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Hydrodechlorination of Et₃NBCl₃ Catalyzed by Amorphous Nickel Boride – A Mechanistic Approach

Christian Reller^[a] and Florian O. R. L. Mertens^{*[a]}

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The catalytic hydrodechlorination of BCl_3 with molecular hydrogen in the presence of tertiary amines is a viable strategy for the energy-efficient generation of valuable B–H bonds. A mechanistic study based on experiments with isolated intermediates and deuterium labeling experiments is presented. The occurrence of the rate-limiting reverse reaction from the insoluble Et_3 NHCl adduct was identified as a major cause of

Introduction

An important objective in sustainable chemistry is the replacement of precious and expensive reducing agents such as NaBH₄, LiAlH₄, R₃SnH, R₃SiH, and N₂H₄ by earthabundant hydrogen through the use of appropriate catalysts. The number of heterogeneous hydrogenation catalysts developed and their use in a large range of hydrogenation procedures is legion.^[1] Hydrodehalogenation reactions are a related problem but provide a much more complicated task in respect to catalyst requirements.^[2] In addition to the mentioned hydrogen donors, saltlike hydrides such as NaH,^[3] LiH,^[4] CaH₂,^[3] and other complex hydrides of the group 1 and 2 elements are also well established as reducing agents in hydrodehalogenation reactions.^[5–8] The progress of these reactions is thermodynamically favored by the formation of a simple stable metal halide or in the cases of alkyl stannanes (R₃SnH)^[9] or alkyl silanes (R₃SiH)^[10] by the corresponding halogen compounds R₃SnX or R₃SiX. If a hydrodehalogenation is performed with molecular hydrogen in the presence of a catalyst, gaseous HX is obtained. The reaction only proceeds in the presence of a catalyst such as Pt, Pd, or Ni.^[2] Of these elements, palladium is preferentially used as the catalytically active metal, because it catalyzes both the CX bond cleavage and the subsequent hydrogenation.^[11] As they can form very stable MX bonds with the metal centers, halogens usually act as strong catalyst poisons for precious-metal-based catalysts.^[2] The corresponding chloride surface coverage data were published by

low Et_3NBH_3 yields. In addition, amines with NCH₂ units, which also serve in the corresponding cases as solvents, have a strong influence on the reaction kinetics; they are directly involved in the hydrogen transfer at elevated temperatures and assume the role of a cocatalyst. A catalytic cycle for the reaction on a nickel boride catalyst is proposed.

Urbano, and the order of the halogen affinity was determined to be Ru>Rh>Pd and Os>Ir>Pt.^[2] In many hydrodehalogenation reactions, as was observed, for example, in the case of aryl halogenides, the hydrogen halide formed during the reaction can also deactivate the catalyst;^[12] therefore, it is necessary to reliably remove the hydrogen halide.^[2] If the hydrodehalogenation occurs in the liquid phase, the removal of the HX is commonly achieved by the addition of a base, such as NaOH,^[13,14] or an amine $(R_3N)^{[15-17]}$ In the case of NaOH, the product of the acidbase reaction is NaX, and in the case of a trialkylamine, it is corresponding hydrochloride (R₃NHX). If the reaction is performed in organic solvents such as hydrocarbons or even in pure amines, an increased salt concentration is obtained, and this leads to the generation of an additional insoluble phase in the reactor.^[15] Through such effects, the catalyst can clump together or pores can be blocked, which in turn suppresses or even prevents the adsorption of reactants on reactive areas of the catalyst.^[18] Hydrodehalogenation reactions are known from the field of "green chemistry" and have a special meaning for the disposal and the reduction of halogenated environmental pollutants with increased bioaccumulation potential such as 2,4-dichlorophenol, chlorobenzene, bromobenzene, and 4-chlorohypnon.^[16] In contrast to this field of application, the transfer of the catalytic procedure with molecular hydrogen to other reaction systems, such as the hydrodehalogenation of amine-BX₃ adducts has not yet been made. As already mentioned, the presented catalytic dehydrohalogenation of these adducts has the potential to become an important tool for the generation of highly active reducing agents by an energy-efficient procedure. The production of high-energy boron hydride compounds from gaseous BCl₃ was presented by Schlesinger in the early 1930s.^[19] In this procedure, dibor-

[[]a] Institut für Physikalische Chemie, TU Bergakademie Freiberg, Leipziger Str. 29, 09596 Freiberg, Germany E-mail: florian.mertens@chemie.tu-freiberg.de www.tu-freiberg.de

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ane and chlorodiborane (B₂H₅Cl) were obtained from a gas mixture of BCl₃/H₂ exposed to an electric arc at 15 kV between two cooled copper electrodes. In general, all gasphase processes known to date run at high temperature (T > 350 °C), which entails low product selectivities; therefore, a specific and defined production of boranes by these methods is unfavorable and unattractive for commercial use. In addition to the gas-phase concepts,^[19-21] several other hydrodehalogenation methods that were performed in the liquid phase have been described in the literature.^[22,23] In these procedures, BX₃ was first precomplexed with an amine to form a Lewis acid-base adduct and then reacted with hydrogen at a pressure of 2000 bar and temperatures of 180-250 °C; the best cases reported 25% yield of Me₃NBH₃ after 60 h.^[23] In continuation of our previous studies on the catalytic generation of boranes from boron halides with molecular hydrogen,^[24] we focus in this contribution on detailed mechanistic investigations to get a better

understanding of the procedure with the aim to optimize

the hydrodehalogenation reaction of Et₃NBX₃ adducts.

