Metal–Organic Frameworks

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Magnesium Borohydride Confined in a Metal–Organic Framework: A Preorganized System for Facile Arene Hydroboration**

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Confinement of a reactive moiety in the extended structure of a metal–organic framework (MOF) can considerably enhance the stability of otherwise inaccessible or short-lived species.[1–3] Conceptually, the opposite is also feasible, with framework confinement enforcing a structural arrangement that destabilizes a molecular functionality. Destabilization would be particularly beneficial for metal borohydrides ($M(BH_4)_x$), which have great potential as hydrogen-storage materials but are in general limited by undesirably high decomposition temperatures.[4–6] The addition of weak acids as stoichiometric reagents to $M(BH_4)_x$ species enables lower-temperature reactivity to proceed by relatively facile dehydrocoupling (combination of protic and hydridic hydrogen atoms). For example, $Mg(BH_4)_2$ decomposes at temperatures above 270 °C,[7] in contrast to 150 °C for $[Mg(BH_4)_2(NH_3)_2]$.[8] Invariably the extended solid-state structures of these mixed protic–hydridic species are dominated by dihydrogen bonding ($H^{\delta-}\cdots H^{\delta+}$ hydrogen-bonding interactions).[8–10] Extensive studies, particularly on aminoborane complexes,[9,11–13] have demonstrated that dihydrogen bonding markedly affects physical properties (e.g., melting temperature) and, more importantly, facilitates dehydrocoupling.[12,14,15] Our interest has focused on the generation of $[BH_4]^-$-based dihydrogen-bonded systems in which the second component of the dihydrogen bond involves the less acidic but still significantly protic hydrogen atom of a $C{-}H^{\delta+}$ bond, with the aim to investigate how $C{-}H^{\delta+}\cdots H^{\delta-}{-}B$ interactions modify the propensity for reaction of borohydride anions. Confining $M(BH_4)_x$ units in the extended structure of a MOF is an ideal method for generating dihydrogen interactions, and the resulting materials are readily accessible by simple pillaring of $M(BH_4)_x$ units with rigid polydentate amines or ethers.[16] Herein, we report our initial findings on the reactivity of a $Mg(BH_4)_2$-based MOF, the extended structure of which is comprised of extensive $C{-}H^{\delta+}\cdots H^{\delta-}{-}B$ dihydrogen bonding.

Direct combination of $Mg(BH_4)_2$[17] and pyrazine (ca. 3 equiv) in Et_2O rapidly yielded an insoluble material that was a single phase (as determined by powder X-ray diffraction, pXRD), with elemental microanalysis giving a $Mg(BH_4)_2$/pyrazine molar ratio of 1:2. Precise structural identification was forthcoming from single crystal X-ray diffraction studies, which confirmed the formation of the extended framework $[Mg(BH_4)_2(pyrazine)_2]$ (**1**). The coordination environment at the magnesium center in **1** (Figure 1 a) is pseudo-octahedral ($[BH_4]^-$ ions are treated as occupying one site), consisting of four pyrazine units coordinating in the equatorial plane and two borohydride counterions in the axial sites. Hydrogen atoms bound to carbon were placed in calculated positions, while boron-bound hydrogen atoms in **1** were located in the penultimate difference Fourier map and freely refined. The $[BH_4]^-$ ion binds in a bidentate manner (through two Mg-H-B bridges) to the Mg center. The Mg–B separation (2.675(2) Å) is long compared to $Mg(BH_4)_2$,[18,19] indicating a weakened $Mg\cdots BH_4$ interaction (consistent with reduced Lewis acidity of Mg^{2+} coordinated by four Lewis bases). The $[BH_4]^-$ ions occupying the axial magnesium sites

