

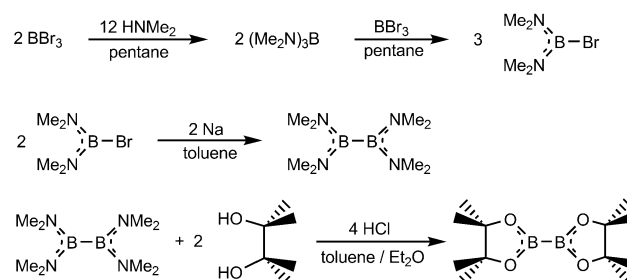
Transition-Metal-Catalyzed Synthesis of Diboranes(4)

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Organoboranes are organic molecules featuring an sp^2 -hybridised BR_2 group. This BR_2 fragment, with its well-documented σ basicity and π acidity, lends the C–B bond a unique reactivity that has been impressively exploited by organic chemists. In the early 20th century, organoboranes featured in organic chemistry merely as placeholders for hydroxy groups, the oxidation of a C– BR_2 bond to C–OH being a reliable method for the synthesis of alcohols. However, it was only after the discovery of the Suzuki–Miyaura cross-coupling of organoboranes with aryl halides that this functional group became widely used in organic chemistry.^[1] This method has since developed into one of the most versatile synthetic methods available for C–C bond formation and it was the subject of the Nobel Prize in Chemistry in 2010.^[2] Consequently, the need for convenient and economical methods for the installation of the BR_2 group in organic molecules has fuelled research into organoborane chemistry for some time.

The hydroboration of unsaturated organic substrates developed by Brown and co-workers in the 1950s brought organoborane chemistry out of obscurity and added boron to the organic chemist's repertoire.^[3] For a long time, simple hydroboration remained the method of choice for the synthesis of organoboronates. In the 1980s, the groups of Sneddon, Marder, and Nöth reported the transition-metal-catalyzed hydroboration reaction, thus providing access to borane products with alternative chemo- and regioselectivity to complement those prepared by classical hydroboration.^[4] Furthermore, catalytic diboration of unsaturated compounds^[5] as well as the borylation of arenes^[6] and alkanes^[7] gave access to a much broader variety of organoboronates.

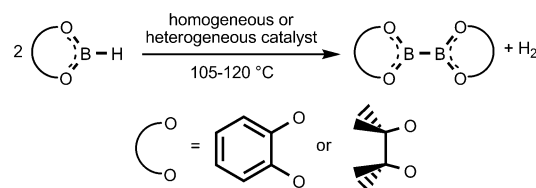
An indispensable starting material in many of these reactions is a tetraalkoxydiborane(4) of the general formula $(RO)_2B-B(OR)_2$. The two most commonly used reagents of this class of compounds are bis(catecholato)diborane (B_2Cat_2 ; **1**) and bis(pinacolato)diborane (B_2Pin_2 ; **2**), which are currently synthesized by a method established by Brotherton in 1960,^[8] which has been modified several times over the intervening decades.^[9] Starting from boron tribromide, bromobis(dimethylamino)borane is synthesized in two steps. Subsequently, formation of the boron–boron bond is achieved by reductive coupling with sodium to yield $B_2(NMe_2)_4$ (**3**), which is further converted into **1** and **2** upon reaction with the corresponding diols (Scheme 1).^[9a,d,10] Alternatively, **1** can be



Scheme 1. Typical synthesis of bis(pinacolato)diborane.

directly obtained from reductive coupling of chlorocatecholborane with sodium amalgam, while the pinacol derivative **2** is not accessible by this route.^[11] However, owing to the harsh conditions and toxicity of the reagents, reductive coupling procedures have distinct disadvantages. Furthermore, these multistep methods are tedious, and owing to the loss of the dimethylamino groups, the overall process leads to large amounts of waste material, making the diboranes(4) relatively expensive.

