Solid Molecular Frustrated Lewis Pairs in a Polyamine Organic Framework for the Catalytic Metal-free Hydrogenation of Alkenes

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Abstract: We report for the first time a metal-free heterogeneously catalyzed hydrogenation using a semi-solid frustrated Lewis pair (FLP). The catalyst consists of a solid polyamine organic framework and molecular tris(pentafluorophenyl)borane (BCF) that form a semi-immobilized FLP *in situ* in the catalytic hydrogenation of diethyl benzylidenemalonate. ^{11}B NMR spectroscopy proves the successful hydrogen activation by the FLP. Furthermore, the B-N interactions between the polyamine and BCF are investigated by IR and solid state NMR spectroscopy. The FLP 1,4-diazabicyclo[2.2.2]octane (DABCO)/BCF, which combines the features of a FLP and a classical Lewis adduct, functions as molecular reference in both, catalysis and characterization. Furthermore, computational studies enable a better insight into the hydrogen activation through DABCO/BCF and polyamine/BCF.
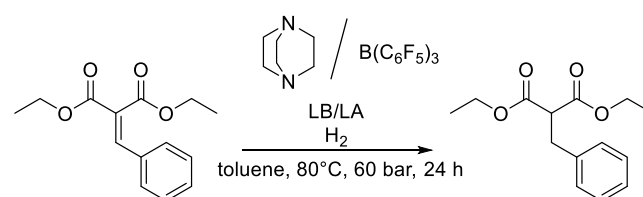
Introduction

Hydrogenation reactions represent a crucial step in the synthesis of many bulk and fine chemicals.[1] The use of transition metal catalysts like organometallic Pd and Ni complexes as well as early transition metals such as Ti and Nb in hydrogenation reactions is widely known.[2,3] However, even traces of metal are unfavorable in fine chemicals and pharmaceuticals.[4] Stephan et al. were the first to report a reversible metal-free H_2 activation using the concept of frustrated Lewis pairs (FLP) in 2006.[5] FLPs consist of sterically hindered Lewis acids and bases which do not form adducts but rather "frustrated complexes". Due to the unquenched acidity and basicity they are capable of activating small molecules such as SO_2[6], CO_2[7], N_2O,[8] H_2[5,9,10], in the case of H_2 via a heterolytic cleavage.[3,11] Since the first publication a lot of effort has been put into the research field of FLPs and numerous examples of FLPs and their application in homogeneous catalysis have been shown. In 2012, Inés et al. reported a system of DABCO/$B(C_6F_5)_3$ (BCF) as FLP which catalyzes the hydrogenation of electron-poor allenes and alkenes in very good yields (Scheme 1).[12,13]

In general, due to their convenient processing and separation from the reaction solution heterogeneous catalysts are favored for process implementation. Hence, solid FLP recently emerged as a hot topic in this field. Some examples of either solid, immobilized or semi-immobilized FLPs have been published recently. Supported FLPs for heterogeneously catalyzed hydrogenation reactions are mentioned by Szeto et al. as well as Xing et al.[4,14] Szeto et al. report a silica-based FLP for the Z-selective reduction of alkynes. For immobilization they stirred an ether solution of (4-hydroxyphenyl)biphenyl phosphine and $[(\equiv SiO)_2Al(iBu(Et_2O)]$ at 25°C for 12 h. The resulting silica-supported surface phosphine is then combined with Piers' reagent or BCF to give the supported FLP. This FLP was characterized by DRIFT spectroscopy as well as MAS NMR spectroscopy. It shows a remarkable activity and selectivity in the hydrogenation of alkynes.[4] In contrast, Xing et al. describe a procedure to obtain silica-supported BCF (s-BCF), although silica-supported BCF was already reported earlier on.[14–16] However, their procedure differs from the procedures described before and further they combine this s-BCF with a Lewis base, tri-*tert*-butyl phosphine, to yield a solid FLP. In the example mentioned before they proved the successful heterolytic cleavage of H_2 under mild conditions by the immobilized FLP by NMR studies.[14] Recently, Trunk et al. reported for the first time a semi-immobilized FLP in microporous polymer networks. BCF is immobilized in two different polyphosphines, i.e., triarylphosphine polymers.[17] Interactions between P and B and the "frustrated" character are proven by ^{31}P solid state NMR. They report a chemical shift in comparison to the pure polymer due to a "less frustrated" state of the solid and solvent-free FLP. Furthermore, they proved a successful solid FLP-catalyzed H_2/D_2 activation and exchange by ^{1}H NMR experiments.

Herein, we report for the first time a semi-solid molecular FLP consisting of an insoluble polyamine organic framework exhibiting Lewis base sites in combination with molecular BCF. This semi-solid FLP successfully activates H_2 and enables the heterogeneously catalyzed hydrogenation of the electron-poor alkene diethyl benzylidenemalonate as model substrate.

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Scheme 1. Catalytic hydrogenation of diethyl benzylidenemalonate.[12,13]

Results and Discussion

Materials synthesis and characterization

Our concept of supported FLPs is similar to the approach of Trunk et al.[17] It is composed of a polymeric organic framework, which exhibit heteroatoms as connectors, which function as Lewis acid or base centers, and the corresponding counterpart. To form a FLP, the polymer requires appropriate electronic and structural features. On the one hand, the Lewis base sites need to be accessible for the Lewis acid, but also sterically hindered enough so that the Lewis acid cannot form the adduct but rather only a weak "frustrated" interaction. In this work, we obtained a solid frustrated Lewis Pair, which consists of a polyamine organic framework, which exhibits tertiary amine groups as the Lewis base centers in combination with tris(pentafluorophenyl)borane as the Lewis acid part. The novel polyamine organic framework is synthesized by a N-alkylation of *p*-xylylenediamine with 1,4-bis(bromomethyl)benzene inspired by a synthesis route of Singh et al., who reported aqueous-mediated N-alkylations of various primary and secondary amines with halides by using $NaHCO_3$ as a base in aqueous solution.[18] This procedure was adjusted to our purpose of obtaining an insoluble, crosslinked polymeric organic framework by a convenient synthetic approach (Scheme 2).
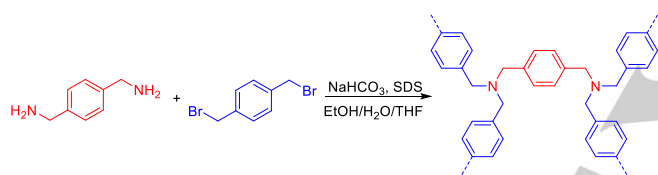
Scheme 2. Synthesis of polyamine organic framework: p-xylylenediamine/1,4-bis(bromomethyl)benzene/$NaHCO_3$=1/2.2/4.4; H_2O/EtOH/THF (1/1/1), SDS = sodium dodecyl sulfate.

