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Authors: Heinz Berke, Smair Barman, Arndt Remhof, Ralph Koitz, Marcella Iannuzzi, Olivier Blacque, Yigang Yan, Thomas Fox, Jürg Hutter, and Andreas Züttel

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Post-synthesis amine borane functionalization of metal-organic framework and its unusual chemical hydrogen release phenomenon

Samir Barman,^{[a],[b]} Arndt Remhof,^[c] Ralph Koitz,^[a] Marcella Iannuzzi,^[a] Olivier Blacque,^[a] Yigang Yan,^{[c],[d]} Thomas Fox,^[a] Jürg Hutter,^[a] Andreas Züttel^{[c],[e]} and Heinz Berke*^[a]

Dedicated to Roald Hoffmann on the occasion of his 80th birthday especially acknowledging with this contribution his EHT based theoretical work of 1964 on boron, nitrogen compounds

We report a novel strategy for post-synthesis amine borane functionalization of MOFs under gas-solid phase transformation utilizing gaseous diborane. The covalently confined amine borane derivative decorated on the framework backbone is stable when preserved at low temperature, but spontaneously liberates soft chemical hydrogen at room temperature leading to the development of an unusual borenium type species ($-\text{NH}=\text{BH}_2^+$) ion-paired with hydroborate anion. Furthermore, the unsaturated amino borane ($-\text{NH}=\text{BH}_2$) and the α -iminodiborane ($-\alpha\text{-NHB}_2\text{H}_5$) were detected as final products. A combination of DFT based molecular dynamics simulations and solid state NMR spectroscopy, utilizing isotopically enriched materials, were undertaken to unequivocally elucidate the mechanistic pathways for H_2 liberation.

Metal-organic frameworks (MOFs) are hybrid organic-inorganic materials whose pore size, shape and functionalities can be tuned amenably through judicious selection of organic linkers.¹ MOFs are the subject of intense research due to their enormous potential applications.² Concomitant development of post-synthetic modification (PSM) strategies further enriched the possibilities to immobilize versatile functional entities with unique physical and chemical properties that are difficult to achieve under typical one-pot MOF synthesis conditions.³ Successful PSMs are accomplished *via* photochemical, thermal and synthetic transformation routes to obtain desired functional units while preserving framework integrity.³ Here we disclose an unique modification approach for a rapid post-synthetic amine borane functionalization of MOFs using gaseous diborane (B_2H_6). The

incorporation of amine borane functionalities in a MOF backbone is the first example of a novel method of post-synthetic modification by gas-solid phase reactions, which opens new possibilities to manipulate the chemistry of MOFs towards the development of new functional materials. Particularly, in this contribution we demonstrate a unique strategy for post-synthesis amine borane derivatization of the activated DMOF-1- NH_2 ⁴ under gas-solid phase transformation and a full characterization of the modified materials with the aid of infrared, UV-Vis, elemental microanalysis, and solid state NMR (SS NMR) spectroscopy. To our surprise, the covalently bonded amine borane derivatives of the modified material (designated DMOF-1- NH_2BH_3 here after) are found to liberate chemical H_2 at room temperature. This is evidence for chemical hydrogen desorption at unusually low temperature, as compared to pristine ammonia borane under physically confined state in the pore of solid supports.⁵ Some mechanistic insight based on density functional theory (DFT) calculations⁶ and SS ^{11}B and ^{15}N NMR spectroscopic studies, performed on isotopically labelled analogue of DMOF- NH_2BH_3 , are discussed. Which allowed us to comprehend a plausible hydrogen release pathways and their effect on the overall transformation of the framework material.

