intermediacy of radicals in the process, corroborated by DFT calculations, which rationalized the mechanism of the N₂ functionalization by R₂B radicals.

Introduction

Ammonia is one of the most abundantly produced chemicals worldwide. This compound is an essential component of fertilizers, providing nitrogen for plants to grow. Without fertilizers, the growing world's population could not be fed. Currently, 150 million t/y of NH₃ is produced worldwide; this figure is expected to more than double by 2050.^[1] Ammonia is also a promising material as a transportation fuel.^[2] Ammonia is a prime candidate for energy storage in the hydrogen economy; Indeed, the energy density of liquid ammonia (11.5 MJ/L), is higher than for liquid hydrogen (8.491 MJ/L) and for compressed H₂ at 690 bar and 15°C (4.5 MJ/L).^[3]

Around 78% of our planet's atmosphere is made up of nitrogen gas (N₂) but its activation and conversion to NH₃ remains a challenging task due to the inertness of the dinitrogen. Plants have developed mechanisms to activate and fix nitrogen from N₂ using nitrogenase enzymes, but the process is slow and does not lend itself to industrialization. The industrial production of NH₃ uses the Haber-Bosch (HB) process, during which hydrogen and

nitrogen react at a high temperature and pressure over a metal catalyst.^[4,5] The process uses natural gas as raw material and has a heavy CO₂ footprint of 1.9 t of CO₂ per t NH₃. The HB process contributes 1.4% of the world's CO₂ emissions.^[6] The process can only be run economically in large, capital-intensive units.

Decarbonizing the HB process can potentially be done by sequestering and storing the generated CO₂,^[7] or by using the hydrogen gas produced by water splitting from renewable energy.^[8] However, the primary step of the process – the actual HB ammonia production – remains energy and capital intensive. The process does not lend itself easily to medium-sized production units that are aimed at using locally available renewable energy.

A clear need exists for a process to convert nitrogen to ammonia without the use of high temperatures and high pressures.

Researchers have been looking into developing processes for N₂ transformation into N-containing derivatives (i.e., N₂ fixation) under mild, homogeneous conditions for several decades, especially processes that use carefully designed transition metal complexes (Figure 1, A).^[9] The classical method for N₂-activation at a metal center relies on a two-way electron flow. Donation of electron density from N₂ to an empty orbital at the metal and back donation from a filled orbital of the metal to π* orbitals of N₂, weakens the strong N≡N bond.^[10–14] Despite impressive results obtained recently, only a few complexes have been demonstrated to efficiently reduce N₂ to NH₃ using carefully optimized sources of protons and electrons.^[15–17] Notably, this strategy was successfully applied most recently to main group boron species (borylene derivatives).^[18–20]

On the other hand, theoretical calculations show that the incorporation of N₂ can take place in some organic molecules.^[21,22] The lack of experimental proof demonstrating the feasibility of such a direct insertion process is obviously due to kinetic limitations, i.e., the involvement of high-energy transition states and intermediates (Figure 1, C).