The resulting polymer was characterized using CHN elemental analysis, SEM, EDX, solid state NMR, N_2 physisorption, TG/DSC, XRD and IR measurements and further applied in the hydrogenation of diethyl benzylidenemalonate in combination with the Lewis acid BCF. SEM measurements show polydisperse particles with a flaky structure, which agglomerate due to electrostatic charge (Figure S2). According to elemental analysis the content of C, H and N is lower than theoretically calculated for an ideal structure. This discrepancy results partially from hydrolyzation as well as unreacted residual bromine which is also detected by EDX spectroscopy. ^{13}C CP MAS NMR (Figure S 4) confirms the proposed structure. However, the small signal at -36.2 ppm indicates residual bromine at the terminal building blocks of the polyamine. The signals above 200 ppm and also at 74 ppm and 62 ppm are spinning sidebands of the main signal at 132.8 ppm and 142.5 ppm. The asymmetry of the spinning sideband at 62 ppm is due to an overlay with a peak originated from the carbon atoms directly bonded to the N atoms.

For three-dimensionally crosslinked polymers a high specific surface area is expected as can be seen for different examples such as hypercrosslinked polymers[19–21] and polyphosphines, which are also applied in catalytic reactions.[22,23] However, the herein synthesized amorphous polyamine does not exhibit a permanent porosity in dry state although it is three-dimensionally crosslinked. Nitrogen physisorption isotherms exhibit a type II behavior (Figure S1) and reveal only external surface area with a low specific surface area of 10 m²g⁻¹. As both monomers exhibit a methylene group between the functional groups and the aromatic ring, respectively, the framework is apparently not sufficiently rigid to exhibit permanent porosity. However, as in the catalytic experiments toluene is applied as the solvent, the polyamine swells to a certain extent opening up the pore system and the nitrogen centers get sufficiently accessible for the molecular Lewis acid during catalysis to form an *in situ* FLP. Even small amounts of toluene result in a slight but observable extension of the polymer volume due to swelling of the framework structure. For other solvents this behavior is even more pronounced. TG/DSC measurements (Figure S3) reveal that the polymer is thermally stable under the reaction conditions of the catalytic hydrogenation of diethyl benzylidenemalonate. The decomposition of the polyamine starts at around 293 °C in argon, whereas the catalytic hydrogenation is carried out at 80 °C which is far below the decomposition temperature.

To obtain more information about the interaction of BCF with the polyamine, the latter was impregnated with BCF and examined by means of ATR IR spectroscopy (Figure 1). A new IR band appears at 1276 cm⁻¹ which can be assigned to neither the pure polyamine nor BCF but rather to the B-N interaction between the polyamine and BCF, indicating weak LA-LB interactions as evidenced by comparison with interactions between DABCO/BCF (Figure 2). To prove this, the literature-known molecular FLP DABCO/BCF was investigated in comparison by ATR IR spectroscopy as well as liquid state ^{11}B NMR studies. DABCO and BCF are considered as a FLP in a toluene solution being able to activate hydrogen for the catalytic reduction of electron-poor allenes and alkenes.[12,13] However, when combining a solution of DABCO in toluene with a BCF solution at r.t., a white precipitate is obtained which is not expected for the formation of a molecular FLP. IR investigations show a new IR absorption band at 1279 cm⁻¹, which is assigned to the boron-nitrogen interaction between DABCO and BCF (Figure 2). The hypothesis that this band indicates a Lewis adduct formation is underlined by the fact that a precipitate is formed. Nevertheless, catalytic activity is obtained for both, the molecular and the solid FLP.

Catalytic performance

The polyamine organic framework in combination with BCF was applied in the catalytic hydrogenation of diethyl benzylidenemalonate as model reaction. The procedure and reaction conditions were based on publications by the Alcarazo group.[12,13] Therefore, the autoclave with glass inlet was charged with a magnetic stirrer and evacuated at 120°C in high vacuum to remove air and moisture. Diethyl benzylidenemalonate, LA and LB were weighed into a Schlenk tube and dissolved in toluene inside the glovebox. After transferring the solution into the autoclave, it was pressurized with H_2. The catalytic experiments were carried out at different temperatures with varying catalyst amounts and different reaction times (Table 1). After the reaction, the solid was filtered off and the reaction solution was analyzed by GC using ethyl heptanoate as an internal standard to obtain the yield of diethyl benzyl malonate.
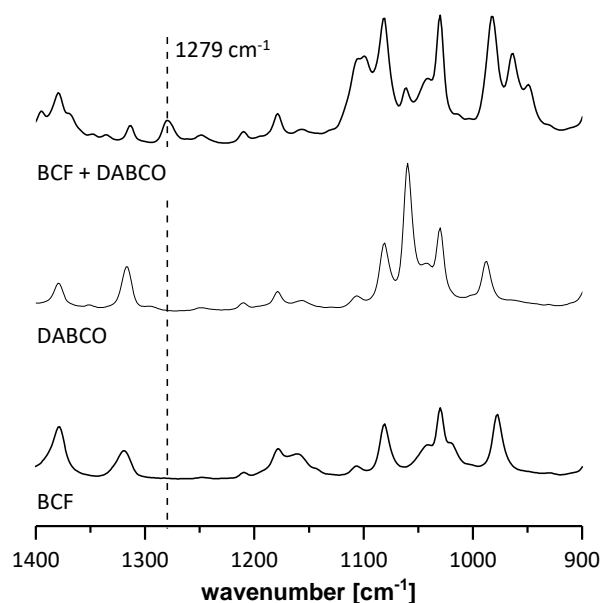
Figure 1. ATR-IR absorption spectra of pure BCF, polyamine and BCF-impregnated polyamine measured under inert gas atmosphere. The dashed line shows the position of the new absorption band at 1276 cm^{-1} of the BCF-impregnated polyamine due to the weak LA-LB interactions.
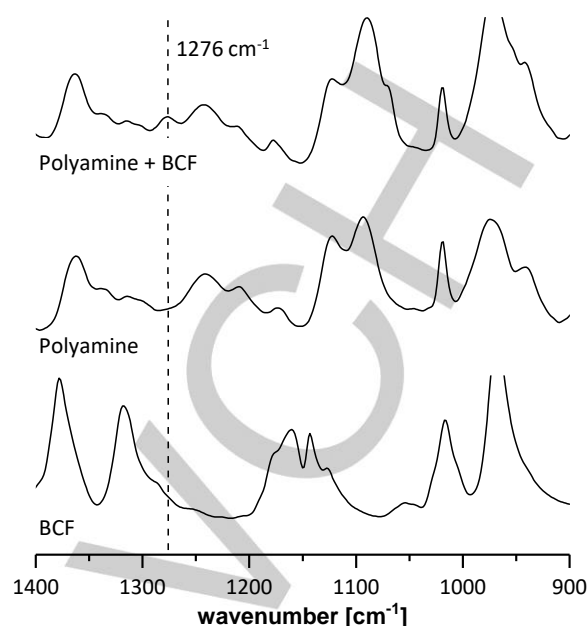

Figure 2 ATR-IR absorption spectra of BCF in toluene, DABCO in toluene and BCF and DABCO in toluene at r.t. The dashed line shows the position of the new absorption band at 1279 cm^{-1} of the combination of BCF and DABCO in toluene.