We succeeded to perform single crystal X-ray diffraction analysis of the guest free (activated) DMOF-1- NH_2 ,⁷ which reveals a similar framework connectivity (Figure 1a) as reported for its as-prepared form, but the tetragonal space group changes from $I4/mmm$ to $P4/mmm$ (See Section S3, SI for detail).⁴

To accomplish the desired amine borane functionalization, we strived to carry out the gas-solid phase reactions between the

- [a] Dr. S. Barman, Dr. R. Koitz, Dr. M. Iannuzzi, Dr. O. Blacque, Dr. T. Fox, Prof. J. Hutter, Prof. H. Berke
Chemisches Institut, Universität Zurich, Winterthurerstrasse 190, CH-8057, Zurich (Switzerland). Fax: (+41) 44 635-6802; E-mail: hberke@chem.uzh.ch
- [b] Present address: Physical Sciences and Engineering, KAUST Catalysis Center, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia
- [c] Dr. A. Remhof, Dr. Y. Yan, Prof. A. Züttel
Empa, Materials Sciences and Technology Department of Mobility, Überlandstrasse 129, 8600 Dübendorf (Switzerland)
- [d] Present address: Interdisciplinary Nanoscience Center (iNANO), Aarhus University, DK-8000 Aarhus C, Denmark.
- [e] Present address: EPFL Valais Wallis, EPFL SB ISIC LMER, Rue de l'Industrie 17, CH-1951 Sion (Switzerland)
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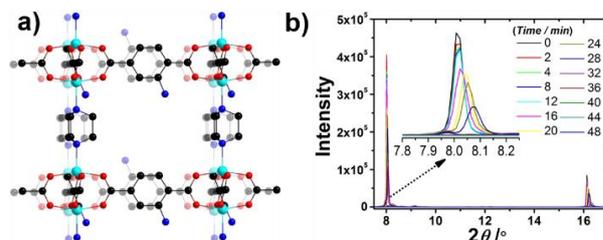


Figure 1. a), partial view of the single crystal X-ray structure of activated DMOF-1- NH_2 consisting of the DABCO pillared cuboid cages. The dicarboxylate linkers are disordered and only one of the possible conformations is shown. Atom colors: Zn, aqua; O, red; C, gray; N, blue. Hydrogen atoms are omitted for clarity. b), Time dependent *in situ* PXRD investigation of the stability of DMOF-1- NH_2 under gaseous $\text{H}_2/\text{B}_2\text{H}_6$ (2 bar) at room temperature. The inset magnified portion of the figure emphasizes the change in the selected peak position with diborane exposure time.

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activated DMOF-1-NH₂ (Figure 1a) and B₂H₆. The diborane source was prepared from the decomposition of LiZn₂(BH₄)₅ as described in the literature (Section S2, SI).⁸ Initial attempts to derivatize the pendant amine groups of DMOF-1-NH₂ with .BH₃ units employing an excess of diborane and at higher temperatures resulted in the loss of structural coherence as evidenced by powder X-ray diffraction (PXRD) analysis (Figure S6, SI). Therefore, to investigate the structural response of activated DMOF-1-NH₂ to B₂H₆ exposure in detail, we carried out room temperature *in situ* PXRD experiments (See Figure S5, SI for a schematic sketch of the setup). The obtained results are depicted in Figure 1b, which clearly reveals that increasing diborane exposure time induces a shift of the indicated PXRD reflections to higher angles along with a gradual decrease in intensity. This suggests shrinking of the lattice parameters before collapse of the framework occurs at about 30 min of diborane exposure.

A first indication of the successful modification is a distinct colour change (Figure 2). When the activated DMOF-1-NH₂ was exposed to diborane atmosphere at room temperature for 15 min (see Section S2, SI for synthetic details), an intense colour change of the materials became visible (shifted UV-vis absorptions, see spectra in Figure S3, SI). Thus, yellowish crystals of activated DMOF-1-NH₂ (Figure 2a) changed to bright yellow for DMOF-1-NH₂BH₃ (Figure 2b) with no noticeable change in the PXRD patterns (Figure S7, SI). Elemental analysis study indicates a Zn, N and B percent content of 20.02%wt, 9.11%wt and 3.55%wt respectively, which corresponds to a N/Zn and B/Zn molar ratio of 2.12 and 1.07 (theoretical: 2.0 and 1.0). These results suggest a quantitative reaction between the pendant amine groups and the -BH₃ moieties.