Starting from catecholborane (HBCat) and pinacolborane (HBPin), which can be prepared and handled with relative ease,^[12] we sought to develop catalytic syntheses for B_2Cat_2 and B_2Pin_2 . Homonuclear dehydrocoupling reactions of this kind have been established for the formation of several element–element bonds, such as silicon,^[13] phosphorus,^[14] and others.^[15] The formation of a boron–boron bond was reported by Sneddon and Corcoran, Jr. in the reaction of boranes and carboranes with $PtBr_2$, while Himmel et al. recently obtained a doubly base-stabilized diborane(4) from a corresponding diborane(6) by a rhodium-catalyzed dehydrogenation.^[16] During the catalytic borylation of C–H bonds with HBPin, Marder et al. observed the formation of small amounts of **2** as a byproduct, whereas an equilibrium between HBPin and **2** + H_2 is assumed under these reaction conditions (Scheme 2).^[17] Although there is no significant thermodynamic driving force for this dehydrocoupling,^[18] removal of H_2 from the reaction mixture is expected to shift the equilibrium to the side of the diboranes(4), thus facilitating their accumulation. Herein we present our successful studies on the dehydrocoupling of HBCat and HBPin to give the corresponding diboranes(4) by homogeneous and heterogeneous catalysis.^[19]



Scheme 2. Transition-metal-catalyzed synthesis of diboranes(4).

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To obtain a proof-of-principle for the catalytic homocoupling, HBCat and HBPIn were combined with various late transition-metal complexes in a variety of solvents. We detected the diboranes(4) by GC/MS, although at best only in trace amounts. We reasoned that a higher concentration of monoborane in the reaction solution may promote the formation of B_2Cat_2 and B_2Pin_2 , in accordance with the observations of Marder et al.^[17] This hypothesis was key to the development of the coupling procedure: conducting the reactions in neat borane led to a dramatic improvement in diborane(4) formation (Table 1).

Table 1: Synthesis of B_2Cat_2 using homogeneous catalysts.^[a]

Entry	Catalyst (loading [mol %])	TON
1	[(dppm)PtCl ₂] (0.05 %)	90
2	[(dcpe)PtCl ₂] (0.05 %)	65
3	[(dcpe)PdCl ₂] (0.05 %)	75
4	[(dcpe)NiCl ₂] (0.05 %)	35
5	[(dppm)PtCl ₂] (0.025 %)	160
6	[(dcpe)PtCl ₂] (0.025 %)	90
7	[(dcpe)PdCl ₂] (0.025 %)	90
8	[(dcpe)NiCl ₂] (0.025 %)	50

[a] Reaction conditions: neat borane is heated with the catalyst to 110 °C for 20 h.

Initially, synthesis of B_2Cat_2 was attempted under homogeneous catalytic conditions. When employing a typical catalyst loading of 0.05 mol % (Table 1, entries 1–4), [(dppm)PtCl₂] (dppm = bis(diphenylphosphino)methane) appears to be the most efficient catalyst, yielding a turnover number (TON) of 90. With [(dcpe)PdCl₂] (dcpe = bis(dicyclohexylphosphino)ethane) and [(dcpe)PtCl₂], slightly lower TONs of 75 and 65 were observed. A larger excess of HBCat (0.025 mol % of catalyst; Table 1, entries 5–8) significantly improved the TONs to a maximum of 160 for [(dppm)PtCl₂].

The next logical step was to investigate the reactivity of HBCat with common heterogeneous catalysts. When using 0.05 mol % of catalyst (Table 2, entries 1–3), the best results were achieved with platinum on charcoal (10 wt %) and platinum on alumina (0.5 wt %), affording 105 and 95 turnovers, respectively. In contrast to the homogeneous catalysts, palladium appears to be far less efficient than platinum, as palladium on charcoal (10 wt %) yielded a TON of only 35. Again, by decreasing the catalyst loading, the formation of B_2Cat_2 was improved significantly (Table 2, entries 4–6), since

Table 2: Synthesis of B_2Cat_2 using heterogeneous catalysts.^[a]

Entry	Catalyst (loading [mol %])	TON
1	Pd on charcoal (0.05 %)	35
2	Pt on charcoal (0.05 %)	105
3	Pt on alumina (0.05 %)	95
4	Pd on charcoal (0.025 %)	75
5	Pt on charcoal (0.025 %)	190
6	Pt on alumina (0.025 %)	220
7	Pt on alumina (0.006 %)	350

[a] Reaction conditions: neat borane is heated with the catalyst to 110 °C for 20 h.

platinum on charcoal and platinum on alumina afforded TONs of 190 and 220, respectively. Reducing the catalyst loading even further to only 0.006 mol %, we showed that the TON can be again significantly increased, giving a TON of 350 (based on isolated **1**).