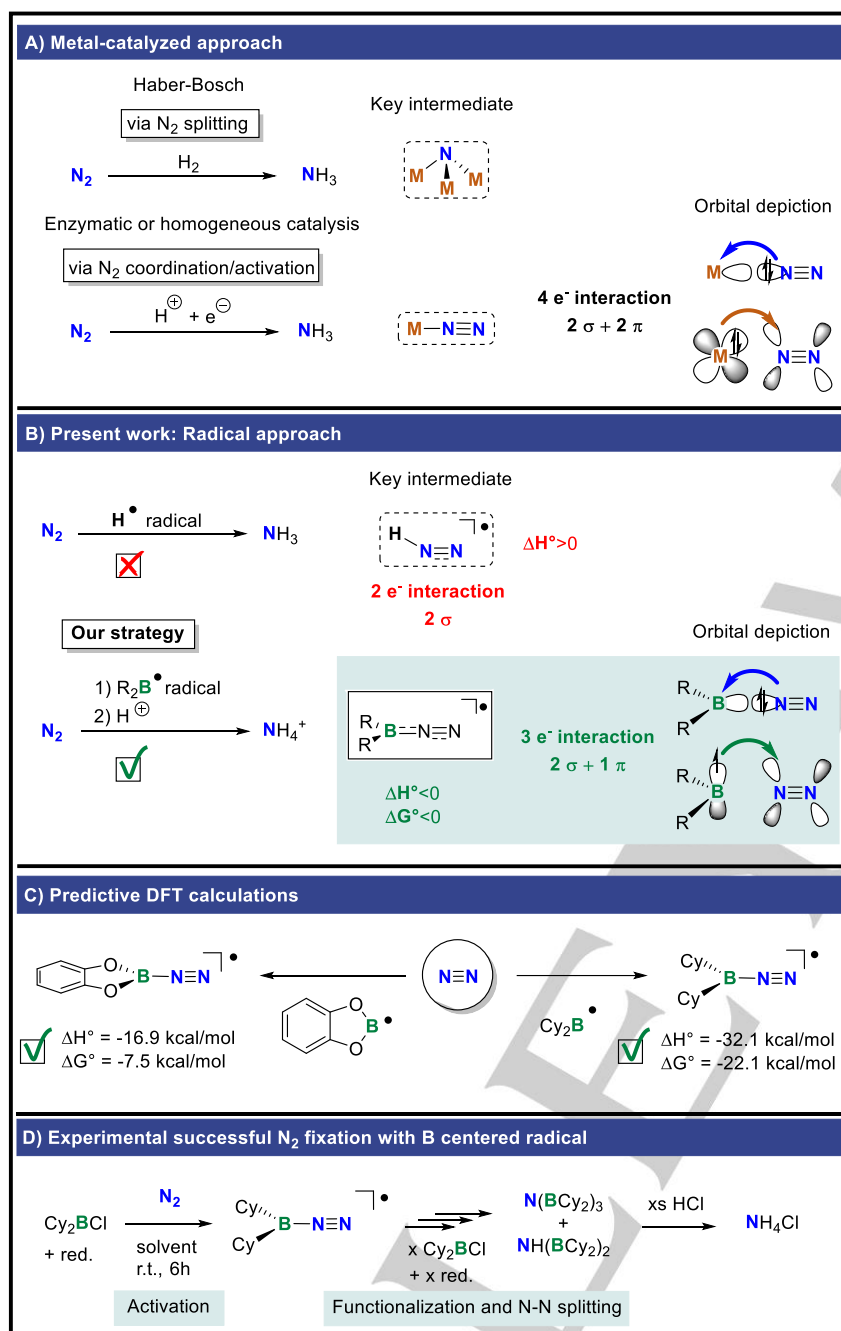


Figure 1. A: Known catalytic N_2 to NH_3 transformations. B: Radical approach to N_2 -activation: our strategy. C: Computed additions of R_2B radicals on N_2 . D: Successful N_2 to NH_4^+ transformation via B-centered radicals.

For example, the addition of H_2 across N_2 to afford NH_3 implies the formation of diazene, $HN=NH$, as the first intermediate. Although this step leads to the formation of two strong NH bonds, calculations show that the reaction is far too endothermic to become feasible ($\Delta H^\circ = 56.0$ and $51.0 \text{ kcal.mol}^{-1}$ for *cis* and *trans* diazene, respectively).

We reasoned that the use of high-energy radicals might provide a kinetically and thermodynamically favorable pathway to N_2 functionalization. The reaction between N_2 and the high-energy radical H^\bullet is, however, known to be endothermic ($\Delta H^\circ = 9.0$

kcal.mol^{-1}), which precludes a radical chain process initiated by H atom transfer.^[23] To develop the first N_2 functionalization process based on radical addition, we performed a computational study (using density functional theory, DFT) to identify radicals (R^\bullet) forming compounds of the type RN_2^\bullet in an exothermic (and exergonic) reaction. We inferred that, in addition to creating a strong σ -interaction, delocalization of the radical onto the π^* system of N_2 could be the key to such an exergonic process (Figure 1, B).^[24] Calculations, therefore, focused on various R_2B^\bullet derivatives. Experimental work was subsequently dedicated to generating such radicals under mild conditions. We report here the first functionalization of N_2 with three radical derivatives, namely Cy_2B^\bullet , (DIP) B^\bullet (DIP = Di-isopinocampheyl) and Bis(bicyclo[2.2.1]-2-heptyl) B^\bullet , generated at room temperature in the presence of potassium (K). NMR and EPR spectroscopies and DFT calculations have unambiguously established the in-situ formation of borylamines from N_2 and boron-centered radicals. NH_4^+ was then obtained by simple hydrolysis of the borylamine intermediates, thereby providing an unprecedented strategy for the transformation of dinitrogen to ammonia under mild conditions.

Results and Discussion

Reaction optimization: NH_4^+ synthesis from N_2

As a first step, the additions of $CatB^\bullet$ (Cat = catechol) and Cy_2B^\bullet on N_2 were computed by DFT (Figure 1, C).^[25] Both radicals are computed to have an exothermic ($\Delta H = -16.9 \text{ kcal.mol}^{-1}$, $CatB$; $\Delta H = -32.1 \text{ kcal.mol}^{-1}$, Cy_2B) and exoergic ($\Delta G = -7.5 \text{ kcal.mol}^{-1}$, $CatB$; $\Delta G = -22.1 \text{ kcal.mol}^{-1}$, Cy_2B) reaction with N_2 . According to these calculations, both radicals were promising candidates to react with N_2 and we set out to generate them in solution

under N_2 upon one-electron reduction of the corresponding R_2BCl derivative. It should be noted, however, that few R_2B-Br_2 compounds are known to be synthesized via this reductive strategy under N_2 , implying favored radical coupling rather than addition on N_2 .^[26a-c] The efficiency of the BB bond formation appeared to depend on the substituents at B, with the presence of donor atoms being very favorable.^[27] The donor atoms likely stabilize the radical, thereby increasing its concentration and thus the radical coupling. Accordingly, several $(RO)_2B-B(OR)_2$ compounds have been synthesized in good to excellent yields from $(RO)_2BCl$ and Na/Hg under N_2 in toluene at $90^\circ C$.^[28] Therefore, the reduction of Cy_2BCl to form a higher-energy non-stabilized boryl radical was chosen as the more promising candidate.^[29] Thus, as a preliminary investigation a stoichiometric mixture of Cy_2BCl and K (2.0 mmol) in THF (12 mL) was stirred for 12 h under N_2 (1 bar), followed by hydrolysis with

RESEARCH ARTICLE

an excess of HCl in Et₂O to convert all N containing species into NH₄Cl. Quantification was achieved by dissolution of the solid residue and integration vs 1,3,5-trimethoxybenzene as internal standard by ¹H NMR spectroscopy (see ESI for details on the quantification method). It revealed that NH₄⁺ is indeed produced, albeit in a small yield (0.046 mmol, 7% yield, Table 1, entry 1). Further studies then showed that this yield could be significantly improved, up to 41%, by lowering the concentration of the reagents and by using an excess of K (entry 2). A thorough screening of solvents and reducing agents was carried out under these conditions.