The FT-IR spectrum of DMOF-1-NH₂BH₃ clearly indicated covalent binding of the incorporated .BH₃ group by the appearance of several new and strong bands (Figure 2c). The characteristic band at 2377 cm⁻¹ with two shoulders at 2325 and 2273 cm⁻¹ were identified as B-H antisymmetric and symmetric stretching frequencies, respectively. The symmetric $\chi_{(B-H)}$ vibration appears at 1167 cm⁻¹. To further corroborate these assignments, a deuterium analogue, DMOF-1-NH₂BD₃, was prepared (Section S2, SI) and studied by FT-IR spectroscopy. As expected, for DMOF-1-NH₂BD₃, no bands were observed in the wavelength range of 2273-2377 cm⁻¹ and the band at 1167 cm⁻¹ was also absent, instead, a new characteristic infrared band

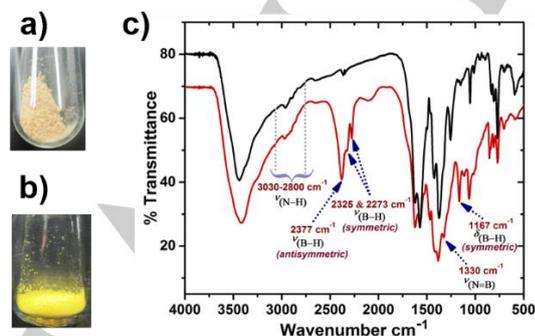


Figure 2. Photo of activated DMOF-1-NH₂ (a) and freshly prepared DMOF-1-NH₂BH₃ (b). c), The FT-IR spectra of activated DMOF-1-NH₂ (red) and as-prepared DMOF-1-NH₂BH₃ (black).

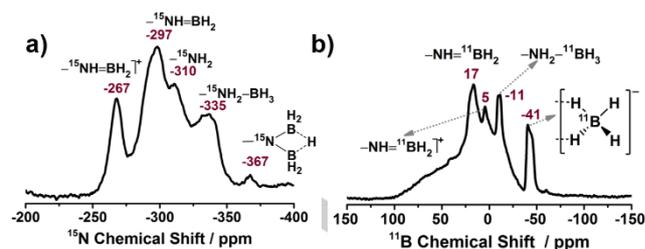


Figure 3. a), the room temperature solid state ¹⁵N CP/MAS NMR spectrum of DMOF-1-¹⁵NH₂BD₃; b), the room temperature solid state ¹¹B MAS NMR spectrum of DMOF-1-NH₂BH₃.

appeared at 1784 cm⁻¹ ascribable to the covalently bonded B-D vibration (Figure S8, SI). Surprisingly, the IR spectrum of DMOF-1-NH₂BH₃ further displayed bands at 1330 cm⁻¹ (Figure 2c), attributable to the N-B⁹ stretching vibration; indicating by this band a state of the sample with some subsequent chemical transformations demonstrated also by the solid state NMR spectra (*vide infra*). The amine borane groups have partially depleted in H atom content forming amino borane functional groups. Indeed, quite interestingly, when the freshly prepared bright yellow DMOF-1-NH₂BH₃ was stored at room temperature under nitrogen atmosphere, a second colour change (Figure S2, SI) of the crystalline material occurred accompanied by a slow spontaneous and soft chemical release of H₂ (confirmed by GC-TCD analyses, see section S7 and Figure S9 for details) was ascertained. Successive PXRD analyses of the hydrogen desorbed materials of DMOF-1-NH₂BH₃ obtained at different time intervals at room temperature indicated a slow partial loss of the framework integrity. However, the process can be stopped by preserving the as-prepared material at lower temperatures

To gain insight into the reaction mechanism involving the unusual low temperature H₂ release, we performed room temperature SS ¹⁵N CP/MAS measurements using the isotopically labelled material DMOF-1-¹⁵NH₂BD₃ (see Section S2 for preparation). This study was further supported by room temperature SS ¹¹B NMR measurements performed on DMOF-1-NH₂BH₃. In line with the suppositions as featured in the infrared spectrum (Figure 2c), the ¹⁵N and ¹¹B NMR spectrum (Figure 3a and 3b) also exhibited unexpectedly complicated spectral features. In both cases four clearly identifiable broad resonances spanning between -267 ppm to -335 ppm for ¹⁵N NMR and between 17 ppm to -41 ppm for ¹¹B NMR were observed. The intense ¹⁵N resonance at -297 ppm (Figure 3a) was assigned to a tricoordinate nitrogen site .NH=BD₂ generated by liberation of one molecule of HD from the amine borane species.¹⁰ The corresponding ¹¹B resonance for .NH=BD₂ functional moiety was assigned to the most downfield shifted signal resonating at 17 ppm (Figure 3b) based on solution NMR data of related structural units.^{10,11} Considering this assignment we believe that the ¹⁵N NMR signal appearing at -335 ppm is due to the pristine amine borane substituents (-NH₂BD₃). The ¹¹B signal for the -NH₂BH₃ unit could be assigned at -11 ppm; again both signals (¹⁵N and ¹¹B NMR) appear in the chemical shift range of amine boranes in solution.^{11b,12,13} The most down field shifted ¹⁵N NMR signal at -267 ppm (Figure 3a) was attributed to the development of a species with a trivalent nitrogen site