Given the surprising success of the B_2Cat_2 synthesis, we sought to apply this catalytic dehydrocoupling method to pinacolborane (HBPIn). However, this reaction is much less straightforward than the synthesis of B_2Cat_2 , especially under homogeneous catalysis conditions. The aforementioned catalysts suitable for the formation of B_2Cat_2 afforded TONs of no more than 10 in the case of B_2Pin_2 . Furthermore, the formation of the latter is accompanied by various side products, of which PinBOH and (PinB)₂O were identified by mass spectrometry and NMR spectroscopy.^[20] Nevertheless, we managed to synthesize B_2Pin_2 under heterogeneous catalytic conditions using palladium on charcoal and platinum on charcoal (0.025 mol %), both catalysts affording TONs of 60. As in the case of **1**, the output of **2** could be improved by further reducing the catalyst loading. In the reaction of HBPIn with 0.005 mol % of platinum on alumina, a TON of 93 (based on isolated **2**) was achieved after 8 h.

For the dehydrocoupling reactions described herein, the reaction temperature must be chosen carefully. In general, formation of the diboranes(4) can be observed at temperatures as low as 75 °C, but higher temperatures enhance their formation significantly. However, boranes such as HBCat are known to decompose under prolonged heating,^[12a] and HBPIn is no exception. Our experiments showed that the best results could be achieved at temperatures between 105 °C and 110 °C, which is only marginally below the boiling points of HBCat and HBPIn. Although the rate of the dehydrocoupling decreases as the reaction progresses, the yield of diborane(4) can still be increased slightly by prolonged heating. However, reaction times exceeding 24 h are best avoided, as degradation of HBCat and HBPIn increases and starts to predominate over the formation of B_2Cat_2 and B_2Pin_2 .

Complete conversion of borane to diborane(4) was not observed, however. Although strong evolution of hydrogen occurs initially, a significant decrease is apparent after several hours. Investigation by GC-MS showed that the rate of formation of **1** and **2** decreases with increasing reaction time, and the overall yield does not exceed 5 %.

Therefore, we carried out additional experiments to establish the reason for the decreasing rate of formation of diboranes(4). The most apparent reason, that is, deactivation of the catalyst, could be ruled out, as reactions of used heterogeneous catalyst with fresh borane resulted in almost identical TONs. Given that a large excess of borane yielded the best results to date, we reasoned that an increasing concentration of diborane(4) accumulating in the reaction mixture might inhibit the reaction. In this case, continuous removal of the diboranes **1** and **2** from the reaction mixture should drive the dehydrocoupling forward. We achieved this by using a Soxhlet-type reaction vessel, in which freshly distilled, neat borane is continuously reacted with the hot heterogeneous catalyst, whereas **1** and **2** are purged out of the reaction zone immediately after their formation (for details and experimental setup, see the Supporting Information).

The use of this alternative procedure resulted in dramatic increases in the TONs. The catalysts of choice were Rh, Pd, and Pt supported on alumina (0.5 wt%), as they are commercially available in pellet form and can thus be kept within the reaction chamber with ease. For the formation of B₂Pin₂, TONs of 460, 670, and 1850 were determined by GC. In the case of B₂Cat₂, the TONs could be raised even further to 11 600 for Pt and 6500 and 3920 for Rh and Pd, respectively (Table 3). A typical experiment for the synthesis of **1** starting from 30.0 g of HBCat yielded 8.05 g (27 %; 8854 TONs) of analytically pure B₂Cat₂ after workup, and about 10 g of pure HBCat could be recovered by distillation for further use (see the Supporting Information for full details).

Table 3: Heterogeneous catalysis with continuous removal of **1** and **2**.^[a]

Catalyst (reaction time)	Product	TON [GC]	TON (isolated)
Rh on alumina (20 h)	1	6500	3707
Pd on alumina (40 h)	1	3920	2157
Pt on alumina (20 h)	1	11 600	8854
Rh on alumina (20 h)	2	460	284
Pd on alumina (40 h)	2	670	513
Pt on alumina (48 h)	2	1850	1050

[a] Reaction conditions: neat borane is continuously distilled into a heated Soxhlet-type reaction vessel equipped with catalyst.

In summary, we have reported a new one-step procedure for the synthesis of two of the most widely used and synthetically relevant diboranes(4), B₂Cat₂ and B₂Pin₂, by metal-mediated, catalytic dehydrocoupling of the commercially available boranes HBCat and HBPin. Although the homocoupling of both boranes using both homogeneous and heterogeneous catalysts was successful, the practice of continuous removal of B₂Cat₂ and B₂Pin₂ provided a marked increase in efficiency. This effect was particularly salient in the synthesis of B₂Cat₂ with platinum on alumina, which proceeded with TONs of up to 11 600. Further studies, including the use of different catalysts and boranes, are ongoing in our laboratory.

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