Results and Discussion

Hydrodehalogenation

In a previous study,^[24] it was demonstrated that BCl₃ can be directly hydrodehalogenated to Et₃NBH₃ with molecular hydrogen in the presence of the catalyst Ni₃B and the amine Et₃N with good yields and under fairly mild conditions. Particularly remarkable in respect to this reaction is the tolerance of the catalyst to the strong transition-metal-catalyst poisons, chloride and amine. To learn more about the underlying reaction mechanism, it is necessary to identify all intermediates, their time of occurrence, and their mutual interactions. Consequently, as the first step to obtain this information, the time-dependent composition of the reaction mixture was monitored by periodically taking samples from the liquid reaction phase as a constant hydrogen pressure was maintained. The determination of the composition of the extracted samples was then performed by ¹¹B NMR spectroscopy. Our first objective was to establish the temperature and pressure dependence of the reaction. The hydrodechlorination experiments showed that the partially hydrogenated intermediates Et₃NBHCl₂ and Et₃NBH₂Cl can selectively be prepared by temperature adjustment. For example, the experiment at 100 °C and a H₂ pressure of 40 bar resulted in almost exclusive formation of the monohydrogenated Et₃NBHCl₂ adduct after a reaction period of 270 min (Figure 1). After the completion of the reaction, the product was quantitatively isolated and no other byproducts except Et₃NHCl were detected in the residue.

As can be seen from the ¹¹B{¹H} NMR spectra (Figure 1, left), the signal of Et₃NBCl₃ at $\delta = 10$ ppm decreases over time in correlation with the increase of the doublet signal at $\delta = 4.7$ ppm, which can be attributed to the monohydrogenated Et₃NBHCl₂ product. The analytical results for the reaction at the somewhat higher temperature

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Figure 1. Left: Time-resolved ¹¹B{¹H} NMR measurements of the hydrodehalogenation of Et₃NBCl₃. Right: Kinetic plot based on the integrated ¹¹B{¹H} NMR signals. The experiment was performed at $p(H_2) = 40$ bar, T = 100 °C, 10 mol-% nickel boride, n = 650 rpm.

of 130 °C over a reaction period of 1000 min are shown in Figure 2. Within the first 90 min, only Et_3NBHCl_2 is formed, and it then continues to react to form Et_3NBH_2Cl . The transfer rate of the second hydrogen atom in the interval 360–1000 min is significantly lower. After ca. 360 min, the formation of Et_3NBH_3 commences. From the temporal development of the reaction, it can additionally be assumed that a limitation must underlie the formation of Et_3NBH_3 and Et_3NBH_2Cl , as the reaction rate is much lower in comparison to that for the formation of Et_3NBHCl_2 and, more importantly, instead of a complete conversion to Et_3NBH_3 , a steady state with partial conversion was reached after ca. 24 h.

An increase of the reaction temperature (T = 160 °C) led to further acceleration of all partial reactions, so that the generation of the first intermediate Et₃NBHCl₂ was completed after 30 min. In the 160 °C experiment measured after 24 h, the equilibrium state possessed slightly higher mole fractions of Et₃NBH₂Cl and Et₃NBH₃ than were observed in the experiment at T = 130 °C. To determine the equilibrium composition precisely and to test whether or not the equilibrium state was really reached, we conducted a longterm experiment over 3 d and found the same composition as that after 24 h: 63% Et₃NBH₂Cl and 37% Et₃NBH₃. These results suggest that a reverse reaction is responsible for the observed conversion limitation. Control experiments starting with the presynthesized final products of the BCl₃ hydrodechlorination experiment, Et₃NBH₃ and Et₃NHCl (corresponding to those in Figure 2), demonstrate that the assumed reverse reaction of the last reaction step conducted under the same reaction conditions with Et₃N present as solvent and amorphous nickel boride catalyst as in the original experiment can proceed at significant reaction rates. The progress of the reaction was monitored by liquid sample collection and subsequent ${}^{11}B{}^{1}H{}$ NMR analysis. The results are displayed in Figure 3 and compared to those for the last hydrodehalogenation step of Et₃NBCl₃, that is, the