In addition to the polyamine/BCF system, also catalytic tests using only the Lewis acid in combination with DABCO as molecular base were performed to better compare to the experiments from earlier reports on that model reaction.[12,13] It should be noted that only the reduction of the C-C double bond was observed in our experiments. Applying the pure LA BCF (10 mol%) in the catalytic reaction already leads to conversion of diethyl benzylidenemalonate achieving a yield of 61 % after 24 h of reaction time. This behavior was not described by Nicasio et al. who reduced electron-poor alkenes and allenes including diethyl benzylidenemalonate, previously. They describe the cycloisomerization of an allene catalyzed by solely BCF, but not the hyrdogenation.[12,13] However, the Lewis acid is not capable of activating hydrogen on its own as the counterpart to absorb the proton is missing, which was also proven by ^{11}B NMR experiments, in which no BCF-hydride could be detected (see below). It is highly likely that BCF forms a FLP with the substrate itself which is capable of splitting hydrogen to auto-catalytically hydrogenate diethyl benzylidenemalonate. A similar behavior is already reported in literature for BCF in combination with imines.[24–31] Experimental evidence of the autoinduced catalysis of imine reduction with BCF was reported by Tussing et al.[30,31] However, as soon as substrate, H$_2$ and BCF are present during the reaction, the reduction of diethyl benzylidenemalonate occurs. As a result, no BCF-hydride is observable in the ^{11}B NMR spectrum after the reaction as the activated hydrogen reduces the substrate. However, applying a combination of LB/LA leads to even higher yields than obtained by the semi-autocatalytic reduction of the substrate. The combination of BCF and DABCO (10 mol %) leads to an increase in yield of diethyl benzylmalonate up to 95 % which is only slightly lower than the yield reported in literature (98 %) but within the GC error of ~3 %. This implies that the FLP formed by DABCO and BCF is more active than the one consisting of the substrate alkene and BCF.

For homogeneous systems it is rather challenging to separate the catalyst from the reaction solution. Because of this, we replaced one part of the FLP by an appropriate solid, namely the solid polyamine organic framework. Due to the lack of porosity, an excess (referred to the nitrogen content) of polymer is used to ensure the sufficient accessibility of Lewis base centers. The experimental procedure was modified for the application of polyamine as the autoclave is charged with the polyamine first and heated up to 120 °C in high vacuum to remove the residual moisture and air adsorbed on the polymer. Subsequently, the FLP was formed *in situ* in the toluene reaction mixture splitting hydrogen for the efficient catalytic hydrogenation of diethyl benzylidenemalonate. Applying 10 mol-% of BCF and 50 mg of polyamine a yield of 100 % was achieved under the same reaction conditions (500 rpm, 80 °C, 24 h) as used for the DABCO/BCF (10 mol-%) system. Full conversion was achieved already after six hours (Table 1, entry 9), rendering the combination of the polyamine with BCF an even more active catalyst compared to the molecular counterpart. Hence, the electronic and structural features of the polyamine are appropriate to form an *in situ* FLP in combination with BCF to catalyze the hydrogenation. Furthermore, studies by liquid phase ^{11}B NMR show proof of the capability of hydrogen splitting through the polyamine and BCF as the NMR spectrum shows a characteristic doublet for the BCF-hydride at around -25 ppm (Figure 3).

As mentioned above, the polymer exhibits a very low specific surface area in dry state. However, in catalysis it shows an excellent activity due to swelling in toluene which allows appropriate accessibility of the borane to the nitrogen centers of the polymer. Furthermore, the reaction shows no pressure dependence above 20 bar hydrogen pressure (Table 1).

Table 1. Catalytic hydrogenation of diethyl benzylidenemalonate with varying hydrogen pressure and reaction time using 10 mol% LA and 50 mg polyamine.

Entry[a]	LA [mol%]	Base	H_2 [bar]	t [h]	Yield[d] [%]
1	-	-	60	24	0
2	10	-	60	24	61
3	10	DABCO[b]	60	24	95
4	-	Polyamine	60	24	0
5	10	Polyamine[c]	60	24	100
6	10	Polyamine[c]	40	24	100
7	10	Polyamine[c]	20	24	100
8	10	Polyamine[c]	40	18	96
9	10	Polyamine[c]	40	6	100

[a] Reaction conditions: 45 mL Hastelloy autoclave, glas inlet, magnetic stirrer, 8 mL toluene solution, 80°C, 500 rpm. [b] 10 mol%. [c] 50 mg. [d] Yield determined via GC using ethyl heptanoate as standard.

Table 2. Catalytic hydrogenation of diethyl benzylidenemalonate using 5 mol% LA and 25 mg polyamine.

Entry[a]	LA [mol%]	Base	H_2 [bar]	Yield[d] [%]
1	5	DABCO[b]	60	67
2	5	-	60	15
3	5	-	40	11
4	5	-	20	2
5	5	Polyamine[c]	60	33
6	5	Polyamine[c]	40	51
7	5	Polyamine[c]	20	24
8	5[e]	Polyamine[c]	40	0
9	5[e]	-	40	0
10	-	Polyamine[c]	60	0

[a] Reaction conditions: 45 mL Hastelloy autoclave, glas inlet, magnetic stirrer, 8 mL toluene solution, 80°C, 24 h, 500 rpm. [b] 5 mol%. [c] 25mg. [d] Average yield determined via GC using ethyl heptanoate as standard. [e] BPh₃.

When lowering the H_2 pressure to 20 bar, still 100 % product is obtained. Shortening the reaction time shows that the hydrogenation takes place fast using this catalyst amount. After 6 h and 18 h the yield was 100 % and 96 % (Table 1, entries 7, 8), respectively. The variation in yield is within the GC error which can be assumed to be ~3% for the applied method.