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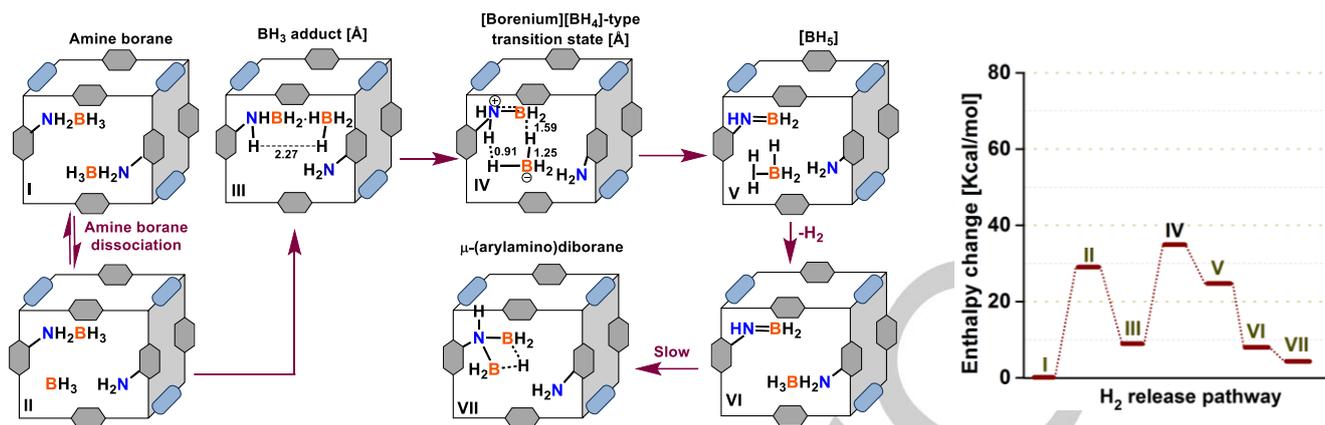


Figure 4. A schematic sketch of the proposed mechanism for the release of chemical hydrogen from DMOF-1-NH₂BH₃ at room temperature (left) proceeding along a proposed energy profile diagram of the chemical hydrogen release from DMOF-1-NH₂BH₃ at room temperature using the notations of the mechanistic sketch (right).

constituting an adduct of BH₃ to the amine borane at a H_B atom. This unexpected adduct possesses secondary type bonds: a more or less symmetric B^{δ+}H^{δ-}B^{δ-}H^{δ+} bond and according to the DFT calculations also a dihydrogen bond (H(X⁺)^{δ+}H(X⁻), 2.27 Å) (Figure S13, SI)^{14d} approaching the structure of an amine stabilized borenium hydroborate molecular unit. The ¹⁵N signals of borenium cations cover a great range of chemical shifts due to the variability of the stabilizing base. For the BH₃ adduct the ¹⁵N resonance was attributed to the signal at -267 ppm. The ¹¹B resonance of the borenium part was assigned to a signal at 5 ppm and the hydroborate part of the BH₃ adduct was attributed to the signal at -41 ppm¹⁵ in an upfield chemical shift range related to [BH₄]⁻ units. DFT calculations for free [BH₄]⁻ caged in the MOF gave a ¹¹B resonance at 37 ppm. The arylamine species are anticipated to correspond to a ¹⁵N signal at around -310 ppm,¹⁶ The small ¹⁵N resonance at 367 ppm is suggested to belong to an amino diborane moiety (·NHB₂D₅), which is reported to be a species stable at room temperature^{11b,c}. The corresponding ¹¹B resonance for this moiety would be expected to appear - also as a signal of low intensity - at around 20 ppm^{11c}, which however became not visible presumably being buried under the left tailing of the broad amine borane resonance (Figure 3b).

