Synthesis of Catechol-, Pinacol-, and Neopentylglycolborane through the Heterogeneous Catalytic B−B Hydrogenolysis of Diboranes(4)

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Abstract: A new synthetic approach to hydroboranes catechol-, pinacol-, and neopentylglycolborane has been developed. Starting from diboranes(4) B_2cat_2, B_2pin_2, or B_2neop_2, the respective boranes were obtained by heterogeneously catalyzed cleavage of the B−B bond in the respective diboranes with hydrogen. Group 10 metals were found to be effective catalysts for this reaction.

Keywords: boron · cleavage reactions · diboranes · heterogeneous catalysis · hydrogenolysis

Introduction

As organoboronate esters grow in importance, owing to their great utility in organic synthesis, interest in the reagents that are used in borylation reactions has increased accordingly. Hydroboranes are commonly used compounds in functionalization reactions, such as hydroboration,[1] the borylation of arylhalides,[2] and the catalytic C−H activation of aromatic hydrocarbons, alkenes, or even alkanes.[3] By far the most prominent of these hydroboranes are catecholborane (HBcat) and pinacolborane (HBpin). The standard synthesis of these boranes involves the reaction of BH_3−Lewis-base adducts, such as BH_3−THF or BH_3−SMe_2, with the respective diol, that is, pinacol or catechol (Scheme 1).[4] Durin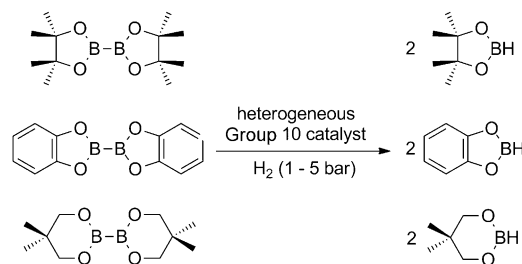g this reaction, only one of the reactive hydrides on the BH_3 moiety remains in the reaction product, whilst the other two are lost as gaseous H_2. HBcat can also be obtained from a ligand-scrambling reaction between B_2cat_3 and B_2H_6 or BH_3−Lewis base adducts.[5]

Hydroboranes, such as HBcat and HBpin, are known to be air- and moisture-sensitive compounds[4b] and they decompose through disproportionation over time, even if they are stored at low temperatures under an inert atmosphere. Hydrogenolysis of the respective diboranes(4) could represent an attractive in situ method for the synthesis of hydroboranes to avoid such decomposition issues. This reaction would make stable, solid diboranes simple synthons for hydroboranes.

A reductive procedure for the synthesis of diboranes was first published by Brotherton et al. and Nöth and Meister in the early 1960s and it has been improved and optimized a number of times since then, thereby making these compounds available on a large scale.[6] We recently developed a new route to diboranes(4) that proceeded through a dehydrocoupling reaction under hetero- or homogeneous catalysis.[7] This development was based on the earlier observations of Marder and co-workers of the catalytic formation of small amounts of B_2pin_2 during the rhodium-catalyzed borylation of aromatic compounds by using HBPin.[3e] The fact that this reaction was an equilibrium, which was confirmed by mechanistic studies,[8] led us to attempt the synthesis of hydroboranes through the hydrogenolysis of diboranes(4) (Scheme 2).
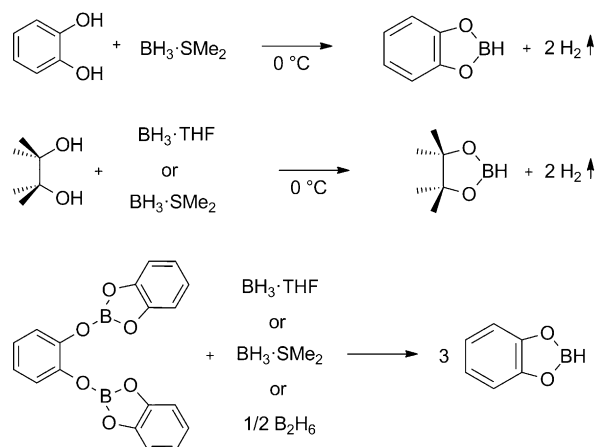
Scheme 1. Currently employed syntheses of HBcat and HBpin.

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Scheme 2. Synthesis of HBcat, HBpin, and HBneop through the hydrogenolysis of diboranes.