Reducing the amount of catalyst to half, i.e., 25 mg of polyamine combined with 5 mol-% of BCF, leads to lower conversions as expected in most cases. Using fresh BCF and applying a hydrogen pressure of 40 bar yields up to 86 % in the

catalytic hydrogenation of diethyl benzylidenemalonate. However, the average yield is around 50 % (Table 2, entry 6) under these reaction conditions. The yield fluctuates to a certain degree which is attributed to the sensitivity of the catalytic system. Even small amounts of moisture lead to deactivation of the LA due to its high Lewis acidity. Besides, the LA catalyzes the reaction in combination with the substrate as stated above. Nonetheless, the yield obtained using a combination of LB and LA is always higher than when only applying the LA (Table 1, entries 2, 3, 5-9; Table 2). To lower the moisture sensitivity of the system in future developments, a feasible method might be to substitute the BCF with compounds that exhibit a lower Lewis acidity and, hence, a higher moisture tolerance. In literature, there are already some examples for moisture-tolerant FLPs, in which the LA exhibits, e.g., partial chlorine instead of fluorine substitution.[32,33]

H_2 activation
Liquid phase ^{11}B NMR spectra show a new signal at around -3 to -4 ppm (Figure 3) for the combination DABCO/BCF in toluene, whereas the signal of pure BCF in toluene-d_8 is located at around 60 ppm. A chemical shift of -3 to -4 ppm can be assigned to signals of either boron complexes, trivalent or tetravalent boron species and in systems where there is direct bonding of nitrogen to boron. The distinct shift from 60 ppm to -3/-4 ppm indicates a major change in the chemical environment of the boron atom. That implies that DABCO and BCF do not form a FLP to common comprehension but rather a Lewis adduct with a more pronounced interaction. This behavior has already been shown, e.g, for lutidine/BCF by Geier et al.[34] In their study, lutidine/BCF is explored for H_2 activation, despite the fact that a [11]B chemical shift is observed at -3.9 ppm for the lutidine/BCF adduct,[34] which is in the same range as the signal for the DABCO/BCF adduct. However, they proved H_2 activation and claimed that the adduct and the FLP exist in equilibrium.[34] As the catalytic reduction of the electron-poor alkene diethyl benzylidenemalonate is possible using the combination of DABCO and BCF, a similar behavior regarding the hydrogen activation is expected.

For experimental proof, the molecular FLP of DABCO and BCF was used to activate hydrogen and analyzed by means of ^{11}B NMR (Figure 3). The resonance of BCF at 60 ppm as well as the signal assigned to the DABCO-BCF adduct at -3/-4 ppm was not visible in the ^{11}B NMR spectrum while a doublet at -24.3 ppm was observed. This doublet is assigned to the BCF-hydride which is in accordance with its literature-known chemical shift.[35–37] Hydrogen activation through BCF and DABCO is not only possible at 60 bar H_2 and an elevated temperature of 80 °C. When exposing the DABCO/BCF system in toluene-d_8 to a hydrogen pressure of 0.3 bar (rel.), slightly above atmospheric pressure, at 80°C, the ^{11}B NMR spectrum shows again the doublet at -24 ppm indicating the presence of $[HB(C_6F_5)_3]^-$ in the solution. Certainly, the hydrogen splitting under these conditions is not as efficient as at 60 bar and 80 °C as there is still precipitated adduct present as proven by the peak at -3/-4 ppm in the ^{11}B NMR spectrum. A similar behavior is observed when exposing the DABCO/BCF adduct to 60 bar H_2 at 25 °C. Clearly, hydrogen activation is observable but also there is a distinct signal that proves the presence of the DABCO/BCF adduct.
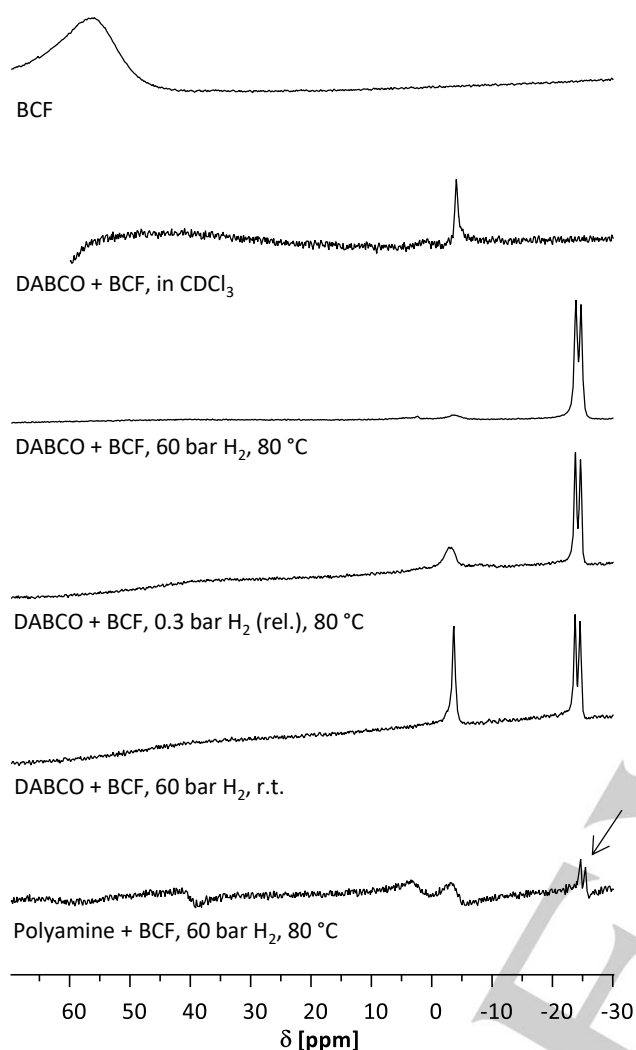
Figure 3. Liquid ^{11}B NMR measured in toluene-d_8. An autoclave equipped with magnetic stirrer and glass inlet was charged with Lewis base, Lewis acid and toluene-d_8, pressurized with H_2 and left to stir for 24 h. The mixture of DABCO and BCF was measured in CDCl$_3$ because it dissolves the precipitate better. The mixture as well as pure BCF were measured after mixing without the autoclave procedure.

Thus, the DABCO/BCF system is capable of activating hydrogen at room temperature and also under very low H_2 pressures. The hydrogen activation takes place efficiently under elevated pressures at elevated temperatures.

Substituting the molecular Lewis base with the solid polyamine organic framework under the same conditions (60 bar H_2, 80°C, 24 h), ^{11}B NMR investigations of the liquid phase show only weak signals (Figure 3, bottom) indicating a low concentration of the boron species in solution. This implies that the boron species is adsorbed and immobilized within the pore system of the organic framework to a large extent, but there is still a molecular boron species in the liquid phase that would result in tremendous leaching under continuous processing conditions. The adsorption of the BCF-hydride is assigned to an electrostatic interaction between the BCF-hydride anion and the positively charged polymer due to the heterolytic cleavage of hydrogen. However, a small doublet at around -25.1 ppm is observed that indicates the formation of $[HB(C_6F_5)_3]^-$. This

proves the capability of the herein synthesized polyamine combined with BCF for hydrogen activation.

Solid-state MAS NMR

For a comprehensive investigation of the solid FLP and its hydrogen activation behavior, solid-state ^{1}H, ^{11}B and ^{14}N MAS NMR experiments were carried out on the polyamine and the BCF-loaded polyamine in dry and wetted samples. For the latter, the materials were wetted with dry and oxygen-free toluene-d_8 to create a paste-like sample.