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Figure 2. ¹¹B{¹H}NMR spectroscopy (C₆D₆) tracking of the hydrodehalogenation of Et₃NBCl₃ conducted at T = 130 °C and $p(H_2) = 60$ bar. $\delta = 10$ ppm, Et₃NBCl₃ (s); $\delta = 4.7$ ppm, Et₃NBHCl₂, $J_{B,H} = 151.4$ Hz (d); $\delta = -4.2$ ppm, Et₃NBH₂Cl, $J_{B,H} = 126$ Hz (t); $\delta = -12.1$ ppm, Et₃NBH₃, $J_{B,H} = 98.2$ Hz.

reaction from Et_3NBH_2Cl to Et_3NBH_3 . In addition to hydrogen gas, the solvent Et_3N , and the catalyst, only presynthesized Et_3NBH_2Cl was used for the latter reaction; the advantage of this is that one can examine the formation of Et_3NBH_3 from Et_3NBH_2Cl in the absence of Et_3NBCl_3 , Et_3NBHCl_2 , and larger amounts of Et_3NHCl . Figure 3 clearly indicates that the initial reaction rate in the period from 90 to 200 min is very high and is followed by a massive decline in reaction rate directly afterwards.

This effect can be explained by the onset of the reverse reaction. Both experiments together clearly substantiate the importance of the described reverse reaction for the last hydrodechlorination step in the presence of the hydrochloride and, thus, for the overall Et₃NBH₃ production by es-



Figure 3. Temporal development of the Et_3NBH_3 mole fraction in the control experiments related to the last step of the BCl₃ hydrodehalogenation in the presence of Et₃N [T = 160 °C, $p(\text{H}_2) = 60$ bar], i.e., the forward (lower curve, starting from Et₃NBH₂Cl and hydrogen) and the reverse reactions (upper curve, starting from a mixture of Et₃NBH₃ and Et₃NHCl).

tablishing an equilibrium between the Et_3NBH_3 and Et_3NBH_2Cl content.

The influence of the catalyst on the kinetics of the reverse reaction was also examined as shown in Figure 4. The composition of the reaction mixture of the reaction conducted at T = 160 °C and $p(H_2) = 60$ bar without the use of a catalyst was 70:30 (Et₃NBH₃/Et₃NBH₂Cl) after 2400 min. By using a catalyst, the composition after the same reaction period was modified to 35:65. The amorphous nickel boride is apparently able to activate the Et₃NHCl adduct that is formed during the hydrodehalogenation and, thus, promotes the reverse reaction. The same experiment, but at 130 °C, leads to a ratio of the two products Et₃NBH₂Cl and Et₃NBH₃ of 80:20 after 3 d. The observed increase of the hydrogen pressure in the reactor can be seen as further evidence for the occurrence of the reverse reaction. From these results, one has to conclude that a separation of the Et₃NHCl adduct by filtration is necessary to improve the total yield of Et₃NBH₃ in the original hydrodechlorination reaction as we previously demonstrated.^[24] In contrast to the effectiveness of this measure to improve the Et₃NBH₃ yield, an attempt to improve the reaction kinetics by the increase of the reaction temperature finds its limits at a temperature of ca. 180 °C because of the formation of several undesired byproducts. As most of the corresponding ¹¹B NMR signals are above $\delta = 29$ ppm, a first assumption that these byproducts are mainly borazine derivatives can be made. To gain more information on these byproducts, we performed pyrolysis experiments with the relevant compounds present in the reaction mixture, namely, Et₃NBCl₃, Et₃NBHCl₂, Et₃NBH₂Cl, and Et₃NBH₃ (see control experiment in Figure 5).

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Figure 4. Reverse reaction: comparison of the compositions of the reaction mixture with and without the use of the amorphous nickel boride catalyst [T = 160 °C, $p(H_2) = 60$ bar]. The ¹¹B NMR (C_6D_6) spectra on the right were recorded after 2400 min.

From the presented ¹¹B NMR spectra (Figure 5), a clear relationship can be stated between the hydrodechlorination experiment at T = 190 °C (Figure 5, a) and the pyrolysis experiment of the presynthesized adducts (Figure 5, b) in regard to the observed byproducts. As the mayor byproduct

of the thermal decomposition of Et₃NBCl₃, *N*-alkyl-*B*-chloroborazine was detected at $\delta = 32 \text{ ppm}$ (ref. $\delta = 31.4 \text{ ppm}$).^[25] A signal with the same chemical shift was also found in the hydrodehalogenation experiment at T = 190 °C after 24 h. As a second byproduct, a species with a



Figure 5. (a) Comparison of the ¹¹B{¹H} NMR (C₆D₆) spectra of the hydrodechlorination of Et₃NBCl₃ performed at T = 190 °C, p = 60 bar after 3 h and after 24 h. (b) ¹¹B{¹H} NMR (C₆D₆) spectra of products generated by the thermal decomposition (pyrolysis; T = 200 °C, t = 4 h) of the relevant adducts. (c) Reactions pathways compatible with the product spectra obtained from the pyrolysis of the Et₃N adducts at T = 200 °C and 4 h.