The hydrogenative cleavage of E−E bonds has been demonstrated in a number of different systems. Reactive Ga−Ga, In−In, and Al−Al bonds can be broken without transition-metal (TM) catalysts,[9] as can E−E bonds in digermylenes and distannylenes.[10] An example of the cleavage of a more-stable E−E bond is the hydrogenolysis of $ClMe_2Si-SiMe_2Cl$. The Si−Si bond is broken under homogeneous catalytic conditions with $[Pt(PEt_3)_4)]$ at 5 bar H_2 pressure.[11] A very similar reaction to the intended hydrogenolysis of B_2cat_2/B_2pin_2 is the deuterolysis of B_2pin_2 reported by Hartwig and co-workers. In that case, DBpin was generated in a homogenous catalytic reaction with an iridium catalyst; however, this technique was used only in one instance and was not developed further.[12]

Hartwig et al. reported that the reductive elimination of HBpin from $[CpRhH_2(Bpin)_2]$ was favored over the elimination of B_2pin_2.[13] Thus, we reasoned that the equilibrium should lead to the respective hydroborane on the introduction of dihydrogen gas to diboranes(4). Herein, we present our results concerning the synthesis of hydroboranes Bpin, HBcat, and HBneop through the hydrogenolysis of the B−B bonds in their respective $B_2(OR)_4$ compounds under heterogeneous catalysis.

Results and Discussion

Because our best dehydrocoupling results were obtained by using heterogeneous Group 10 catalysts, such as platinum or palladium, on charcoal or aluminum oxide,[7a,b] we used these catalysts in our initial attempts at the hydrogenolysis of diboranes(4). These catalysts had the additional benefit of being easily removable and reusable after the reaction. For proof of principle, the catalyst was added in quite large amounts (2–3 mol%) to a suspension of the diborane in toluene. After degassing the mixture, hydrogen gas was introduced and the pressure, reaction temperature, and reaction time were varied. The reaction was monitored by GCMS and by ^{11}B NMR spectroscopy; the latter technique confirmed the formation of the respective hydroborane by the appearance of a doublet signal. Initial qualitative evaluation of the progress of the reaction was made by assessment of the relative intensities of the signals of the diborane, the borane, and the decomposition products. The turnover numbers (TONs) were estimated by using GCMS measurements.

Our first attempts were performed by using Pt on aluminum-oxide pellets, which we had previously found to be the most-effective catalyst for the synthesis of diborane(4). Because the reaction of B_2cat_2 at 80 °C under 1 bar H_2 pressure in toluene showed no formation of borane after 5 h or even after a prolonged reaction time with a higher catalyst loading, we used Pt on charcoal (10 wt.% Pt, 2.5 mol%) to increase the surface area that was available for the reaction and to ensure better mixing of the reactants (Table 1, entry 1–4). After stirring for 1 h at 80 °C under an atmospheric pressure of H_2 in toluene, a weak doublet signal at $\delta = 28.8$ ppm $(J = 192$ Hz)[5b] was detected for HBcat. GCMS

Table 1. Synthesis of HBcat and HBpin with Pt/C as a catalyst; reactions were carried out in toluene, unless otherwise stated.

Entry	Borane	Catalyst loading [mol%]	H_2 pressure [bar]	T [°C]	t [h]	TON (GC)
1	HBcat	2.5	1	80	1	2
2			1	80	5	4
3			5	80	1	4
4			5	80	5	13
5	HBpin	2.5	1	80	1	8
6			1	80	5	15
7			1	80	5	10[a]
8			5	80	1	11
9			5	80	5	21
10			5	80	5	18[a]

[a] THF was used as the solvent.

measurements confirmed the formation of trace amounts of HBcat (m/z: 120 $[M]^+$), which corresponded to a very small TON of 2. Prolonging the reaction time to 5 h doubled the TON to 4. Under higher H_2 pressure (5 bar), TONs of 4 (1 h) and 13 (5 h) were obtained.

For the synthesis of HBpin, slightly better results were obtained with Pt/C (Table 1, entries 5–10). On heating the reaction at 80 °C under 1 bar H_2 pressure in toluene, the TON was 8 after 1 h and 15 after 5 h. By increasing the hydrogen pressure to 5 bar, the TON was improved to 11 (1 h) and 21 (5 h). The formation of HBpin was confirmed by the appearance of a doublet at $\delta = 28.4$ ppm $(J = 173$ Hz)[4c,d] in the ^{11}B NMR spectra and by GCMS measurements (m/z: 128 $[M]^+$). Because of its superior solubility, B_2pin_2 could also be reacted with H_2 in other solvents; for example, reaction in THF gave similar TONs (Table 1, entries 7 and 10).