Despite the fact that the chloroborane is reduced, as attested by the formation of BH species in the crude mixture by ¹¹B NMR (vide infra), in none of cases, NH₄⁺ was observed after hydrolysis of the crude mixture (entries 8-12). To ascertain that all reagents were needed for the reaction to proceed, the control reactions (under Ar; without K; and without Cy₂BCl) were carried out. As expected, in none of these cases was NH₄⁺ observed after hydrolysis. Further optimizations were carried out to increase the efficiency in N-B bond formation, and thus the yield of NH₄⁺ after hydrolysis. Due to the use of solid K, the stirring efficiency was found to be particularly important. A strong agitation was most likely required to prevent passivation of the K surface.

	[R ₂ BCl] (mol/L)	Solvent	Reducing agent	Stoich. Red	PN ₂ (bar)	Yield
1	0.17	THF	K	1	1	7
2	0.04	THF	K	2.5	1	41
3	0.04	MeTHF	K	2.5	1	0
4	0.04	Pentane	K	2.5	1	0
5	0.04	Toluene	K	2.5	1	0
6	0.04	Et ₂ O	K	3.3	1	0
7	0.04	Dioxane	K	3.3	1	Trace
8	0.04	THF	Na	2.5	1	0
9	0.04	THF	Na/Hg	2.5	1	0
10	0.04	THF	Na/naphtalene	2.5	1	0
11	0.04	THF	KC ₈	2.5	1	0
12	0.04	THF	Sml ₂	2.5	1	0
13 ^a	0.04	THF	K	2.5	1	0
14 ^b	0.04	THF	K	2.5	1	0
15 ^c	0.02	THF	K	2.5	1	56
16	0.02	THF	K	1	1	30
17 ^d	0.04	THF	K	2.5	1	56
18	0.04	THF	K	2.5	20	60
19	0.04	THF	K	2.5	40	76
20	0.04	THF	K	2.5	80	94
21 ^e	0.04	THF	K	2.5	1	48
22 ^f	0.08	THF	K	2.5	1	38
23 ^g	0.04	THF	K	2.5	1	0
CatBCl						
24 ^h	0.04	THF	K	2.5	1	28
DIP-Cl						
25 ⁱ	0.04	THF	K	2.5	1	43
BCHBCl						

Table 1 : Exploring the reaction parameters: step 1) N₂ + R₂BCl + x red. (6h, solvent, temperature, N₂ pressure); step 2: hydrolysis with excess HCl; step 3 quantification of NH₄⁺. Standard reaction conditions: 0.16 mmol Cy₂BCl unless otherwise specified; stirring at 700 rpm at room temperature for 6h, open flask in glove box. Yield is calculated as $3 \times n(\text{NH}_4^+)/n(\text{Cy}_2\text{BCl}) \times 100$ thus considering only N(BCy₂)₃ to be formed during the reaction (see text). All reactions were reproduced at least twice (entry 2, done 6 times). Yield accuracy was estimated at $\pm 4\%$. a) reaction at 60°C; b) reaction at -70°C; c) reaction conducted on a 0.08 mmol scale; d) K was cut into 5 pieces; e) reaction conducted on a 10 times scale compared to standard; f) reaction conducted on a 100 times scale compared to standard; g) CatBCl = catechol-chloroborane; h) DIP-Cl = Di-isopinocampheyl-chloroborane; i) BCHBCl = Bis(bicyclo[2.2.1]-2-heptyl)chloroborane.

No NH₄⁺ production was observed in toluene, Et₂O, pentane or 2Me-THF, no matter what the reducing agent was, while trace amounts were observed in 1,4-dioxane (entries 3-7). We then tested the use of several strong one-electron reducing agents, such as Na, Na/Hg, Na/naphtalene, KC₈ and Sml₂ in THF.

The first parameter evaluated was the stoichiometry between K and Cy₂BCl (entries 16 vs 1). A 2.5-fold excess of K was found to be favorable, although some of it remained unconsumed at the end of the reaction. Decreasing the concentration of chloroborane from 0.04 to 0.02 mol/L led to a significant increase in yield

RESEARCH ARTICLE

(entries 15 vs 2), which was, however, counterbalanced by cutting the K into several pieces (entries 17 vs 15).

The effect of N_2 pressure was also tested. Increasing the pressure to 20 and 40 bars resulted in major improvements in the yields: up to 60% and 76%, respectively (entries 18 and 19 vs 2). At 80 bar, a 94% yield was obtained (entry 20), attesting a highly efficient N_2 functionalization by the Cy_2B radicals. Running the reaction on a ten-fold scale provided a slightly improved yield (entry 21, 48% vs 41% entry 2), while a hundred-fold scale reaction (with doubled concentration) showed a very moderate decreased yield (entry 22, 38% vs 41% entry 2). Finally, two experiments were carried out with $^{15}N_2$ gas, either mixed with $^{14}N_2$ or pure (ESI). $^{15}NH_4^+$ was observed after hydrolysis when pure $^{15}N_2$ was used, while both $^{15}NH_4^+$ and $^{14}NH_4^+$ were obtained as expected from the mixture providing definitive evidence of the direct functionalization of N_2 under these conditions. The kinetics of the reaction were measured by hydrolysis and 1H NMR quantification of aliquots under conditions of entry 2. These studies led to the conclusion that the reaction is essentially completed after 2h (ESI), even though the color of the medium continues to darken over time.

NMR monitoring: identification of borylamines and boron containing side products.