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chemical shift of 40 ppm (s) was observed and identified as cyclic (EtN–BEt)₃ (ref. δ = 37.3 ppm)^[26] after the pyrolysis of Et₃NBCl₃. However, the thermal decomposition of Et₃NBHCl₂ also led to (EtN-BEt)₃ but mainly to the formation of an unidentified species with a chemical shift of δ = 21 ppm (s). The decomposition of Et_3NBH_2Cl provided a variety of decomposition products including Et₃NBHCl₂ $[\delta = 4.7 \text{ ppm } (d, J_{B,H} = 150 \text{ Hz})], (NC_2H_5BCl)_3 [\delta = 32 \text{ ppm}]$ (s, ref. 31.4 ppm)],^[25] (NC₂H₅BH)₃ [δ = 33.5 ppm (d, J_{B,H} = 166.8 Hz, ref. δ = 33.1 ppm)]^[26] and cyclic (EtN–BEt)₃ [δ = 40 ppm (s, ref. δ = 37.3 ppm)].^[26] The species with the chemical shifts of 46.3 (s) and 54 ppm (s) could not be identified. The decomposition of Et₃NBH₃ led mainly to the formation of a species with a chemical shift of 44 ppm (d, $J_{\rm B,H}$ = 118 Hz). The corresponding ¹H and ¹³C NMR spectra can be found in the Supporting Information in Figures S2 and S3. A list of decomposition reactions compatible with the observed product spectrum of the pyrolysis experiments is given in Figure 5c. It has been assumed that ethene and HCl were formed in the first step of the decomposition of the chlorine-containing adducts. Furthermore, it was demonstrated that the addition of HCl to ethene leads, as it was expected, to chloroethane (Figure 5, c, no. 3). Ethene itself can react with boranes/chloroboranes according to reaction nos. 4-6 in Figure 5c. As documented in the literature, the reaction between ethene and trimerized (BHNEt)₃ (Figure 5, c, no. 4) finally leads to the formation of B-alkylated borazine derivatives.^[26] Ethene generally provides a basis for the formation of various byproducts owing to its tendency to undergo hydroboration. At even higher temperatures ($T = 200 \,^{\circ}\text{C}$), traces of B-alkylated compounds, detected by ${}^{11}B{}^{1}H{}$ NMR (C₆D₆), with chemical shifts of >50 ppm are formed during the thermal decomposition of Et₃NBH₂Cl.

Role of the Amine

As solvents fulfill simultaneously the role of amine-derived bases for the hydrodehalogenation of R₃NBX₃, trialkylamines should be used instead of aromatic amines, because the latter compounds very often lead to the formation of the undesired BCl₄⁻ ion, which poses an obstacle to successful hydrogenation.^[24] For example, the use of N,N-diethylaniline can lead to the BCl₄⁻ containing diammoniate [PhEt₂NBCl₂NEt₂Ph]BCl₄ or the simple PhEt₂NHBCl₄ salt. The addition of Et₃N in excess to the ionic product [Et₃NH][BCl₄] results in the almost complete conversion of the latter compound to Et₃NHCl and Et₃NBCl₃. These results indicate that BCl₄⁻ ions are unstable in Et₃N as was also observed by Gutmann, who attributed the effect to the low dielectric constant of the solvent (relative permittivity of Et_3N : 2.45).^[27–29] By the use of Et_3N as the solvent, the entire boron content becomes accessible as Et₃NBCl₃ adduct. In addition to its role as a solvent, the main purpose of the amine, however, is the removal of the hydrogen chloride produced by the formation of a sparingly soluble Et₃NHCl adduct. From the thermodynamic point of view, a direct hydrogenation reaction of uncomplexed BCl₃ to di-

borane is highly unfavorable as expressed by its positive free energy of reaction $[\Delta_R G(298 \text{ K}) = +148.0 \text{ kJ/mol}]$.^[30] Therefore, Et₃N has to be seen as an auxiliary base for the reduction of the free reaction energy by the formation of the HCl adduct. In addition, the amine also fulfills the task of stabilizing the borane products and keeps all reactants, except Et₃NHCl, in solution. Furthermore, the adduct formation probably contributes to an expansion of the B-X bond lengths and may ultimately lead to a destabilization of this bond, an assumption that still needs either to be evidenced experimentally or by quantum chemical calculations. The adsorption of Et₃N molecules on the catalyst surface may form a layer that protects the catalyst against inhibition by free HCl, interestingly without itself inhibiting the catalyst. This phenomenon is also described in the literature for elemental nickel and palladium catalysts and has been studied extensively.^[13] A corresponding hydrodehalogenation experiment of Et₃NBCl₃ in the solvent CH₂Cl₂ without a corresponding excess of amine led to the formation of the Ni- $(NEt_3)_3Cl_2$ dimer complex, which had previously been synthesized from Et₃N and NiCl₂ and characterized by Tandon.^[31] Apparently, an initial formation of NiCl₂ on the catalyst surface was the cause for the observed complexation. Another advantage of Et₃N compared to other organic solvents such as dichloromethane and toluene is the higher solubility of hydrogen and connected to it the reduction of its mass transport limitations in these multiphase reactions. A graph representing the hydrogen solubility in Et_3N is displayed in Figure S1. It can be seen that the H_2 solubility even increases with the increase of temperature over a wide pressure range. From this behavior, a positive value of the enthalpy of solution, describing an endothermic process, can be concluded ($\Delta_{\rm L} H^{298} = +5.285 \, \rm kJ/$ mol).^[32] To investigate the influence of the different amine bases, two other trialkylamines, Me₂EtN and Me₃N, were used in addition to Et₃N as auxiliary bases. A comparison of the corresponding experiments, that is, the hydrodehalogenation of Et₃NBCl₃, Me₂EtNBCl₃, and Me₃NBCl₃ in their corresponding solvents or bases, is presented in Figure 6. The graph displays the temporal development of the corresponding product of the first hydrogenation stage. The reaction rates follow the order: Et₃NBCl₃>Et₂- $MeNBCl_3 > Me_3NBCl_3$. It needs to be emphasized that no hydrodehalogenation products for Me₃N could be detected even after a reaction period of 24 h. It is somewhat surprising that the structurally and electronically related amines cause such drastic changes in the reaction rates. Therefore, it was decided to address this issue by additional mechanistic investigations such as labeling and solvent-variation experiments.