In addition to the doublet signal for HBcat (29 ppm) and the signal for B_2cat_2 (30 ppm),[14] another broad signal at $\delta = 22$ ppm was detected in every spectrum, which we assumed to be the decomposition product B_2cat_3, as well as trace amounts of catBOBcat and/or HOBcat.[5b,15,16] The generation of these side products is well-documented in cases in which these diboranes and boranes are exposed to harsh reaction conditions. The longer the reaction solutions were stirred at 80 °C and the higher the H_2 pressure, the more of these side products that were formed. The same observations were made for the pinacol derivative. Aside from the doublet signal for HBpin ($\delta = 28$ ppm) and B_2pin_2 ($\delta = 30$ ppm),[6d] a broad signal, which corresponded to B_2pin_3, pinBOBpin, and/or HOBpin, was observed at $\delta = 21$ ppm.[16,17]

To improve on these results, analogous palladium catalysts were applied to these reactions (Table 2). Under the same conditions as implemented for Pt on charcoal, palladium on charcoal gave much-better results for both boranes. ^{11}B NMR spectra of the reaction solution showed the quantitative transformation of diborane into borane. After stirring for 1 h at 80 °C with 1 bar H_2 in toluene, a tenfold-higher TON (48) was found for HBcat compared to the corresponding Pt-catalyzed reaction. A signal for B_2cat_2 was not detected by GC. Longer reaction times decreased the TON, owing to the increased formation of side products.

Table 2. Synthesis of HBpin and HBcat with Pd/C as a catalyst; reactions were carried out in toluene, unless otherwise stated.

Entry	Borane	Catalyst loading [mol %]	H_2 pressure [bar]	T [°C]	t [h]	TON (GC)
1	HBcat	2.5	1	40	1	32
2			1	80	1	48
3			1	80	5	44
4			5	40	1	32
5			5	80	1	35
6	HBpin	2.5	1	40	1	24
7			1	80	1	24
8			1	80	5	31
9			1	80	5	0[a]
10			5	40	1	27
11			5	80	1	33

[a] THF was used as the solvent.

When the temperature was lowered to 40 °C, a TON of 32 was obtained after 1 h. Performing the hydrogenolysis reaction at higher H_2 pressures (5 bar) did not improve the TONs.

Comparable results were obtained for the synthesis of HBpin (Table 2, entries 6–11). Under a H_2 atmosphere (1 bar) at 40 °C, a TON of 24 was obtained for the hydrogenolysis of B_2pin_2 in toluene after 1 h. The same TON was obtained when the temperature was increased to 80 °C and prolonging the reaction time to 4 h caused the TON to increase to 31. When THF was used as the solvent for the synthesis of HBpin, only decomposition products, which were presumably due to ring-opening of the THF, were observed, whereas the reaction in *n*-hexane afforded comparable TONs to those in toluene.

To complete the comparison of Group 10 metals, Raney nickel was applied as a heterogeneous catalyst in the B–B hydrogenolysis reaction (Table 3). Thus, Raney nickel

Table 3. Synthesis of HBpin and HBcat catalyzed by Raney nickel; reactions were carried out in toluene.

Entry	Borane	Catalyst loading [mol %]	H_2 pressure [bar]	T [°C]	t [h]	TON (GC)
1	HBcat	5.50	1	80	5	10
2	HBpin	4.30	1	80	5	3

(92 wt. % Ni) and the respective diborane(4) were stirred in toluene for 5 h at 80 °C under 1 bar hydrogen pressure. ^{11}B NMR analysis indicated that both reactions produced the desired hydroborane products. The TONs were comparable to those with Pt/C, but, because Raney Ni is much more sensitive towards water and air, the other two Group 10 metals were preferred as catalysts for this reaction.

To demonstrate the applicability of this reaction, the syntheses of HBcat and HBpin were conducted on a larger scale with palladium on charcoal as the catalyst (Table 4). Owing to the very similar boiling points of toluene and HBcat, pentane was used for the synthesis of this borane.

Table 4. Synthesis of HBcat, HBpin, and HBneop with Pd/C.

Entry	Borane	Catalyst loading [mol %]	H_2 pressure [bar]	T [°C]	t [h]	TON[a]
1	HBcat	0.27	1	RT	21	196[b]
2	HBpin	0.18	1	RT	20	504[b]
3	HBneop	0.41	1	80, RT	13, 30	86[c]

[a] TON for the isolated borane. [b] Pentane was used as the solvent. [c] Benzene was used as the solvent.