The ^{11}B NMR spectra (Figure S 5) of the dry BCF-impregnated polyamine show no presence of free BCF. Instead, all signals have shifted to lower fields and we propose that this is mostly due to interactions somewhere in between the "frustration" and adduct-formation. The more downfield shifted signals could also arise from π-π interactions. In the spectra, multiple [11]B species are observable. A greater number of species may originate from the distribution of different sites, namely due to interactions of the borane with different (e.g. primary or secondary) amine species and other species as residual bromine terminal groups. The signal at approximately 8-14 ppm may result from the formation of a bromide complex with the aromatic borane. The rather upfield shifted signals could occur due to interaction of B with stronger nucleophiles such as the N sites in the polyamine.

To obtain well-resolved spectra, the materials were wetted with toluene-d_8. Due to the addition of the solvent the polymer swells, thus rendering higher mobility of the molecular borane species in the framework pore system and allowing better-resolved signals. For a more suitable evaluation, the peaks were assigned by deconvolutions of the spectra of the dry and wetted material (Figure 4). The sharp signals at -4.9 ppm (dry) and -4.6 ppm (wetted) can be assigned to direct bonding between B and N. These chemical shifts are near the chemical shifts of the DABCO/BCF adduct and the lutidine/BCF.[34] Therefore, it is likely that the polyamine/BCF and the DABCO/BCF system both exist in equilibrium as an adduct and a FLP similar to the scenario reported by Stephan et al.[34] We propose that the two broad signals in both spectra most likely arise from subsurface-level incorporation of the borane species embedded within the polyamine framework. In this regard, the signals with the most upfield shifts at -8.7 ppm (dry) and -10.5 ppm (wetted) are probably indicative of borane species embedded in the polymer framework that are interacting with amines by a dative bond. A fraction of embedded active sites is suggested to be less accessible to reactants and solvents. Upfield chemical shifts have also been attributed to anions like $[HB(C_6F_5)_3]^-$. However, this is not probable due to the fact that the sample was not exposed to hydrogen and these shifts are usually even more upfield-shifted as they normally appear at around -25 ppm which was also observed for molecular FLPs (Figure 3) and in previous reports.[35–37]

Certainly, to exclude this possibility, the evaluation of the amount of exchangeable H in primary and secondary amines would be beneficial. The broad [11]B resonances at 12.2 ppm (dry) and 17.1 ppm (wetted) are also assigned to boranes on subsurface-level but not with close proximity to the nitrogen sites. Downfield shifts in [10]B NMR spectra have been observed for sterically hindered, bulky secondary and tertiary amines which were complexed with boranes. These did not form adducts in
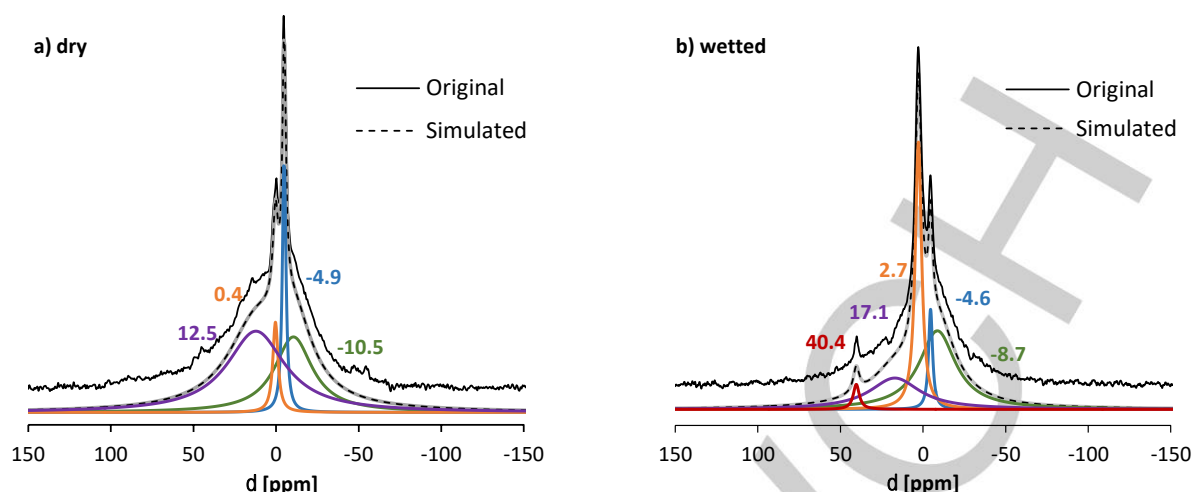
Figure 4. Spectral deconvolutions showing [11]B chemical shift assignment for the dry (a) and wetted (b) BCF-impregnated polyamine.

contrast to the studied primary amine.[38] We propose that these signals shed light into the "frustrated interactions" expected for our system, as also Trunk et al. showed in the case of ^{31}P NMR spectroscopy for their polyphosphine/BCF FLP.[17] In their study, they directly used changes in ^{31}P chemical shifts to account for frustrated type of interactions in their system. Another possibility is that the chemical shift is indicative for interactions between the electron-rich aromatic rings of the polyamine and the electron-poor ones in borane, resulting in π-π stacking. The π-π stacking has been suggested for such FLPs containing aromatic rings.[35,39,40] N-benzyl imines and N-phenyl imines complexed with BCF have shown restricted rotation in the B-N bond due to sterical hindrance and π-π stacking.[39] Besides, intermolecular π-π stacking between catalysts containing C_6F_5 and aromatic groups has been demonstrated to affect the catalytically active conformation even in organic solvent and hence, the enantioselectivity.[40] However, there is no literature example of π-π stacking with NMR evidence. At 40 ppm in the ^{11}B NMR spectrum of the wetted BCF-impregnated polyamine there is an additional small peak. The BCF itself has a chemical shift of 65-59 ppm (in CD_2Cl_2/C_6D_6, CD_2Cl_2, C_6D_6, $CDCl_3$).[41–44] Because of this, it is hypothesized that this signal results from the appearance of a borane species with less interaction with the polymer when the solvent is added. This would also match with

the fact that the $[HB(C_6F_5)_3]^-$ is detectable after H_2 activation using the combination of polyamine and BCF in toluene-d_8, as can be seen in Figure 3. However, it should be noted that in literature a minor signal at 30-40 ppm has been observed for a borane-tetrahydroquinoline adduct in its [10]B spectrum in addition to the B-N signal at approximately -4 ppm. This signal has not been assigned.[44] Table 3 gives an overview of all assigned signals.

The ^{1}H MAS NMR spectra of the polyamine and the BCF-impregnated polyamine (Figure 5) both in dry (a) and wetted (b) state were measured to probe changes in chemical shifts due to the addition of the BCF. The spectra show broad signals due to strong dipolar interactions as is often the case in a 3D polymeric network that contains interacting protons. The most intense signal of dry polyamine (Figure 5a) is observed at 6.7 ppm and does not change significantly through the impregnation with BCF. This signal is assigned to aromatic protons which typically show chemical shifts at ~ 7 ppm. The signal at 1.3 ppm appears due to aliphatic protons. However, the latter is well-resolved for the BCF-impregnated polyamine but not for the polyamine itself. The spectrum of the wetted polyamine (Figure 5b) also shows broadening and less-resolved signals. Through impregnation with BCF the signals become much better resolved, although also here the chemical shifts do not change. This implies that the incorporation of the BCF reduces the rigidity of the polymer network, presumably by decreasing the amount of π-π interactions between adjacent aromatic pore walls. This effect appears to be even more pronounced in the wetted material compared to the dry one.