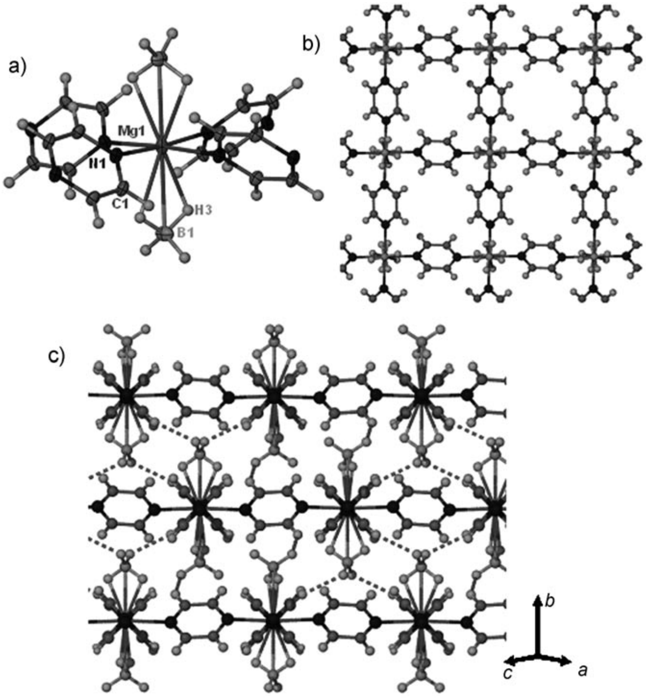

Figure 1. a) Local environment at magnesium (thermal ellipsoids at 50 % probability). b) The extended 2D layer of framework **1** showing the Mg_4py_4 square grids. c) A segment of the extended structure of **1**, the interlayer dihydrogen interactions distinguished by dashed lines.

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are terminal, and no extended Mg-[BH_4]-Mg chains are formed. The extended structure of framework **1** comprises a 2D square grid (4^4 Schläfi notation) constructed by the pillaring of adjacent $Mg(BH_4)_2$ units by pyrazines (Figure 1 b). Successive 2D layers of framework **1** are offset, with each BH_4 unit directed into a pocket constructed by {Mg_4py_4} units from the adjacent layer, generating an ABAB layered nonporous structure.[20] Adjacent 2D layers are linked by extensive dihydrogen bonding from arene C–$H^{\delta+}$ units of one layer to terminal B–$H^{\delta-}$ units of the next layer; the positive charge on the aryl C–H moiety is enhanced by pyrazine coordination to two Lewis acidic Mg^{2+} ions. The shortest H···H contact in **1**, as determined by X-ray diffraction data, is 2.24(3) Å, significantly shorter than the sum of the van der Waals radii (2.65 Å).[9] Although rare, other intermolecular examples of C–H···H–B bonding have been reported (ca. 2.25 Å).[9,21,22] The interlayer dihydrogen bond in **1** (2.24(3) Å) is also appreciably shorter than those present in the molecular analogue [$Mg(BH_4)_2$(pyridine)$_4$] (shortest C–H···H–B contact 2.595 Å),[16] thus suggesting that the extended framework structure is essential for generating these short $H^{\delta+}\cdots H^{\delta-}$ interactions.

In light of the inherent uncertainty in hydrogen positions from X-ray diffraction, a computational study was undertaken to independently verify the close $H^{\delta-}\cdots H^{\delta+}$ contacts. On optimization, DFT calculations utilizing a starting geometry based on **1** refined to a minimum-energy structure very similar to **1**.[20] The multiple interlayer C–H···H–B contacts were also observed in the optimized structure, with interlayer $H^{\delta-}\cdots H^{\delta+}$ distances of 1.812 and 2.243 Å, thus confirming the presence of the dihydrogen interactions detected by single crystal X-ray diffraction. These extensive short dihydrogen bonds assist in orienting the proximal arene rings of the adjacent layers towards the BH_4 moiety, thus generating a close arene–BH_4 arrangement (the closest interlayer C···B distance in **1** is only 3.58 Å). Thus, the extended MOF structure of **1** holds an unsaturated nucleophilic moiety (arene π electron density) in close proximity to the reducing BH_4 group.