All of the above reactions were monitored by ^{11}B NMR with the aim to characterize the products prior to hydrolysis. Unfortunately, the N-B-containing products were not observed, most likely because of signal broadening due to N-B coupling. On the other hand, side products corresponding to the known $Cy_2BH_2^-$ ($\delta = -9.0$ ppm, triplet) and Cy_2BH ($\delta = 17.0$ ppm, doublet) could be observed in variable proportions, depending on the applied conditions. When stoichiometric amounts of K and Cy_2BCl were used (entry 16), only Cy_2BH was observed, forming colorless crystals of $(Cy_2BH)_2$ upon concentration of crude mixtures. On the other hand, the anion $Cy_2BH_2^-$ was formed when an excess of K was used for the reaction. The observation of signals attributed to $Cy_2BH_2^-$ and $(Cy_2BH)_2$ in the 1H coupled ^{11}B spectrum of the reaction carried out in THF-D8 demonstrated that intramolecular H migration to the B-centered radical is faster than the intermolecular abstraction of D atom from the solvent.^[29] We also found that the intensity of these two signals is inversely proportional to the yield in NH_4^+ obtained after hydrolysis, indicating that the formation of B-H derivatives competes with the coupling of the B-based radical with N_2 .

Multinuclear NMR experiments (1H , ^{15}N , ^{15}N - 1H HMBC) demonstrated that a mixture of two borylamine compound(s), $N(BCy_2)_3$ and $NH(BCy_2)_2$ were generated by the reduction process, with relative ratios also depending on the experimental conditions (see ESI). Above all, NMR analyses carried out on samples taken before hydrolysis of a reaction performed under the conditions of entry 20, previously found to give the best yield in NH_4^+ without BH-type secondary products, revealed that $N(BCy_2)_3$ is formed with a yield exceeding 90%. The ^{15}N - 1H HMBC spectrum of a reaction carried out in THF-D8 showed a cross-signal for the $NH(BCy_2)_2$ compound, thereby pointing to a faster intramolecular HAT (H atom transfer) process at a generated N radical, than D abstraction from the solvent.

With these results in hand, other halogeno boranes were tested under optimized conditions. The chlorocatecholborane did not lead to formation of any NH_4^+ after hydrolysis (entry 23), which implies, in accord with earlier reports,^[28] that the B-B bond forming

process is favored over that of the N-B bond. On the other hand, two other dialkylchloroborane were used successfully to achieve this transformation. Using DIP-Cl under the standard conditions used in entry 2 resulted in the formation of NH_4^+ in 28% yield (entry 24), to be compared with the 41% and 43% yields obtained under the same conditions with Cy_2BCl and Bis(bicyclo[2.2.1]-2-heptyl)chloroborane (entry 25), respectively. These results clearly bring to light the major influence of the alkyl substituents at B, an effect which will be the subject of a subsequent study.

EPR monitoring: evidence of organic radical formation

The proposed reaction scheme, involving formation of organic radicals, was further confirmed by EPR measurements (X band) carried out either at room temperature or at 110 K. The samples were prepared under the same conditions as above, i.e., in a dedicated glove box under N_2 , upon mixing at room temperature under vigorous stirring Cy_2BCl and K in dry THF (entry 17). EPR analyses were conducted on aliquots collected at different reaction times. The spectra collected after 90, 150 and 210 minutes of stirring are shown in Figure 2.

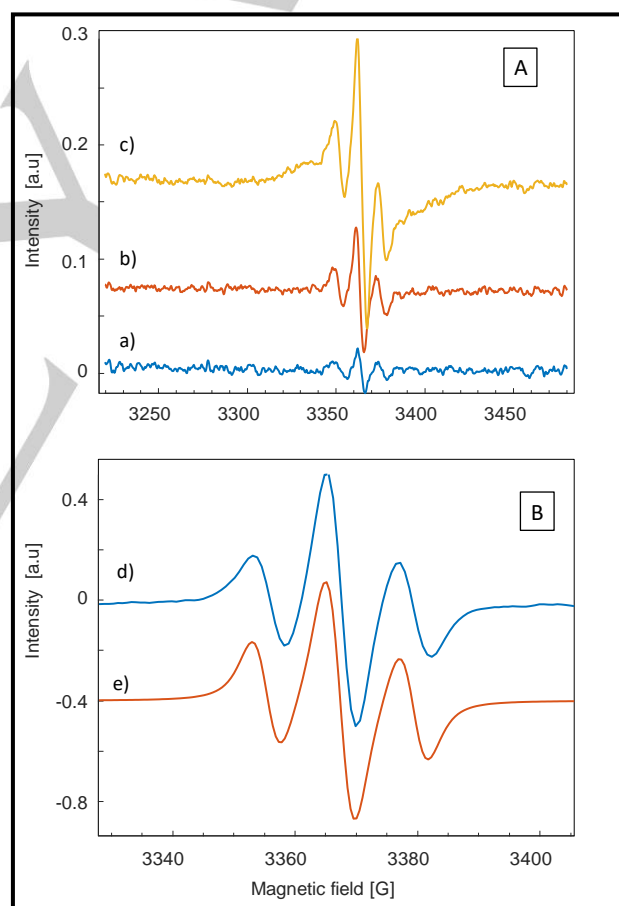


Figure 2. EPR spectra recorded at RT after stirring a mixture of Cy_2BCl/K in THF under N_2 for a) 90; b) 150; c) 210 minutes. d) Experimental spectrum recorded at 110 K after 4h of stirring; e) simulated spectrum using easyspin (Matlab toolbox).