After stirring the suspension for 21 h at room temperature under a hydrogen atmosphere (1 bar) with a catalyst loading of only 0.27 mol %, HBcat was isolated by distillation, with a TON of 196. Hartwig's synthesis of DBpin through the homogeneous Ir-catalyzed deuteration of B_2pin_2 with the same catalyst loading gave a TON of 155.[12] HBpin could also be isolated in the same way. Stirring B_2pin_2 in pentane for 20 h under a H_2 atmosphere with Pd/C allowed HBpin to be obtained by distillation. The TON reached 504 with a catalyst loading of 0.18 mol %. This result was more than twice as high as that for HBcat and more than three times higher than for the synthesis of DBpin by deuterolysis.[12]

Similarly, bis(neopentylglycolato)diborane(4) (B_2-neop$_2$)[14a] was examined for cleavage of its B–B bond by hydrogenolysis to form neopentylglycolborane (HBneop).[18] Reaction of B_2neop_2 in toluene for 1–5 h under a hydrogen atmosphere of 1 bar at 80 °C in the presence of Pt/C or Pd/C resulted in a doublet signal at $\delta = 25.6$ ppm ($J = 172$ Hz) in the ^{11}B NMR spectra. GCMS measurements also confirmed the formation of HBneop (m/z: 114 $[M]^+$). The synthesis of HBneop was more successful with Pd as the catalyst than with Pt, as already observed for the synthesis of HBcat and HBpin. However, the ^{11}B NMR spectra indicated that the transformation of HBneop proceeded much more slowly than those of HBcat and HBpin. HBneop was isolated by using Pd/C as the catalyst (Table 4, entry 3). Because B_2neop_2 was not very soluble in either pentane or *n*-hexane, benzene was used as the solvent. After stirring the solution for 13 h at 80 °C and then for 30 h at room temperature under a hydrogen atmosphere of 1 bar, HBneop was obtained. At a catalyst loading of 0.41 mol %, the TON was 86.

Conclusion

We have shown that the synthesis of hydroboranes, such as HBcat and HBcat, is possible through the hydrogenolysis of diboranes(4) under heterogeneous catalysis. All of the Group 10 catalysts (Pt/C, Pd/C, Raney Ni) that were tested were able to catalyze the hydroborane formation. For Pt/C and Raney Ni, only low TONs were obtained. The most-active catalyst for this reaction by far was palladium on charcoal, with which the boranes could be synthesized under mild conditions (room temperature, atmospheric H_2 pressure). Reactions on a larger scale were carried out by using

this catalyst and all three boranes (HBcat, HBpin, HBneop) were isolated as pure materials. The TONs were estimated to be 196 for HBcat, 504 for HBpin, and 86 for HBneop.

Experimental Section

General procedures and materials: Reactions were carried out under a dry argon atmosphere by using standard Schlenk techniques. Reactions under increased H_2 pressure were carried out in an autoclave that was purchased from BASF. The solvents were dried by distillation over appropriate drying agents and stored over molecular sieves. Diboranes(4) were provided by AllyChem Co. Ltd. and used without further purification. Pd/C and Pt/C were purchased from commercial suppliers and Raney nickel was synthesized according to a literature procedure.[19] Hydrogen gas was purchased from Linde (purity $\geq 99.9992\%$). NMR spectra were recorded on a Bruker Avance 400 NMR spectrometer (^{1}H: 400.130 MHz, ^{11}B: 128.385 MHz). Chemical shifts are given in ppm and are referenced to internal Me$_4$Si (^{1}H) and BF$_3$·OEt$_3$ (^{11}B). Turnover numbers were determined by GCMS analysis on an Agilent Technologies GCMS system (GC 7890A, MSD 5975 C) with *n*-dodecane as an internal standard.

General procedure for the synthesis of HBcat with Pd/C or Pt/C: B$_2$cat$_2$, Pd/C or Pt/C (10 wt.%, 10–20 µmol, 2–3 mol%), and *n*-dodecane were suspended in toluene (8 mL). After degassing the mixture, H_2 gas (1 or 5 bar) was introduced and the mixture was stirred for several hours at the chosen temperature (Table 1 and Table 2). The formation of HBcat was confirmed by GCMS, as well as by ^{11}B NMR spectroscopy.

General procedure for the synthesis of HBcat with Raney Ni: B$_2$cat$_2$, Raney Ni (92 wt.%, 70 µmol, 15 mol%), and *n*-dodecane were suspended in toluene (8 mL). After degassing the mixture, H_2 gas (1 or 5 bar) was introduced and the mixture was stirred for 1–5 h at 40 or 80°C (Table 3). The formation of HBcat was confirmed by GCMS measurements, as well as by ^{11}B NMR spectroscopy.