To investigate the effect of this MOF confinement on the thermal stability of the $Mg(BH_4)_2$ groups, thermogravimetric analyses (TGA) were performed under N_2. These revealed a substantial mass loss (onset ca. 110 °C, Figure 2 a), with the largest loss between 120 and 170 °C. The large reduction in mass (greater than 25 %) intrinsically implied loss of a proportion of the organic pillaring ligand. This loss was confirmed by analysis of the volatile products (captured by condensation at 77 K), which were free of boron-containing compounds and consisted exclusively of pyrazine ($C_4N_2H_4$) and, unexpectedly, piperazine ($C_4N_2H_{10}$). The only feasible source of piperazine is the hydrogenation of pyrazine during the thermal decomposition of **1**. With analysis of the released volatiles in hand, the nonvolatile solid that remained after thermal decomposition of **1** (termed **1d**) was spectroscopically studied and found to be amorphous (pXRD, Figure 2 b). IR and ^1H–^{13}C cross-polarization magic-angle-spinning (CP/MAS) NMR spectroscopy revealed that the organic ligand in **1d** had been converted from pyrazine into predominantly piperazine (Figure 2 c, $\delta = 46.1$ ppm). Piperazine present in **1d** is assigned to be in its deprotonated diamide form by the absence of N–H stretches in the IR spectrum (Figure 2 f). No stretches were observed in the B–H region of the IR spectra,

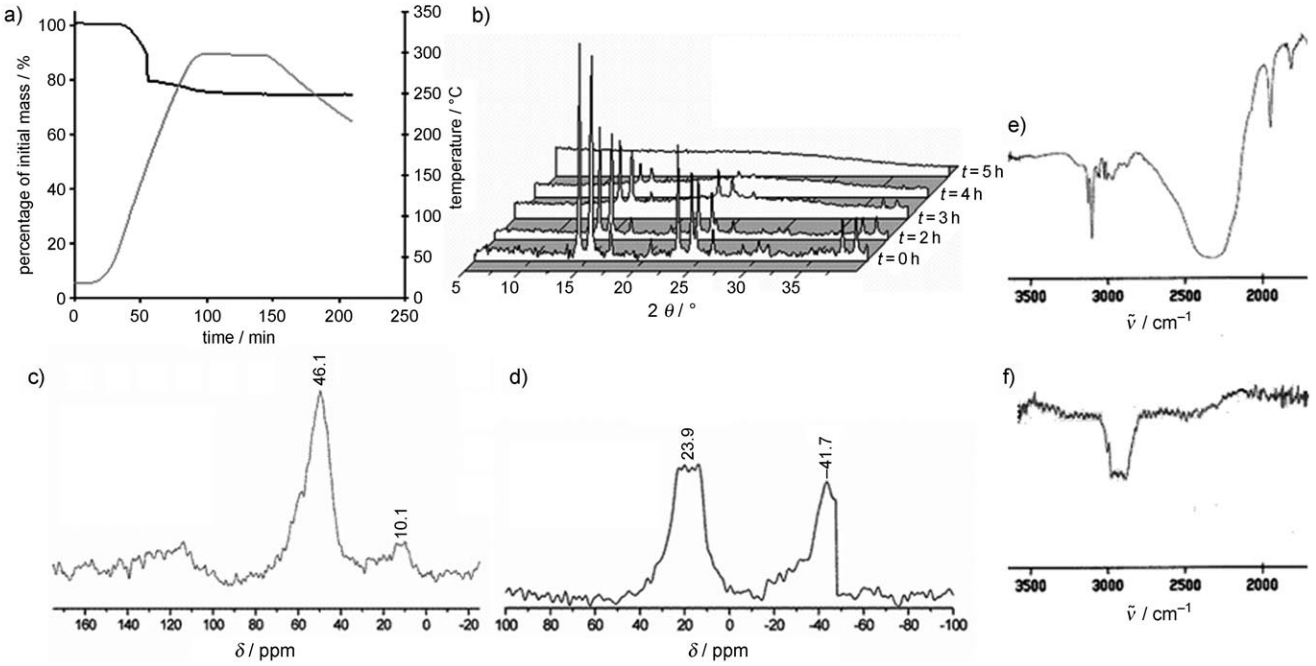
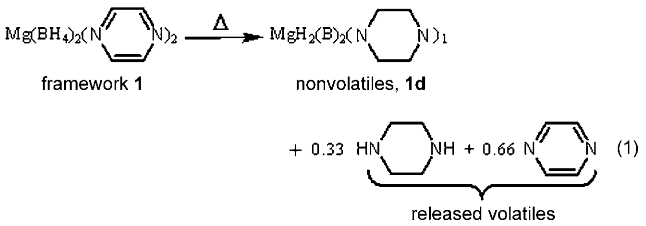