Computational studies

To underline the experimental results, computational calculations were performed for the molecular DABCO/BCF system. The calculations were performed for 80 °C and 25 °C, respectively (Figures S 7-15). In reference to the isolated system (isolated DABCO and isolated BCF, each in toluene) the Gibbs free energy for the formation of an adduct species with strong B-N interaction (to be referred to as adduct) is $\Delta G_{adduct,80} = 7.0$ kcal/mol at 80 °C in toluene. The calculation for the adduct without or with low B-N interaction (to be referred to as FLP) results in $\Delta G_{FLP,80} = 1.7$ kcal, meaning that this state is
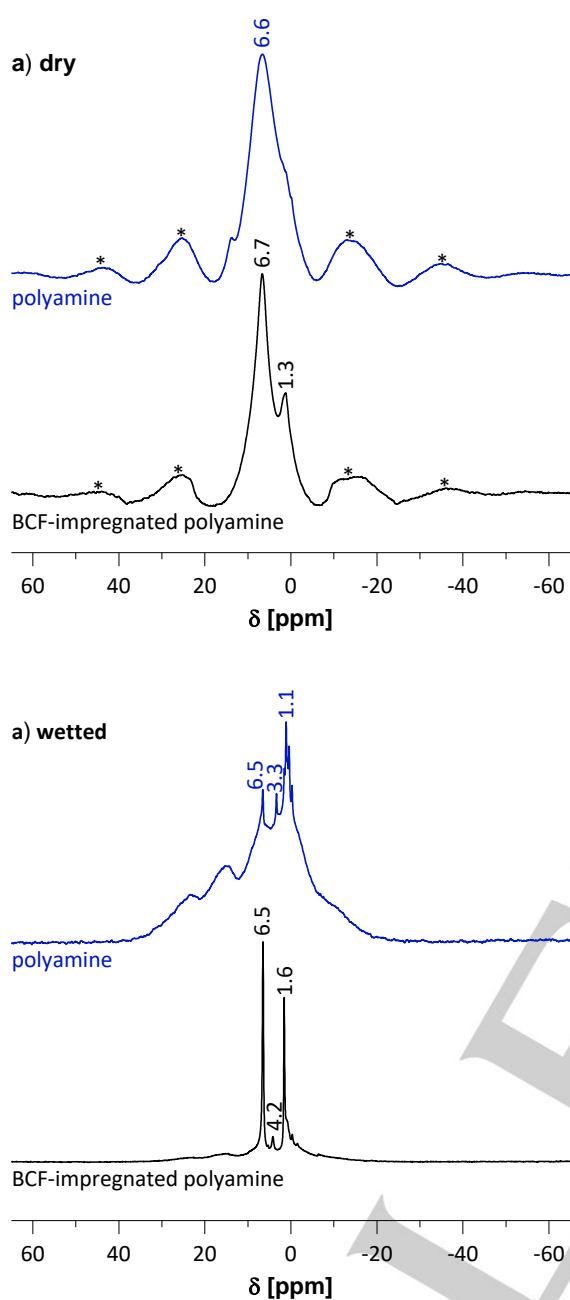
Table 3. Tentative assignments of the resonances in ^{11}B MAS NMR spectra of dry and wetted BCF-impregnated polyamine.

Entry	Observed δ_{11B} [ppm]		Literature δ_{11B} [ppm]	Assignments
	Dry	Wetted		
1	-4.9	-4.6	-3.9[34]	B-N dative bonds, surface-level
2	-10.5 (b)	-8.7 (b)	-	B-N dative bonds, subsurface-level
3	12.2 (b)	17.4 (b)	-	B-N frustrated interactions/ π-π stacking, subsurface-level
4	-	40	65-59	weakly interacting borane

Figure 5: ^{1}H MAS of polyamine (blue) and BCF-impregnated polyamine (black) in dry (a; MAS rate: 8 kHz) and wetted (b; MAS rate: 4 kHz) state. The spinning sidebands are denoted with asterisks.

apparently thermodynamically favored at 80 °C in comparison to the adduct. However, due to molecular motion and collisions interaction, the adduct formation is not completely excluded and in this case the adduct species precipitates under kinetic control, which was observed in the experiment. Nevertheless, due to the lower energetic barrier of the FLP formation, the FLP state of the system is favored, meaning the H_2 activation is feasible based on the thermodynamic properties of the system.

For the calculations at room temperature the Gibbs free energy is lower in both cases, namely $\Delta G_{FLP,RT} = 0.7$ kcal for the FLP and $\Delta G_{adduct,RT} = 4.5$ kcal for the adduct, respectively. This is expected as with lower temperature the molecule motion is

reduced, meaning that the energetic barrier is lower for both FLP and adduct, whereas the FLP formation is favored in comparison to the adduct formation.

The calculated IR spectrum of the DABCO/BCF adduct (Figure S6) with B-N interaction matches the experimental spectrum of the DABCO/BCF system in toluene indicating the presence of the adduct although its formation is energetically less favored. Based on the experimental and computational evidence the FLP is the favored species, but due to the precipitation from the solution, the adduct is formed according to the principle of LeChatelier. However, in solution the FLP is the dominating species.

The H_2 activation of the DABCO/BCF FLP is energetically favored in toluene at 80 °C with a calculated Gibbs free energy of $\Delta G_{FLP,H2,80} = -6.3$ kcal/mol. For comparison of the molecular with the polymeric system an extended model molecule is chosen for the calculations (Figure S12). The FLP (denotation analogous to DABCO/BCF system) formation has a Gibbs free energy of $\Delta G_{sFLP,80} = 3.8$ kcal/mol, meaning that this reaction is slightly endergonic. However, the energetic barrier is low in analogy to the results for the DABCO/BCF system. The H_2 activation starting from the polyamine/BCF FLP results in a Gibbs free energy of $\Delta G_{sFLP,H2,80} = -2.3$ kcal/mol, showing that the reaction is exergonic and the FLP is capable of heterolytically cleaving H_2. These results are similar for the polyamine/BCF and the DABCO/BCF system in toluene and underline the liquid-state ^{11}B NMR experiments in which the formation of $[HB(C_6F_5)_3]^-$ was proven.