As a first step, we tested the interaction of Et_3N , as the amine related to the highest hydrodehalogenation rate, with the catalyst; no reactant other than deuterium was present. The result of the ²H NMR measurements of periodically extracted samples can be seen in Figure 7. One observes the replacement of the H atoms, first in the N–CH₂ units beginning after 3 h (Figure 7, b) and then in the CH₃ groups after 48 h (Figure 7, a).

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The same experiment conducted at lower temperatures (T = 100 and 130 °C) shows almost no replacement of the H atoms in the CH₃ groups by deuterium. Knowing that the exchange of the Et₃N hydrogen atoms is in principle possible in the presence of the catalyst, the question has to be raised to what extent these hydrogen atoms serve as the actual hydrogen source in the reaction. To address this point, we repeated the Et₃NBCl₃ hydrodechlorination experiment at 100 °C with D₂ instead of H₂. Surprisingly, B–



Figure 6. Temporal development of the products of the first hydrodechlorination step of the RBCl₃ adducts, RBHCl₂, (R represents the amine components Me₂EtN, Et₃N, and Me₃N) in the different amine-variation experiments. The experiments were conducted with the same corresponding amines as solvents: Et₃NBCl₃ in Et₃N, Me₂EtNBCl₃ in Me₂EtN, and Me₃NBCl₃ in Me₃N [T = 160 °C, $p(H_2) = 60$ bar, catalyst: amorphous nickel boride].

H species were obtained prior to the B–D species, which appeared after ca. 90 min in the ¹¹B NMR measurement (see Figure 8, left). The spectra on the right of Figure 8 illustrate the reaction progress of the same experiment at 130 °C.

The higher reaction temperature of 130 °C leads to the formation of the more highly deuterated (hydrogenated) intermediates $Et_3NBD_2(H_2)Cl$ and $Et_3NBD_3(H_3)$. The B–D coupling constant $J_{B,D}$ was determined to be 22 Hz for the Et_3NBDCl_2 adduct, but for the more highly deuterated/ hydrogenated species this quantity could not be obtained owing to poor spectral resolution. The labeling experiments very clearly demonstrate that activated amorphous nickel boride is able to activate and transfer molecular hydrogen (or deuterium) directly to the substrate.

To test whether or not N–CH₂ bond changes are associated with the hydrodechlorination, several isotope labeling experiments with subsequent ²H NMR analysis were conducted. The results unambiguously indicate that the hydrogen transfer not only occurs from molecular hydrogen (or deuterium) but also from the hydrogen atoms of the N–CH₂ units of the solvents. As an iminium ion formed during that process will almost certainly be catalytically hydrogenated during the course of the continued hydrodechlorination reaction, we conducted an additional control experiment without the presence of hydrogen/deuterium. If a N–CH₂ hydrogen elimination takes place, as was pointed out before, there must be some evidence of the formation of



Figure 7. ²H NMR spectra (C₆D₆): (a) Sequence of spectra taken during a N–CH₂ deuterium exchange experiment covering a period from 1 to 5 h. (b) Bottom – after (48 h) the exchange of the hydrogen atoms in the CH₃ groups of Et₃N has also taken place. To assign the peak positions, an ¹H NMR spectrum of Et₃N was used as a reference [T = 160 °C, $p(D_2) = 30$ bar].



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Figure 8. Time evolution of the hydrodechlorination experiments of Et_3NBCl_3 traced by ${}^{11}\text{B}[{}^2\text{H}(\text{H})]$ NMR (C₆D₆) measurements. The experiments were performed at T = 100 (left) and 130 °C (right) at $p(D_2) = 30$ bar. The insert visualizes the B–H and B–D coupling of the monohydrogenated intermediate $\text{Et}_3\text{NBD}(\text{H})\text{Cl}_2$.