Figure 2. a) TGA on framework **1** run under N_2. ——: percentage initial mass; ——: temperature. b) pXRD traces of framework **1** heated at 140 °C for different durations; after 5 h, complete conversion to **1d** is detected (*y* axis relative intensity in arbitrary units). c) Solid-state ^1H–^{13}C CP/MAS NMR spectrum of compound **1d** (vs. TMS). d) $^{11}B\{^1H\}$ MAS NMR spectrum of **1d** (vs. $BF_3 \cdot OEt_2$). e) IR spectrum of **1**. f) IR spectrum of **1d** (both KBr disc).

suggesting decomposition of the BH_4 anion and loss of the majority of B–H bonds. This observation is consistent with the observed extensive hydrogenation of pyrazine (hydrogen utilized in hydrogenation has to be produced from BH_4 decomposition, therefore B–H units are consumed to generate predominantly C–H and some N–H moieties). The $^{11}B\{^1H\}$ MAS NMR spectrum of **1d** shows two major resonances at approximately $\delta = 24$ and -41 ppm (Figure 2d). The resonance at $\delta = -41$ ppm is close to that of $[BH_4]^-$ (the spectrum of $NaBH_4$ displays a sharp resonance at $\delta = -41.9$ ppm),[20] but the significant differences in the ^1H–^{11}B selective CP/MAS NMR spectroscopy dynamics for **1d** compared to $NaBH_4$ (in combination with the other direct and indirect evidence) strongly suggest that the line at approximately $\delta = -41$ ppm in the spectrum of **1d** does not correspond to BH_4.[20] Unambiguous identification of the two major resonances has proved difficult; however, the $\delta = +24$ ppm resonance is in the region expected for $B{=}NR_2$[15,23] and so is tentatively attributed to a boron species multiply bonded to a piperazine amide functionality.

Elemental analysis of **1d** corresponded to an empirical formula of $MgH_2(B)_2(C_4N_2H_8)_1$, consistent with the mass loss observed by TGA. Solution NMR spectroscopy studies on **1d** completely dissolved in D_2O or CD_3OD indicated the hydridic nature of the hydrogen centers in **1d**; the formation of HD is detected (a 1:1:1 triplet at $\delta = 4.51$ ppm, $^1J_{HD} = 42$ Hz) in the reaction of a metal hydride with protic $D^{\delta+}$. Combined solution ^{11}B and $^{11}B\{^1H\}$ NMR spectroscopy on dissolved **1d** further supported the consumption of the majority of B–H bonds when **1** decomposes (no resonances displaying B–H coupling are observed). With the absence of any significant B–H-containing material, we tentatively assign the hydridic hydrogen center in **1d** to an {MgH} species.

Species **1d** can alternatively be formed by heating **1** at 140 °C for 5 h, with concomitant loss of organic volatile reaction components (pyrazine and piperazine). The complete decomposition of **1** to form **1d** at this much lower temperature is consistent with the major mass loss observed by TGA occurring in this temperature region. Therefore, the key outcome of heating **1** is the reaction of all the $Mg(BH_4)_2$ units at only 140 °C, involving the consumption of the majority of the B–H bonds, with approximately 75 % of boron-bound hydrogen transferred to the organic pillar (generating piperazine) and the other 25 % utilized in the formation of an Mg–H-containing species. A plausible balanced equation for the overall process is shown in Equation (1), with the unidentified magnesium and boron species present in **1d** depicted as $MgH_2(B)_2$ for simplicity.