Conclusions

In conclusion, a novel insoluble, three-dimensionally crosslinked polyamine organic framework was prepared and successfully applied in the catalytic hydrogenation of diethyl benzylidenemalonate in combination with molecular BCF as strong Lewis acid. It proves that the structural and electronic features of the polymer are appropriate to form a semi-solid *in situ* FLP under the hydrogenation reaction conditions. Hence, our approach to combine a Lewis basic polymer and its counterpart for FLP formation is promising to bridge the gap from molecular to solid FLP catalysis. ^{11}B NMR experiments proved the capability of heterolytic hydrogen cleavage as well as the presence of the respective adduct and the FLP. ^{1}H experiments suggest that the incorporation of BCF increases the accessibility of the swellable polyamine. Upon impregnation with BCF the signals become much better-resolved. This implies that the rigidity of the polymer framework is probably reduced by the impregnation with BCF in the swollen state. Besides, the BCF-impregnated polyamine is more accessible and mobile to the solvents in comparison to the polyamine itself.

Computational studies show a very small energetic barrier for the FLP formation of the DABCO/BCF system in comparison to the isolated adduct. For the latter the Gibbs free energy is higher and hence, its formation thermodynamically less favored. However, also adduct formation takes place to some extent due to precipitation. The H_2 activation starting from the FLP is exergonic. This means H_2 activation through this system is possible which supports the experimental data. The polyamine/BCF FLP shows a similar behavior with a slightly

endergonic Gibbs free energy for the FLP formation and an exergonic Gibbs free energy for the H_2 activation proving that hydrogen activation is thermodynamically favored.

Overall, a polyamine was synthesized and characterized which is capable of H_2 cleavage and furthermore of heterogeneously catalyzing the hydrogenation of the electron-poor alkene diethyl benzylidenemalonate. The DABCO/BCF system acts as a molecular model system. The experimental data is underlined by computational calculations. This proves that organic framework materials and accessible polymers, which exhibit molecular Lewis basic or acidic centers, are a promising class of materials to further develop the heterogenization of molecular FLP and, thereby, bridge the gap from homo- to heterogeneous catalysis for these innovative materials and metal-free catalysts.

Experimental Section

Polyamine preparation

To a suspension of *p*-xylylenediamine, $NaHCO_3$ and SDS in water/ethanol (v/v=1/1) a solution of 1,4-bis(bromomethyl)benzene in THF was added dropwise while stirring. The reaction mixture was left to stir at r.t. overnight. The resulting solid was filtered off and washed several times with water, methanol, THF and acetone. After that, it is washed by soxhlett extraction with EtOAc. Finally, it was dried in vacuo at 60°C. Anal. calcd.(%): C, 84.67; N, 8.23; H, 7.11. Found: C, 70.54; N, 7.42; H, 6.11.

Catalytic hydrogenation

All steps were carried out in Ar inert gas atmosphere using Schlenk-technique and a Glovebox. Diethyl benzylidenemalonate was dried over molecular sieve 4 Å and solvents were dried prior to use over sodium/benzophenone and stored in a Labstar Glovebox by mBraun. For the hydrogenation reaction MRS-5000 autoclaves (45 mL) by Parr equipped with a glass inlet and a magnetic stirrer were charged with the prepared polyamine and evacuated at 120°C using high vacuum. Tris(pentafluorophenyl)borane and diethyl benzylidenemalonate were dissolved in toluene and added to the prepared polymer in the autoclave with a cannula. The autoclave was pressurized with H_2 and the reaction was carried out at 80°C with various reaction times. Yields were determined by GC analytics using ethyl heptanoate as standard.

Impregnation of polyamine with BCF

Polyamine and BCF were transferred into a Schlenk flask equipped with a magnetic stirrer. Toluene was added and the mixture was stirred overnight. Afterwards, toluene was evaporated. The dry material was stored under argon inside a glovebox.

Solid-state NMR

^{11}B, ^{14}N and ^1H solid-state NMR experiments were carried out on a Bruker AVANCE500 WB spectrometer (11.7T) under magic angle spinning conditions at the desired spin. Due to the moisture-sensitive nature of the samples, the samples were prepared and kept under Ar or N_2 atmosphere. The BCF-impregnated polyamine as well as the polyamine were analyzed by solid state ^{11}B, ^1H and ^{14}N MAS NMR. Two types of substrates were investigated: the dry as-prepared samples in addition to wetted samples. The latter one was prepared by wetting 150 mg of BCF-impregnated polyamine with 200 µL of dry and oxygen-free toluene-d_8 to create a paste-like sample. In this way, the dipolar interactions that result in extensive broadening characteristic of solid state NMR spectra were eliminated to a certain degree. Therefore,

better-resolved signals were observed such that changes in chemical shifts are easier to observe. All ^{11}B spectra were measured by single-pulse echo MAS at room temperature using 10 µs of pulse length and 1 s of delay time, at MAS rate of 8 kHz unless otherwise stated. The spectra were calibrated with cubic boron nitride as an external standard. All ^1H spectra were measured at room temperature using single-pulse MAS with 10 µs of pulse length and 1 s of delay time, at MAS rate of 8 kHz. The chemical shifts were calibrated with solid adamantane as external reference. The wetted samples were spun at a lower rate, 4 kHz, due to presence of the solvent in the rotor. All spectra are only qualitative for identification of species rather than for quantification. The number of scans varies from sample to sample because it was chosen according to the best signal-to-noise ratio.

[1] D. Heller, A. H. M. De Vries, J. G. De Vries, *The Handbook of Homogeneous Hydrogenation*, Wiley-VCH Verlag GmbH, Weinheim, Germany, **2006**.

[2] T. L. Gianetti, N. C. Tomson, J. Arnold, R. G. Bergman, *J. Am. Chem. Soc.* **2011**, *133*, 14904–14907.

[3] G. Erker, D. W. Stephan, *Frustrated Lewis Pairs I, Uncovering and Understanding*, Berlin, Heidelberg, **2013**.

[4] K. C. Szeto, W. Sahyoun, N. Merle, J. L. Castelbou, N. Popoff, F. Lefebvre, J. Raynaud, C. Godard, C. Claver, L. Delevoye, et al., *Catal. Sci. Technol.* **2016**, *6*, 882–889.

[5] G. C. Welch, R. R. San Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124–1126.

[6] M. Sajid, A. Klose, B. Birkmann, L. Liang, B. Schirmer, T. Wiegand, H. Eckert, A. J. Lough, R. Fröhlich, C. G. Daniliuc, et al., *Chem. Sci.* **2013**, *4*, 213–219.

[7] N. von Wolff, G. Lefèvre, J.-C. Berthet, P. Thuéry, T. Cantat, *ACS Catal.* **2016**, *6*, 4526–4535.

[8] E. Otten, R. C. Neu, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 9918–9919.

[9] M. Ullrich, A. J. Lough, D. W. Stephan, *Organometallics* **2010**, *29*, 3647–3654.

[10] D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2010**, *49*, 46–76.

[11] G. Erker, D. W. Stephan, K. (Konstantin) Chernichenko, *Frustrated Lewis Pairs. II, Expanding the Scope*, Springer, **2013**.