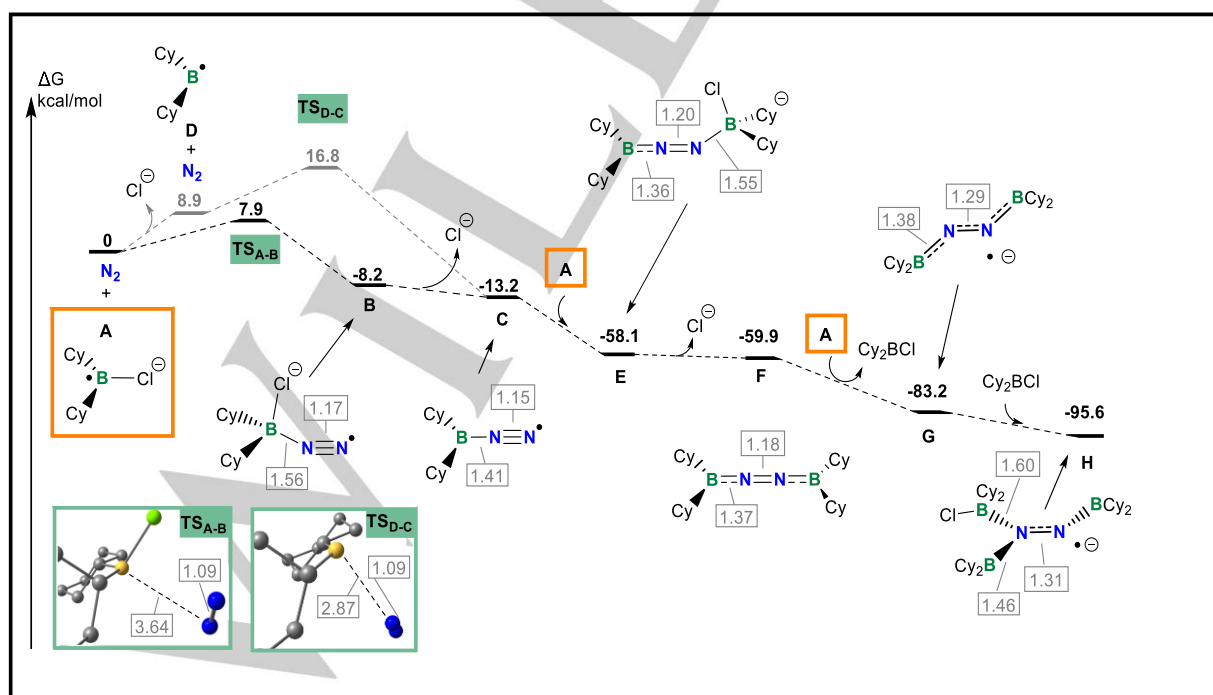
The spectra in Fig. 2.A reveal that stable organic radical(s) accumulate in solution after one hour of reaction. At first sight, those spectra seem to consist of three lines of relative intensity: 1/2/1. Further studies on longer reaction times, however, revealed

RESEARCH ARTICLE

that the intensity of the central signal at $g=2.0034$ increases more rapidly than the two peripheral ones. This outcome is consistent with the conclusion that the apparent triplet developing over time in fact results from the presence of at least two different organic radicals. We also found that the temperature (RT vs 110 K) of the resonator has only a limited effect on the number, shape and relative intensity of those signals and that those signals eventually disappear over time. Key insights into the nature of the radicals involved in solution were provided by simulation of the experimental data. The three-line signal showing a large peak-to-peak line width could be readily simulated with a 1:1:1 triplet at $g=2.0036$ attributed to a ^{14}N ($I=1$)-centered radical featuring a hyperfine constant, $a_{\text{N}}=11.8$ G (see Figure S25, ESI).^[30] The broad and unsmooth character of the experimental lines (Figure 2) is, moreover, consistent with the existence of low, superhyperfine, and thus unresolved, interactions ($<1\text{G}$) with surrounding hydrogen atoms. Such features could correspond to the computed intermediate radicals **I**, or more likely **M** proposed in Figure 3 (vide infra). Attributing the additional central singlet at $g=2.0039$ remains hypothetical at this stage. Based on relevant previous studies involving similar organic radicals,^[31-35] we propose an attribution of that additional signal either to a C- or B-centered radicals featuring low, and thus unresolved, hyperfine coupling constants ($|I[\text{B}^{11}]=3/2$, $|I[\text{B}^{10}]=3$). This attribution was further supported by EPR measurements performed under an Ar atmosphere. In the absence of N_2 , we found that the colorless solution remains EPR silent until a brown red color appears leading to the development of one intense singlet signal at $g=2.0037$ (see fig. S26, ESI) consistent with the formation of the radical discussed above. Taken together, these measurements provide unambiguous evidence supporting the existence of *in-situ* generated organic radicals, most notably nitrogen-centered species as intermediates in the direct chemical reduction of Cy_2BCl by K in THF under N_2 .

DFT calculations: reaction mechanism

To shed light on the reaction mechanism, DFT calculations were carried out. Only the lowest energy pathway leading to $\text{N}(\text{BCy}_2)_3$ is presented here. Not surprisingly, in light of the poor Lewis basic properties of N_2 , attempts to locate an adduct with Cy_2BCl failed. The reactivity between N_2 and the reduced radical anion Cy_2BCl^- (**A**), generated through one-electron reduction of Cy_2BCl by potassium, was investigated (Figure 3). Two pathways were computed from **A**: coordination of N_2 vs Cl^- elimination. The latter pathway is kinetically unfavorable ($\Delta\Delta G^\ddagger = 8.9$ kcal.mol $^{-1}$), as depicted in Figure 3. A transition state **TS_{A-B}** for N_2 coordination was located at $\Delta G^\ddagger = 7.9$ kcal.mol $^{-1}$ above **A**. N_2 coordination is exoergic ($\Delta G = -8.2$ kcal.mol $^{-1}$) and leads to the radical anion **B** with a clear nitrogen-boron interaction ($\text{N-B} = 1.558$ Å). Upon dinitrogen coordination to **A**, the N-N bond elongates from 1.097 Å to 1.174 Å. Analysis of the electronic structure of **B** indicates that the N-B bond results from the donation of the B-centered electron into one π^* orbital of N_2 , in agreement with the elongation of the N-N bond upon coordination. Dissociation of Cl^- from **B** to form the radical $\text{Cy}_2\text{BNN}^\cdot$ **C** is computed to be a favorable pathway ($\Delta G = -5.0$ kcal.mol $^{-1}$), resulting in an even shorter N-B bond (1.413 Å). In **C**, the spin density has significant weight on the terminal nitrogen atom (see Figure S27). Therefore, the creation of a second B-N bond upon interaction with the radical anion **A**, is computed to be strongly exoergic ($\Delta G = -44.9$ kcal.mol $^{-1}$) to form **E**. Diazene **F**, the result of a two-electron reduction of N_2 with concomitant formation of two N-B bonds, is obtained upon chloride dissociation from **E**. These two electrons have populated one π^* orbital on N_2 and, due to the unsaturated nature of boron, a two-electron delocalized π -type interaction develops between the B-N-N-B atoms. This interaction is illustrated by the linear geometry for the four atoms with rather short B-N bonds, an elongated N-N bond ($\text{B-N} = 1.37$ Å and $\text{N-N} = 1.18$ Å; $\text{N-N} = 1.25$ Å in free H_2N_2) and the nature of the HOMO (see Figure S30).^[36]