(1)

The mechanism for the complete decomposition of $Mg(BH_4)_2$ in **1** must be complex and involve multiple steps, though no crystalline phases (other than **1**) are detected on heating to 450 °C. The pXRD pattern for **1** is maintained up to the onset of decomposition (at which point it gradually reduces in intensity, Figure 2b), confirming the persistence of the extended structure of framework **1** up to the point of $Mg(BH_4)_2$ reactivity. Related systems with X–H···H–B dihydrogen bonds (albeit possessing more acidic X–H groups than C–H, X = O or N), decompose at relatively low temperatures by direct combination (dehydrocoupling) of the hydridic B–H and protic X–H hydrogen atoms involved in dihydrogen bonding.[8,9] To determine if dehydrocoupling was operating during the heating of **1**, the products from the thermal decomposition of a partially deuterated analogue $[Mg(BH_4)_2(C_4N_2D_4)_2]$ (**2**) were analyzed by solution $^{13}C\{^1H\}$ NMR spectroscopy. The nonvolatile product generated by thermal decomposition, **2d**, after dissolution in CD_3OD, confirmed the conversion of all nonvolatile pyrazine, with the only observed organic product identified as piperazine. The formed piperazine was dominated (by more than 90 %) by one species possessing a 1:1:1 intensity triplet ($^1J_{CD} = 20$ Hz) centered at $\delta = 46.6$ ppm.[20] This resonance corresponds to a single piperazine regioisomer with each carbon atom bound to one hydrogen and one deuterium atom.[24] This regioisomer (produced effectively stoichiometrically given the 95 atom % D of starting pyrazine) can only be formed in such high yield if there is no C–D cleavage during thermal decomposition. Therefore, the decomposition of **2** (and thus **1**) does not proceed via dehydrocoupling of the hydrogen atoms of the dihydrogen bond (B–H···H–C) but by a mechanism involving cleavage of only the B–H bonds and not the C–H bonds of pyrazine.

The mechanism of hydrogen transfer to pyrazine observed during the thermal treatment of **1** thus presumably proceeds by initial alkene hydroboration, in which a $Mg(BH_4)_2$-derived borane species is transferred to a proximal arene unit, and a subsequent thermal hydrodeboration step,[25] which ultimately generates the observed major organic product, piperazine (Figure 3). A minor resonance at $\delta = 10.1$ ppm in the ^1H–^{13}C CP/MAS NMR spectrum is fully consistent with aliphatic species containing direct C–B bonds that have not undergone hydrodeboration,[14] consistent with the proposed initial hydroboration step. There is significant mechanistic precedence for all proposed steps, while the Lewis base initiated fission of a metal-bound borohydride into metal hydride and BH_3 is well-documented[26,27] and consistent with the indirect evidence for the formation of {MgH} species. Attempts to detect discrete gaseous BH_3 evolved during the decomposition of **1** utilizing an external trapping agent failed,[20] owing to the extremely efficient intrasolid hydroboration of proximal pyrazine in preorganized **1**, thus demonstrating that a two phase gas–solid reaction is not involved in the hydroboration reaction studied herein. A species possessing two B–H bonds is required mechanistically as the hydroborating agent, strongly favoring the intermediacy of BH_3.

Confinement in framework **1** has facilitated the low-temperature production of reactive BH_3 (or an equivalent