Isolation of HBcat: B$_2$cat$_2$ (2.50 g, 10.5 mmol) and Pd/C (10 wt.%, 29.7 mg, 27.9 µmol, 0.27 mol%) were suspended in pentane (15 mL). After degassing the mixture, H_2 gas (1 bar) was introduced and the mixture was stirred for 21 h at RT. Pd/C was separated from the solution and the solvent was removed by distillation under an argon atmosphere (1 bar). HBcat (700 mg, 5.47 mmol, 26% yield) was obtained as a clear, colorless liquid (b.p. 120–125°C) with a TON of 196 (Table 4, entry 1). ^{1}H NMR (400.1 MHz, C$_6$D$_6$): $\delta = 4.57$ (br q, $^1J = 192$ Hz, 1H), 6.98 (m, 2H), 6.75 ppm (m, 2H); ^{11}B NMR (128.4 MHz, C$_6$D$_6$): $\delta = 28.8$ ppm (d, $^1J = 192$ Hz; *B*H); MS (EI): *m/z*: 120 [*M*]$^+$.

General procedure for the synthesis of HBpin with Pd/C or Pt/C: HBpin was prepared as described above for HBcat, by using B$_2$pin$_2$ as the starting material (Table 1 and Table 2).

Synthesis of HBpin with Raney Ni: HBpin was prepared as described above for HBcat, by using B$_2$pin$_2$ as the starting material (Table 3).

Isolation of HBpin: B$_2$pin$_2$ (2.00 g, 7.74 mmol) and Pd/C (10 wt.%, 15.2 mg, 14.4 µmol, 0.18 mol%) were suspended in pentane (15 mL). After degassing the mixture, H_2 gas (1 bar) was introduced and the mixture was stirred for 20 h at RT. Pd/C was separated from the solution and the solvent was removed by distillation under an argon atmosphere (1 bar). HBpin (928 mg, 725 mmol, 47% yield) was obtained as a clear, colorless liquid (b.p. 109–111°C) with a TON of 504 (Table 4, entry 2). ^{1}H NMR (400.1 MHz, C$_6$D$_6$): $\delta = 0.99$ (s, 12H), 4.27 ppm (br q, $^1J = 173$ Hz, 1H); ^{11}B NMR (128.4 MHz, C$_6$D$_6$): $\delta = 28.4$ ppm (d, $^1J = 173$ Hz; *B*H); MS (EI): *m/z*: 128 [*M*]$^+$.

General procedure for the synthesis of HBneop with Pd/C or Pt/C: HBneop was prepared as described above for HBcat, by using B$_2$neop$_2$ as the starting material.

Isolation of HBneop: Bis(neopentylglycolato)diborane(4) (2.40 g, 10.6 mmol) and Pd/C (10 wt.%, 46.4 mg, 43.6 µmol, 0.41 mol%) were suspended in benzene (27 mL). After degassing the mixture, H_2 gas (1 bar) was introduced and the mixture was stirred for 4 h at 80°C, fol-

lowed by 19 h at RT. After degassing the solution again, another portion of H_2 gas (1 bar) was introduced. After stirring for 13 h at 90°C and 32 h at RT, Pd/C was separated from the solution and the solvent was removed by distillation under an argon atmosphere (1 bar). HBneop (429 mg, 3.76 mmol, 18% yield) was obtained as a clear, colorless liquid (b.p. 102°C) with a TON of 86 (Table 4, entry 3). ^{1}H NMR (400.1 MHz, C$_6$D$_6$): $\delta = 0.51$ (s, 6H), 3.20 (s, 4H), 4.51 ppm (br q, $^1J = 172$ Hz, 1H); ^{11}B NMR (128.4 MHz, C$_6$D$_6$): $\delta = 25.6$ ppm (d, $^1J = 172$ Hz; *B*H); MS (EI): *m/z*: 114 [*M*]$^+$.

Acknowledgements

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[16] B$_2$cat$_3$, catBOBcat, and HOBcat cannot be distinguished in the ^{11}B NMR spectra due to the broadened signal. B$_2$cat$_3$ forms through thermal decomposition of HBcat, whereas the formation of small amounts of the hydrolysis products catBOBcat and HOBcat could be caused by traces of H$_2$O. The same applies for B$_2$pin$_2$ and its decomposition products.

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