Figure 9. (a) Time evolution of the ¹¹B{¹H} NMR (C_6D_6) spectra during the hydrodechlorination of Me₂EtNBCl₃ (solvent Et₃N). The Me₂EtNBCl₃ resonance subsequently decreased, and the resonances of Me₂EtNBHCl₂ simultaneously appeared beside small amounts of Et₃NBHCl₂ caused by a gradually occurring base exchange. (b) Time evolution of the ¹¹B{¹H} NMR (C_6D_6) spectra during the hydrodechlorination of Et₃NBCl₃ (solvent Me₂EtN): fast base exchange and slow hydrodehalogenation kinetics. Experiment (a) was monitored for 270 min. Experiment (b) was monitored for 210 min. The interval between consecutive sample extractions was 30 min. Both experiments were conducted at *T* = 160 °C, *p*(H₂) = 60 bar in the presence of amorphous nickel boride (18 mg).

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iminium ions as has been previously reported.^[33,34] For proof of concept, we used ¹H NMR spectroscopy to locate the single proton resonance expected to be found near δ = 8.2 ppm (CD₃OD). In the control experiment, a ¹H chemical shift of $\delta = 8.13$ ppm (CDCl₃) was observed and, given the system and solvent differences, this is close enough to allow the assignment to [Et₂N=CHCH₃]⁺Cl⁻ (see Figure S4). As the dehydrochlorination reaction progresses, the number of N-CD₂ groups continuously grows, so that more deuterium can be offered by the solvent. It is quite remarkable that in both experiments no C-D species were observed in the ²H NMR region of the methyl groups. If the just discussed hydrogen-deuterium exchange is an essential part of the hydrodehalogenation reaction mechanism, the reduction of the number of present N-CH2 units should reduce the overall reaction rate. This interpretation is in line with the observation of the slow reaction rate in the Me₃NBCl₃ adduct case in Figure 6, as no N-CH₂ units are present at all there. To investigate this effect in more detail and to answer the question of which amine species is the relevant hydrogen donor in the overall reaction mechanism, the coordinated amine or the solvent one, we conducted two related experiments. In the first one (Figure 9, a), Me₂EtNBCl₃ was chosen as adduct and Et₃N as the solvent, and in the second one (Figure 9, b), reflecting the reverse situation, Et₃NBCl₃ was used as the adduct and Me₂EtN was used as the solvent. The reaction progress was monitored by ${}^{11}B{}^{1}H{}$ NMR spectroscopy. From the analysis of the first experiment, two effects are noticeable. In contrast to the situation in Figure 6, in which Me₂EtNBCl₃ reacts in the solvent Me₂EtN very slowly, the same reaction in the methylene-rich solvent Et₃N progresses much faster (see Figure S5). The reverse experiment, Et_3NBCl_3 in Me₂EtN, shows a much slower hydrodechlorination and a very fast and essentially complete base exchange. As the situation after the base exchange equals the aforementioned one in Figure 6, one has to conclude that the hydrogen atoms offered by the methylene groups of the solvent are essential for the reaction progress. The particular importance of the methylene hydrogen atoms is also backed by the fact that a Me₃NBCl₃ adduct in Me₃N (Figure 6) essentially does not react.

Conclusions

Catalytically active amorphous nickel boride has the ability to activate molecular hydrogen. It is still unclear whether and to what extent the catalyst is directly involved in a B–Cl bond dissociation. In respect to the solvent triethylamine, one needs to state that the catalyst is able to activate the N–CH₂ hydrogen atoms, as has been demonstrated by deuterium labeling experiments. Although it cannot directly be isolated from the dehydrogenation reaction because of its minute concentration, the formation of an intermediate iminium ion was indirectly demonstrated by the suppression of the subsequent catalytic reaction to Et_3NHCl [Equation (1)] by conducting the experiment without molecular hydrogen.

 $[Et_2N=CH-CH_2]^+Cl^- + H_2 \rightarrow Et_3NHCl$

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(1)

From a scientific point of view, the question of whether there is a homolytic or heterolytic C-H bond cleavage is of importance. The simultaneous presence of Et₃N and palladium catalysts often leads to unexpected reactions [isomerization, reduction (hydrogenation)] in which triethylamine represents the hydrogen source.^[35] The cause of this reaction sequence is probably the formation of a palladium hydride-iminium complex (Figure 10). The abstraction of the N-H₂ hydrogen atoms proceeds in this case clearly heterolytically by the transfer of a hydride ion to the palladium center. A similar mechanism may be responsible for the observed N-CH₂ activation by amorphous nickel boride. If the N-CH₂ hydrogen abstraction proceeds through a homolytic (radical) cleavage of the C-H bond, an α-amino alkyl radical will be formed as an reactive intermediate [Equation (2)]. This phenomenon has already been described by Lalevée for the hydrodehalogenation of CCl₄ in Et₃N.^[33,34]

$$Et_3NC \cdot HCH_3 \rightarrow e^- + Et_2N^+ = CHCH_3$$
(2)



Figure 10. Hydrogenation mechanism of unsaturated carbonyl compounds in the system Pd/C–Et_3 $N^{[31]}_{\rm -}$

The reduction of the Et_3NBCl_3 adduct by the α -amino alkyl radical would in this case proceed by a one-electron transfer mechanism. The incorporation of this aspect into the mechanism of the heterogeneously catalyzed hydrodechlorination of Et_3NBCl_3 is shown in the catalytic cycle in Figure 11.