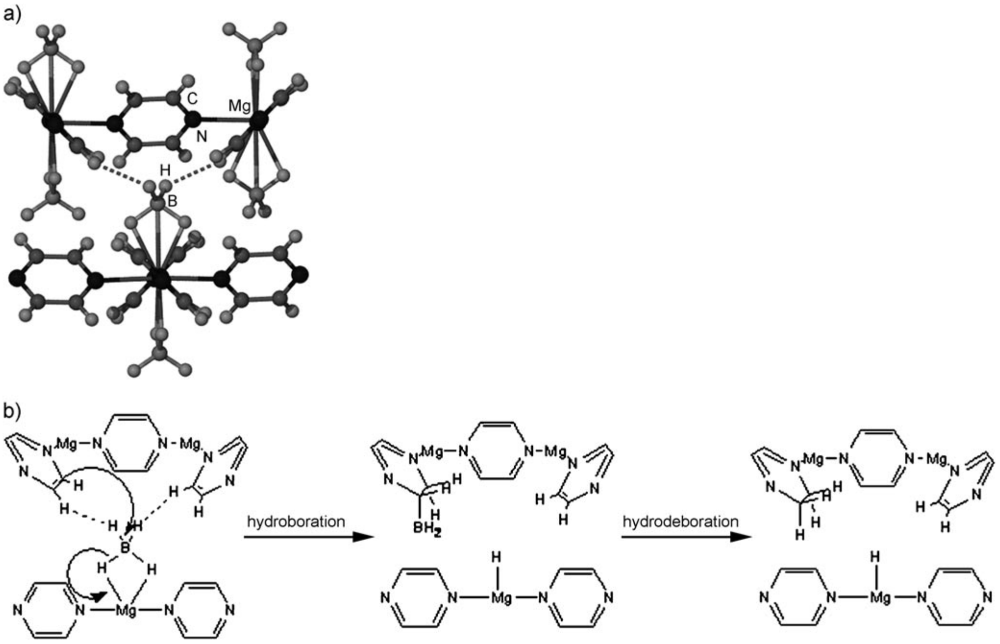


Figure 3. a) A section of framework **1** highlighting the preorganized reactive site and the short dihydrogen bonds. b) The postulated reaction scheme (supported by NMR spectroscopic studies) for BH_3 transfer to a proximal pyrazine unit with subsequent hydrodeboration.

species) from $Mg(BH_4)_2$, enabling the hydroboration reaction to proceed at only 140 °C in the absence of any catalyst. The complete reaction of the $Mg(BH_4)_2$ units in **1** to produce BH_3 and a {MgH} species is in direct contrast to the decomposition behavior of both pure $Mg(BH_4)_2$ and $[Mg(BH_4)_2(NH_3)_2]$, which decompose with quantitative H_2 release and produce no species containing B−H bonds (a prerequisite for hydroboration).[7,8] Thus, framework confinement of $Mg(BH_4)_2$ has enabled an alternative decomposition pathway to be accessed, that is, fission into {MgH} species and BH_3. Separate homogeneous-phase control reactions revealed that $Mg(BH_4)_2$ does not react with naphthalene, pyridine, or a combination of pyridine and naphthalene (starting materials returned unchanged) at 140 °C for 18 h, conditions which for framework **1** result in complete $Mg(BH_4)_2$ decomposition and extensive pyrazine hydrogenation. The absence of any reactivity in the homogeneous control reactions is not surprising, as arenes are well documented to be inert towards metal borohydrides in the absence of a catalyst or coreactant (e.g. $TiCl_4$).[28,29] However, under analogous conditions (ca. 140 °C), neutral borane species (R_2BH, R = alkyl or H) readily hydroborate arenes and undergo subsequent hydrodeboration to produce hydrogenated aliphatic products,[30] consistent with the mechanism proposed for decomposition of **1** and, specifically, the intermediacy of BH_3. Finally, comparison of the thermal reactivity of **1** with a molecular analogue, $[Mg(BH_4)_2(pyridine)_4]$, further confirms the indispensability of framework confinement; this molecular analogue does not hydroborate on heating but simply decomposes by facile loss of pyridine at low temperature.[16] Thus, framework confinement is also important in preventing premature loss of pyrazine (with concomitant structural breakdown and loss of the preorganized reactive site) before the hydroboration reaction can occur, as is the case for $[Mg(BH_4)_2(pyridine)_4]$.[16]