RESEARCH ARTICLE

Figure 3: Computed pathway: the energies are relative to "6 A + N₂". Addition of A (Cy₂BCl^{•-}) to N₂ up to the formation of three N-B bonds (compound H, three-electron reduction of N₂). Note that the energy positioning of the various species does not take into account any potential stabilizing interactions developing between K⁺ and Cl⁻ in the experimental situation.

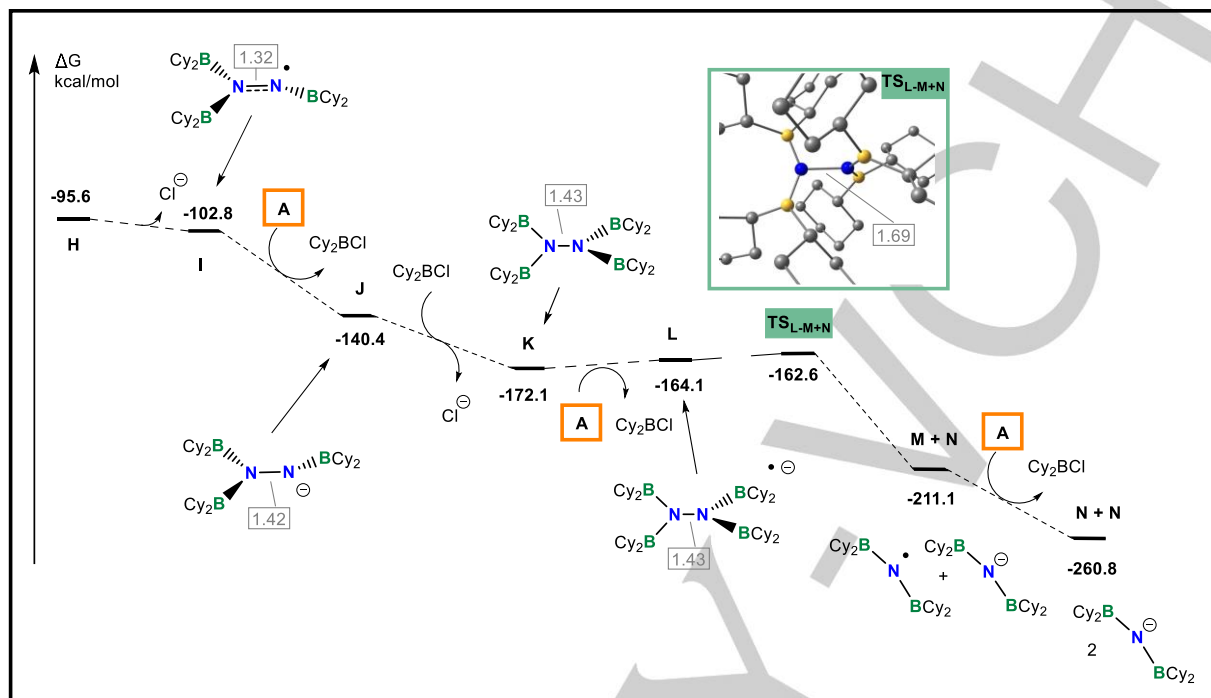


Figure 4: Computed pathway: the energies are relative to "6 A + N₂". Functionalization to the hydrazine (Cy₂B)₂NN(BCy₂)₂ derivative (K) followed by reductive NN bond splitting process leading to bis-borylamide N.

One-electron reduction of F by A populates the remaining N₂-centered π* orbital in an exoergic process ($\Delta G = -23.3 \text{ kcal.mol}^{-1}$) to yield the radical anion G featuring a zig-zag geometry for the B-N-N-B linkage (B-N = 1.380 Å, N-N = 1.284 Å and B-N-N = 136.5°). Coordination of Cy₂BCl affords the radical anion H ($\Delta G = -12.4 \text{ kcal.mol}^{-1}$), from which chloride readily dissociates to yield the neutral radical I featuring three N-B bonds. A strongly exoergic ($\Delta G = -37.6 \text{ kcal.mol}^{-1}$) one-electron reduction of I by A populates the π* orbital between the two nitrogen atoms and yields the anionic system J (Figure 4) featuring an N-centered lone pair on the nitrogen with only one N-B bond (see Figure S31). Subsequent nucleophilic substitution at Cy₂BCl ($\Delta G = -31.7 \text{ kcal.mol}^{-1}$) forms the four boron-substituted hydrazine K.