We then attempted DFT based molecular dynamics simulations of DMOF-1-NH₂-BH₃ to acquire information about the stable and transient MOF attached species involved in the dehydrogenation process. It should be noted at this point that the first quantum mechanical study (Extended Hückel Theory (EHT)) on free boron, nitrogen molecules, including an evaluation of ammonia borane and amino borane, was carried out by Roald Hoffmann in 1964. It was extraordinary and pioneering work within the boron, nitrogen chemistry and within the field of quantum chemistry as a whole¹⁷. Our study stands in direct chemical relationship to Roald Hoffmann's work considering that comparable B,N fragmental molecules attached to the MOF framework are analysed.

Our DFT studies were performed on a cut-off of the DMOF-1-NH₂-BH₃ framework (see details in SI, Section S8). If not noted

otherwise these were conducted at a simulation temperature of 0 K optimizing several configurations containing the possible functional units. The starting system for the simulation contained a DMOF-1-NH₂ partial cage with 16 linker amine groups (4 at each Zn corner, model displayed in the SI, Figure S10), where 8 amine groups were functionalized by BH₃ corresponding to 50% of the available binding sites. The following steps along the proposed process were prepared by modifying the coordinates accordingly. Each guessed structure has been fully relaxed by the geometry optimization at the PBE-rVV10 level of theory¹⁸. Further details about the computational set-up are provided in the SI.

Based on the experimental NMR results, we propose a multi-step reaction course with stable species (Figure 4, left), which could be further complemented particularly in search for transient species by ab initio molecular dynamics simulations (MD)¹⁹. Based on the DFT calculations (Figure 4, right) illustrates an overall energy profile diagram for the important stable species and short-lived intermediates that underlines the computed energy differences. The initial step of the amine borane dehydrogenation is the equilibrium loss of a BH₃ group (see I and II, Figure 4, left). BH₃ is furthermore assumed to possess high mobility within the MOF lattice adding to a H_B atom of the amine borane moiety to form III (Figure 4 and calculated fragmental ball-and-stick plot S13 SI). III turned out to be remarkably stable as revealed by MD/DFT calculations at 300 K. Facile equilibrium dissociation of BH₃ from an amine borane seems reasonable, since the T₀ of aniline-type amine groups are weak Lewis bases, particularly because they are substituted by electron withdrawing metal-carboxylate groups making these amino groups even weaker Lewis bases than the Lewis base aniline expressed by the low aniline basicity with a pK_b (H₂O) of 9.42²⁰. III gains stabilization by a secondary bond of dihydrogen bonding (H(X⁺)^{δ+}H(X⁻), 2.27 Å) and a more or less symmetric B^{δ+}H^{δ-}B^{δ-}H^{δ+} bridging bond (stick and ball sketch S13, SI). Moving further on the reaction coordinate III approaches in its structure the molecular unit of IV (Figure 4, left) to be viewed as composed of an amine stabilized borenium cation and a hydroborate anion held together by tight ion pairing. According to

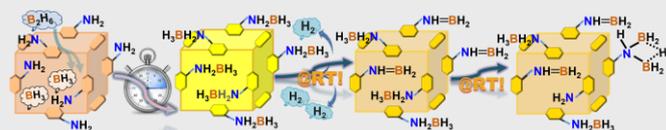
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Post-synthesis amine borane functionalization of metal-organic framework and its unusual chemical hydrogen release phenomenon

Rapid chemical tuning: Novel strategy for rapid post-functionalization of MOFs under gas-solid phase reaction conditions by diborane is revealed, which paves the way to chemically tune surface adorned pendant amine groups with amine borane functionalities confined in the MOF framework exhibiting unusual chemical/physical attributes. Thus, promoting at ambient conditions H_2 evolution and generation of H_2 -containing species.