With the observed low-temperature reactivity specific to $Mg(BH_4)_2$ units confined in framework **1**, interactions only present in the extended structure of **1** (and not in the solution phase) must be the enabling factors. The major factor is likely to be the precise geometric arrangement of the reactive groups enforced by the extended interlayer framework structure (which is in turn dominated by dihydrogen bonding), which holds the reactive groups in close proximity. The close C−H···H−B contacts observed in the experimental and calculated structures of **1** may also play an integral role, weakening the H−B bond (as noted in aminoborane species) and facilitating BH_4 degradation.[14] The proposed generation of BH_3 on heating **1** will be facilitated by release of a hydride as a good leaving group (stabilized by coordination to Mg, Figure 3), analogous to the mechanism elucidated for related intramolecular hydroboration reactions.[31]

In conclusion, the first MOF material constructed from the $Mg(BH_4)_2$ moiety is reported, the structure of which includes extensive dihydrogen bonding and a close arene–BH_4 arrangement. The extensive arene hydrogenation observed during thermal decomposition of **1** operates via an initial hydroboration step that proceeds at this unusually low temperature (140 °C) without a catalyst owing to the exquisite geometric organization of the reactive units in **1**. This behavior is in stark contrast to the heating of $Mg(BH_4)_2$ in the homogeneous phase (no reduction or hydroboration of arenes is observed). Importantly, framework confinement has modified the decomposition pathway of $Mg(BH_4)_2$, with a hydroborating BH_3 species now produced from $Mg(BH_4)_2$ during the decomposition of **1**, thus enabling the low-temperature intrasolid hydroboration. Amine coordination alone (e.g., in $[Mg(BH_4)_2(NH_3)_2]$) does not affect this change in the decomposition pathway; instead, this related species decomposes with no evolution of boranes, quantitatively releasing H_2.[8] Framework **1** is therefore an example of a system in which the stability and reactivity of one of its components (in this case $Mg(BH_4)_2$) has been drastically modified by weak interactions in the solid state, and as such may offer a new direction for enabling low-temperature reactivity of borohydrides in the solid state.

Experimental Section

Single crystals of frameworks **1** and **2** were prepared by the slow diffusion of $Mg(BH_4)_2$ in diethyl ether into pyrazine in the same solvent using an "H-Cell" Schlenk flask. CCDC 699417 (**1**) and 699418 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Crystal data for **1**: $Mg(C_4H_4N_2)_2(BH_4)_2$, $M = 214.18$, colorless prism, $0.10 \times 0.10 \times 0.20$ mm^3, orthorhombic, *Ccca* (No. 68), $a = 10.359(4)$, $b = 11.128(4)$, $c = 10.303(4)$ Å, $V = 1187.7(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.198$ g cm^{-3}, $F_{000} = 456$, Bruker D8 diffractometer with APEX detector, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 100(2)$ K, $2\theta_{max} = 53.2°$, 5327 reflections collected, 687 unique ($R_{int} = 0.0488$). Final GooF = 1.097, $R1 = 0.0426$, $wR2 = 0.0972$, R indices based on 553 reflections with $I > 2\sigma(I)$ (refinement on F^2), 53 parameters, 0 restraints. Lp and absorption corrections applied, $m = 0.121$ mm^{-1}. Crystal data for **2**: $Mg(C_4D_4N_2)_2(BH_4)_2$, $M = 222.19$, colorless prism, $0.40 \times 0.10 \times 0.20$ mm^3, orthorhombic, *Ccca* (No. 68), $a = 10.324(3)$, $b = 11.172(4)$, $c = 10.329(3)$ Å, $V = 1191.3(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.239$ g cm^{-3}, $F_{000} = 456$, Bruker D8 diffractometer with APEX detector, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 100(2)$ K, $2\theta_{max} = 53.6°$, 907 reflections collected, 566 unique ($R_{int} = 0.0143$). Final GooF = 1.322, $R1 = 0.0912$, $wR2 = 0.1810$, R indices based on 535 reflections with $I > 2\sigma(I)$ (refinement on F^2), 67 parameters, 5 restraints. Lp and absorption corrections applied, $m = 0.121$ mm^{-1}.

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