In step II of the proposed reaction cycle, the radical has formed through the catalyzed hydrogen abstraction. The formed α -amino alkyl radical is, according to the investigations of Wayner, a very strong reducing agent owing to its low oxidation potential of $E_{\rm ox} = -1.12$ V.^[36] In reaction step III (with the drawn transition state), a one-electron transfer to the Et₃NBCl₃ adduct leads to the reduction accompanied by the abstraction a Cl ion, which finally causes the formation of the iminium salt.

Although the strongest evidence for the validity of the proposed reaction mechanism would be the direct analytical detection of the α -amino alkyl radical, the results of the D₂ labeling experiments nevertheless substantiate these pathways by the demonstration of the hydrogen transfer through the N–CH₂ groups of the Et₃N solvent. In summary, it can be stated that the presence of N–CH₂ hydrogen atoms of the amine solvent is of great importance for the hydrode-

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Figure 11. Radical-mediated hydrodehalogenation of the B–Cl bond by α -amino alkyl radicals as part of the conversion of Et₃NBCl₃ to Et₃NBH₃.

halogenation reaction. The solvent Et_3N is, thus, a direct part of the reaction mechanism and has to be seen as a separate reactant or, if regenerated, even as a cocatalyst.

Experimental Section

General Methods: All operations were performed by using standard Schlenk and glove-box techniques under an atmosphere of argon (purity 5.0). The hydrodechlorination processes were conducted in a polytetrafluoroethylene-lined (PTFE-lined) 15 mL stainless steel pressure vessel under magnetic stirring. In all time-dependent experiments, the sample extraction of the liquid phase was done with a riser without depressurization of the autoclave. Gases: Hydrogen (5.0; Praxair), BCl₃ (5.0; Linde), deuterium (5.0; Linde) were used without further purification. All solvents were distilled from molten potassium or dried with CaH₂, and the amines were predried with KOH before they were subjected to CaH₂ drying. The ¹H, ²H, ¹³C, and ¹¹B{¹H} NMR spectra were recorded with a Bruker Avance III 500 spectrometer with samples in deuterated solvents (C_6D_6 or CDCl₃) and were referenced to the ¹H or ¹³C resonances of the solvent used. NMR solvents were used without further purification. The ¹¹B NMR spectra were referenced to the external standard Et₂O·BF₃.

Et₃NBCl₃: A 0.5 M solution of BCl₃ in CH₂Cl₂ was used for the preparation of Et₃NBCl₃. BCl₃ (8.2 mL) was condensed into a 10 mL Schlenk vessel and transferred into CH₂Cl₂ (200 mL). This solution (28.8 mL) was added dropwise to a cooled (-78 °C) and stirred solution of triethylamine (13.7 mmol, 1.39 g) in CH₂Cl₂ (20 mL). The solvent was removed by vacuum distillation, and a white precipitate was obtained. ¹H NMR (CDCl₃): δ = 1.41 (t, 3 H, CH₃), 3.42 (q, 2 H, CH₂) ppm. ¹¹B{¹H} NMR (CDCl₃): δ = 10 (s) ppm. ¹³C NMR: δ = 10.3 (CH₃), 52.4 ppm (CH₂).

Et₃NBH₂Cl: Et₃NBH₃ (0.69 g, 6 mmol) and Et₃N (0.445 g, 4.4 mmol) were dissolved in toluene (1 mL) in a 15 mL Schlenk vessel. Afterwards, the mixture was cooled to -78 °C, and a 1M BCl₃ solution in toluene (4.5 mL) was added. The resulting solution

was first warmed to room temperature and then heated to 110 °C for 4 h. The solution was then cooled to room temperature for crystallization (1 d). Afterwards, hexane (10 mL) was added, and the mixture was intensively stirred for 30 min. The precipitation process was then completed by cooling the mixture to -78 °C. In the following step, the supernatant solution was aspirated with a syringe, and the precipitate was washed four times with hexane (10 mL). All volatiles were removed in vacuo, and the white residue was finally extracted with a hexane/toluene (20 mL/2 mL) mixture. ¹H NMR (CDCl₃): $\delta = 1.2$ (t, 3 H, CH₃), 2.9 (q, 2 H, CH₂), 2.7 (s, 2 H, BH) ppm. ¹¹B{¹H} NMR (CDCl₃): $\delta = -4.2$ (s) ppm. ¹³C NMR: $\delta = 8.0$ (CH₃), 48.6 (CH₂) ppm.