The bond-dissociation energy of the N-N bond in hydrazine K is 46.1 kcal.mol⁻¹; reduction is required for subsequent N-N bond breaking. Thus, one-electron reduction of K by A is computed also to be endoergic but by only $\Delta G = 8.0 \text{ kcal.mol}^{-1}$ to yield L. The transition state TS_{L-M+N} associated with N-N bond cleavage is computed with a very small activation barrier ($\Delta G^\ddagger = 1.5 \text{ kcal.mol}^{-1}$) to form the radical (Cy₂B)₂N[•] M and the anion (Cy₂B)₂N⁻ (N) with $\Delta G = -47.0 \text{ kcal.mol}^{-1}$. The one-electron reduction of M by A to form N and Cy₂BCl is computed to be strongly exoergic ($\Delta G = -49.7 \text{ kcal.mol}^{-1}$). This step concludes the six-electron reduction of N₂ to form two equivalents of the anion N. This boron-substituted amide features a linear geometry with two perpendicular B-N π-orbitals similar to the allene structure. Finally, tris-borylamine N(BCy₂)₃ P is formed by a nucleophilic substitution between N and Cy₂BCl (Figure S32).

In summary, these computations highlight the facile and favorable coordination of N₂ to the Cy₂BCl radical anion A obtained by one-electron reduction by K, as the first and crucial step in the functionalization process. Notably, coordination of N₂ to this radical anion prior to chloride elimination appears to be kinetically preferred over the reverse process. The overall transformation is strongly exoergic because of the high reactivity of the radical anion A, Cy₂BCl^{•-}.

Having rationalized the formation of N(BCy₂)₃, as well as NH(BCy₂)₂ (Figure S34), the competing formation of BH-containing byproducts required investigation. The intramolecular H migration from the cyclohexyl to B was thus computed (Figure S33). In accordance with the literature,^[28] this migration proved both facile and thermodynamically favorable. The lowest energy pathway was found via the generation of the radical Cy₂B[•] D. The transition state was found to be only 13.3 kcal.mol⁻¹ higher than Cy₂B[•], and thus 22.2 kcal.mol⁻¹ above A, readily accessible at room temperature. The resulting C-centered radical is computed at -18.5 kcal.mol⁻¹ relative to D (-9.6 kcal.mol⁻¹ vs A). Most importantly, the addition of N₂ to the *in-situ* generated R₂BCl radical anion A to form the first BN bond is lower in energy than the competing HAT from the neighboring Cy to B that creates the BH bond leading to side-product formation. This kinetic preference is crucial in the successful N₂ functionalization.

Conclusion

In conclusion, we present the first successful functionalization of N₂ using boron-centered radicals, at room temperature and low pressures (from one atmosphere). These radicals are efficiently generated *in situ* by reduction of the corresponding, readily available chloroborane derivatives. We believe that these results open new avenues to N₂ functionalization notably different from the high-energy heterogeneous HB process and the bio-inspired homogeneous transformations. These findings could drastically affect the carbon footprint of ammonia production and pave the way for new applications for ammonia, particularly in renewable energy storage and the hydrogen economy.^[37]

See Supporting Information for experimental section, characterization data, spectra, as well as EPR measurements and DFT calculations (details of computations, mechanisms leading to NH and BH bond formations).

Acknowledgements

Financial support from CNRS and Université de Toulouse is acknowledged. CALMIP is gratefully acknowledged for access to supercomputing facilities. C.B. wishes to thank the “région Auvergne-Rhône-Alpes” for financial support. The NMR service of the ICT is gratefully acknowledged, as well as Mrs. C. Absalon for LIFDI MS analysis. We thank T. Personeni for preparing samples for EPR experiments and Dr. W. Schipper from SWAN-H for insightful discussions.

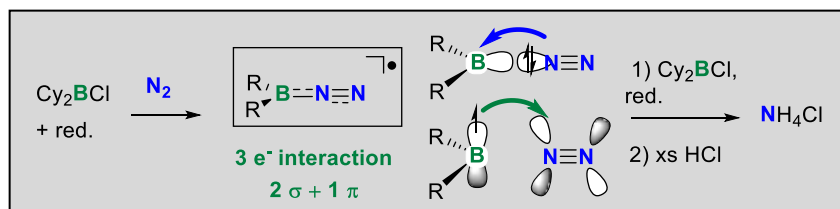
Keywords: N₂ fixation • Boron radical • Reduction • density-functional calculations • Reaction mechanisms

- [1] Ammonia production worldwide 2020 | Statista, (available at <https://www-statista-com/statistics/1266378/global-ammonia-production/>).
- [2] R. H. Dolan, J. E. Anderson, T. J. Wallington, *Sustainable Energy & Fuels* **2021**, *5*, 4830–4841.
- [3] R. Lan, S. Tao, Ammonia as a suitable fuel for fuel cells. *Frontiers in Energy Research* **2014**, *2*, 35.
- [4] Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co. KGaA, **2000**.
- [5] G. Ertl, *Angew. Chem. Int. Ed.* **2008**, *47*, 3524–3535.
- [6] M. Capdevila-Cortada, *Nature Cat.* **2019**, *2*, 1055–1055.
- [7] A. E. Yüzbasıoğlu, A. H. Tatarhan, A. O. Gezerman, *Heliyon* **2021**, *7*, e08257.
- [8] R. F. Service, *Science* **2018**, doi: 10.1126/science.aau7489.
- [9] Y. Nishibayashi, *Transition Metal-Dinitrogen Complexes, Preparation and Reactivity*, (Wiley-VCH, Weinheim), **2019**.
- [10] C. E. Laplaza, C. C. Cummins, *Science* **1995**, *268*, 861–863.