[12] B. Inés, D. Palomas, S. Holle, S. Steinberg, J. a. Nicasio, M. Alcarazo, *Angew. Chem. Int. Ed.* **2012**, *51*, 12367–12369.

[13] J. a. Nicasio, S. Steinberg, B. Inés, M. Alcarazo, *Chem. Eur. J.* **2013**, *19*, 11016–11020.

[14] J.-Y. Xing, J.-C. Buffet, N. H. Rees, P. Nørby, D. O'Hare, D. M. Heinekey, A. Lledós, J. M. Lluch, G. S. McGrady, G. Guilera, et al., *Chem. Commun.* **2016**, *33*, 175–182.

[15] Y.-J. Wanglee, J. Hu, R. E. White, M.-Y. Lee, S. M. Stewart, P. Perrotin, S. L. Scott, *J. Am. Chem. Soc.* **2012**, *134*, 355–366.

[16] J. Tian, S. Wang, Y. Feng, J. Li, S. Collins, *J. Mol. Catal. A Chem.* **1999**, *144*, 137–150.

[17] M. Trunk, J. F. Teichert, A. Thomas, *J. Am. Chem. Soc.* **2017**, *139*, 3615–3618.

[18] C. B. Singh, V. Kavala, A. K. Samal, B. K. Patel, *Eur. J. Org. Chem.* **2007**, 1369–1377.

[19] K. Schute, M. Rose, *ChemSusChem* **2015**, *8*, 3419–3423.

[20] Z. Chang, D.-S. Zhang, Q. Chen, X.-H. Bu, Z. Wei, H.-C. Zhou, A. Coskun, C. D. Wood, B. J. Cox, J. M. Hill, et al., *Phys. Chem. Chem. Phys.* **2013**, *15*, 5430–5442.

[21] M. Rose, *ChemCatChem* **2014**, *6*, 1166–1182.

[22] P. J. C. Hausoul, C. Broicher, R. Vegliante, C. Göb, R. Palkovits, *Angew. Chemie Int. Ed.* **2016**, *55*, 5597–5601.

[23] P. J. C. Hausoul, T. M. Eggenhuisen, D. Nand, M. Baldus, B. M. Weckhuysen, R. J. M. Klein Gebbink, P. C. a. Bruijnincx, *Catal. Sci. Technol.* **2013**, *3*, 2571.

[24] D. W. Stephan, S. Greenberg, T. W. Graham, P. Chase, J. J. Hastie, S. J. Geier, J. M. Farrell, C. C. Brown, Z. M. Heiden, G. C. Welch, et al., *Inorg. Chem.* **2011**, *50*, 12338–48.

[25] S. J. Geier, P. a Chase, D. W. Stephan, *Chem. Commun.* **2010**, *46*, 4884–4886.

[26] Z. M. Heiden, D. W. Stephan, *Chem. Commun.* **2011**, *47*, 5729–5731.

[27] C. Jiang, O. Blacque, H. Berke, I. Pápai, M. Nieger, M. Leskelä, T. Repo, P. Pyykkö, B. Rieger, *Chem. Commun.* **2009**, *131*, 5518.

[28] D. Chen, J. Klankermayer, *Chem. Commun.* **2008**, *17*, 2130–2131.

[29] P. A. Chase, T. Jurca, D. W. Stephan, W. E. Piers, J. D. Masuda, P. Wei, D. W. Stephan, *Chem. Commun.* **2008**, *62*, 1701.

[30] S. Tussing, L. Greb, S. Tamke, B. Schirmer, C. Muhle-Goll, B. Luy, J. Paradies, *Chem. A Eur. J.* **2015**, *21*, 8056–8059.

[31] S. Tussing, K. Kaupmees, J. Paradies, *Chem. Eur. J.* **2016**, *22*, 7422–7426.

[32] Á. Gyömöre, M. Bakos, T. Földes, I. Pápai, A. Domján, T. Soós, *ACS Catal.* **2015**, *5*, 5366–5372.

[33] É. Dorkó, M. Szabó, B. Kótai, I. Pápai, A. Domján, T. Soós, *Angew. Chem. Int. Ed.* **2017**, *56*, 9512–9516.

[34] S. J. Geier, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 3476–7.

[35] G. C. Welch, D. W. Stephan, *J. Am. Chem. Soc.* **2007**, *129*, 1880–1881.

[36] A. C. Malcolm, K. J. Sabourin, R. McDonald, M. J. Ferguson, E. Rivard, *Inorg. Chem.* **2012**, *51*, 12905–12916.

[37] P. A. Chase, D. W. Stephan, *Angew. Chem. Int. Ed.* **2008**, *47*, 7433–7.

[38] G. Erős, H. Mehdi, I. Pápai, T. A. Rokob, P. Király, G. Tárkányi, T. Soós, *Angew. Chemie Int. Ed.* **2010**, *49*, 6559–6563.

[39] J. M. Blackwell, W. E. Piers, M. Parvez, R. McDonald, *Organometallics*, **2002**, 1400–1407.

[40] T. Korenaga, T. Kadowaki, T. Sakai, *J. Fluor. Chem.* **2007**, *128*, 557–561.

[41] G. J. P. Britovsek, J. Ugolotti, A. J. P. White, *Organometallics* **2005**, *24*, 1685–1691.

[42] S. Mitu, M. C. Baird, *Can. J. Chem.* **2006**, *84*, 225–232.

[43] S. A. Llewellyn, M. L. H. Green, A. R. Cowley, A. Guagliardi, M. Muller, G. D. W. Anderson, L. H. Rees, G. Palyi, H.-G. Schmidt, M. Noltemeyer, *Dalt. Trans.* **2006**, *26*, 1776.

[44] G. Erős, K. Nagy, H. Mehdi, I. Pápai, P. Nagy, P. Király, G. Tárkányi, T. Soós, *Chem. Eur. J.* **2012**, *18*, 574–585.

Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

Frustrated frameworks: A solid molecular frustrated Lewis pair was synthesized from a novel polyamine organic framework and a borane. It performs excellent in the metal-free heterogeneously catalysed hydrogenation of alkenes. The frustration and hydrogen activation were proven spectroscopically.
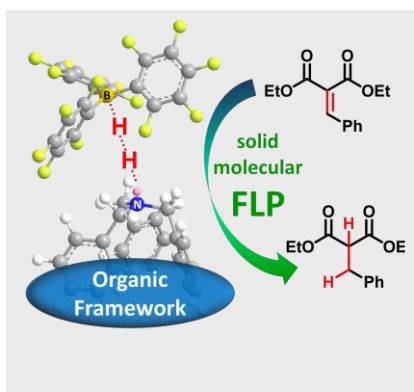
Andrea Willms, Hannah Schumacher, Peter J. C. Hausoul, Tarnuma Tabassum, Long Qi, Susannah L. Scott, and Marcus Rose*

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Solid Molecular Frustrated Lewis Pairs in a Polyamine Organic Framework for the Catalytic Metal-free Hydrogenation of Alkenes