Adduct Pyrolysis: The adduct (Et₃NBCl₃, Et₃NBH₂Cl, Et₃NBHCl₂, or Et₃NBH₃; 4.58×10^{-5} mol) was dissolved in Et₃N (1.37×10^{-4} mol). The mixture was heated in a Pyrex tube at 200 °C for 4 h. The samples were subsequently analyzed by ¹¹B, ¹H, and ¹³C NMR spectroscopy.

Amorphous Nickel Boride: NiCl₂·6H₂O (1.19 g, 5 mmol) was dissolved in ethanol (100 mL), and the solution was transferred to a 250 mL three-necked flask and continuously stirred with a highspeed magnetic stirrer. A 1M solution of NaBH₄ (15 mL) stabilized with NaOH was added dropwise with a dropping funnel over 6 min. The apparatus was continuously flushed with Argon to remove the evolving hydrogen. The black precipitate was collected by filtration and first washed with degassed and distilled water, then three times with absolute ethanol (20 mL), and finally twice with absolute diethyl ether (30 mL). The residue was dried under vacuum (10⁻³ mbar) for 2 h and stored under argon. Analyses were conducted by XRD and X-ray photoelectron spectroscopy (XPS).

Hydrodechlorination of Et₃NBCl₃: Et₃NBCl₃ (300 mg, 1.3 mmol) and nickel boride (18 mg) were added to triethylamine (7 mL), and the mixture was loaded into a sealed PTFE-lined pressure vessel. Samples for ¹¹B NMR analysis were extracted under inert gas atmosphere every 30 min. The last sample was taken after 24 h. ¹¹B{¹H} NMR (C_6D_6) was used to track the hydrodechlorination of Et₃NBCl₃ at T = 130 °C and $p(H_2) = 60$ bar. Et₃NBCl₃ $\delta =$ 10 ppm, Et₃NBHCl₂ δ = 4.7 ppm, Et₃NBH₂Cl δ = 4.2 ppm, Et₃NBH₃ δ = -12.1 ppm. Deuterium labeling: Et₃NBCl₃ (270 mg, 1.2 mmol) and amorphous nickel boride (24 mg) were mixed with triethylamine (7 mL), and the mixture was transferred into a 15 mL stainless steel PTFE-lined pressure vessel. The vessel was equipped with internal stirring and external heating. In all experiments, the manifold was preheated to the desired temperature (before the addition of deuterium). For kinetic NMR studies, samples were first retrieved with a cylindrical riser mounted to the reactor and then transferred under Ar atmosphere to an NMR tube. After each experiment, the pressure vessel was connected to a vacuum line, and triethylamine and the products were removed. The white solid residue in the pressure vessel consisted of a mixture of Et₃NHCl and Et₃NDCl. The experiments were performed at 100 and 130 °C and a deuterium pressure of 30 bar.

Hydrodechlorination of Et₃NBH₂Cl: Et₃NBH₂Cl (0.194 g, 1.68 mmol) was dissolved in Et₃N (7 mL), and amorphous nickel boride (30 mg) was added to the solution. Afterwards, the mixture was heated to 160 °C in a PTFE-lined and magnetically stirred autoclave pressurized with 60 bar of hydrogen and stirred for 24 h under these conditions. Reverse reaction: Et₃NBH₃ (0.184 g, 1.605 mmol) and Et₃NHCl (0.685 g, 4.8 mmol) were dissolved in Et₃N (7 mL). Amorphous nickel boride (30 mg) was finally added, and the mixture was heated to 160 °C in a PTFE-lined and magnetically stirred autoclave, which was pressurized with 60 bar of hydrogen and stirred for 24 h magnetically stirred autoclave, which was pressurized with 60 bar of hydrogen and the mixture was heated to 160 °C in a PTFE-lined and magnetically stirred autoclave, which was pressurized with 60 bar of hydrogen and stirred autoclave.

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gen after the system had reached the desired temperature. The same experiment was repeated without a catalyst.

Supporting Information (see footnote on the first page of this article): Hydrogen solubility in Et_3N , ¹H and ¹³C NMR spectra for the decomposition of Et_3NBH_3 and control experiments.

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Hydrodechlorination

C. Reller, F. O. R. L. Mertens* 1-11

Hydrodechlorination of Et₃NBCl₃ Catalyzed by Amorphous Nickel Boride – A Mechanistic Approach

Keywords: Heterogeneous catalysis / Hydrodehalogenation / Boranes / Nickel boride / Deuterium labeling / Reaction mechanisms



The mechanistic aspects of the generation of borane species from BCl_3 by catalytic hydrodechlorination with molecular hydrogen in the presence of tertiary amines are investigated. The NCH₂ units of the amines are particularly important to the overall reaction kinetics and these units are assigned the role of cocatalyst. Equilibrium investigations guide the way for the improvement of the synthesis.