- [11] J. J. Curley, T. R. Cook, S. Y. Reece, P. Müller, C. C. Cummins, *J. Am. Chem. Soc.* **2008**, *130*, 9394–9405.
- [12] T. J. Hebden, R. R. Schrock, M. K. Takase, P. Müller, *Chem. Commun.* **2012**, *48*, 1851–1853.
- [13] I. Klopsch, M. Finger, C. Würtele, B. Milde, D. B. Werz, S. Schneider, *J. Am. Chem. Soc.* **2014**, *136*, 6881–6883.
- [14] Q. Liao, N. Saffon-Merceron, N. Mézailles, *ACS Catal.* **2015**, *5*, 6902–6906.
- [15] Y. Tanabe, Y. Nishibayashi, *Chem. Soc. Rev.* **2021**, *50*, 5201–5242.
- [16] N. Mézailles, *Comprehensive Coord. Chem. III.* **2021**, 875–958.
- [17] M. J. Chalkley, M. W. Drover, J. C. Peters, *Chem. Rev.* **2020**, *120*, 5582–5636.
- [18] M. A. Légaré, G. Bélanger-Chabot, R. D. Dewhurst, E. Welz, I. Krummenacher, B. Engels, H. Braunschweig, *Science* **2018**, *359*, 896–900.
- [19] M. A. Légaré, M. Rang, G. Bélanger-Chabot, J. I. Schweizer, I. Krummenacher, R. Bertermann, M. Arrowsmith, M. C. Holthausen, H. Braunschweig, *Science* **2019**, *363*, 1329–1332.
- [20] M. A. Légaré, G. Bélanger-Chabot, M. Rang, R. D. Dewhurst, I. Krummenacher, R. Bertermann, H. Braunschweig, *Nature Chem.* **2020**, *12*, 1076–1080.
- [21] J. G. Andino, S. Mazumder, K. Pal, K. G. Caulton, *Angew. Chem. Int. Ed.* **2013**, *52*, 4726–4732.
- [22] L. Li, Z. Wu, H. Zhu, G. H. Robinson, Y. Xie, H. F. Schaefer, *J. Am. Chem. Soc.* **2020**, *142*, 6244–6250.
- [23] A. E. Shilov, *Russ. Chem. Bull.* **2003**, *52*, 2555–2562.
- [24] C. Ling, X. Niu, Q. Li, A. Du, J. Wang, *J. Am. Chem. Soc.* **2018**, *140*, 14161–14168.
- [25] Note: while this work was finalized an article evaluating by DFT calculations the reactivity of B radicals on N₂ was published. J. Zeng, S. Dong, C. Dai, J. Zhu, *Inorg. Chem.* **2022**, *61*, 2234–2241.
- [26a-c] for recent syntheses of B-B derivatives by reduction see for ex. a) A. Hübner, M. Bolte, H.-W. Lerner, M. Wagner *Angew. Chem. Int. Ed.* **2014**, *53*, 10408–10411. b) J. Gilmer, H. Budy, T. Kaese, M. Bolte, H.-W. Lerner, M. Wagner *Angew. Chem. Int. Ed.* **2020**, *59*, 5621–5625. c) T. Trageser, M. Bolte, H.-W. Lerner, M. Wagner *Angew. Chem. Int. Ed.* **2020**, *59*, 7726–7731.
- [27] W. J. Grigsby, P. P. Power, *J. Am. Chem. Soc.* **1996**, *118*, 7981–7988.
- [28] N. R. Anastasi, K. M. Waltz, W. L. Weerakoon, J. F. Hartwig, *Organometallics* **2003**, *22*, 365–369.
- [29] Von Dr. R. Koster und Dr. G. Benedikt, *Angew. Chem.* **1963**, *75*, 346.
- Note: in this article, reduction of a R₂BCl is reported to yield RR'BH compounds, yet it is not mentioned if the reactions were performed under N₂ or Ar.
- [30] Y. Miura, A. Tanaka, K. Hirotsu, *J. Org. Chem.* **1991**, *56*, 6638–6643.
- [31] S. S. Asami, S. Ishida, T. Iwamoto, K. Suzuki, M. Yamashita, *Angew. Chem. Int. Ed.* **2017**, *56*, 1658–1662.
- [32] A. Maiti, F. Zhang, I. Krummenacher, M. Bhattacharyya, S. Mehta, M. Moos, C. Lambert, B. Engels, A. Mondal, H. Braunschweig, P. Ravat, A. Jana, *J. Am. Chem. Soc.* **2021**, *143*, 3687–3692.
- [33] P. Bissinger, H. Braunschweig, A. Damme, T. Kupfer, I. Krummenacher, A. Vargas, *Angew. Chem. Int. Ed.* **2014**, *53*, 5689–5693.
- [34] P. Bissinger, H. Braunschweig, A. Damme, I. Krummenacher, A. K. Phukan, K. Radacki, S. Sugawara, *Angew. Chem. Int. Ed.* **2014**, *53*, 7360–7363.
- [35] P. Bissinger, H. Braunschweig, A. Damme, C. Hörl, I. Krummenacher, T. Kupfer, *Angew. Chem. Int. Ed.* **2015**, *54*, 359–362.
- [36] S. J. K. Forrest, B. Schluschaß, E. Y. Yuzik-Klimova, S. Schneider, *Chem. Rev.* **2021**, *121*, 6522–6587.
- [37] A patent based on the present work was filed on May 20, 2021 by S. Bennaamane and N. Mézailles under the number: FR2105295.

Entry for the Table of Contents

Insert graphic for Table of Contents here.



Boron-centered radicals, generated by reduction of R_2BCl derivatives, react with N_2 all the way to borylamine formation. DFT calculations rationalize the reduction/functionalization process, involving N-N bond splitting. Hydrolysis of the mixture yields NH_4^+ . Radical addition to N_2 provides a new strategy for N_2 fixation.

Twitter: @LhfaShen