Synthetic Methods

Metal-Free HB(C6F5)2-Catalyzed Hydrogenation of Unfunctionalized Olefins and Mechanism Study of Borane-Mediated σ-Bond Metathesis**

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Homogeneous hydrogenation of olefins is of great importance for both laboratory and industry synthesis.[1] While most hydrogenation reactions are catalyzed by transition-metal complexes, the development of metal-free hydrogenation catalysts has recently attracted much attention because of their potential benefits of low cost and toxicity.[2–4] Early efforts towards the metal-free catalytic hydrogenation of olefins or polyarenes employed boranes or diboranes, such as iBu$_3$B,[2b,c] Et$_2$BBEt$_2$, or Pr$_2$BBPr$_2$[2e,f] as catalysts. These reactions require harsh reaction conditions (reaction temperature at 170–225°C and H$_2$ pressure at 100 bar), which often led to unwanted pyrolytic chain cleavage. The recent emerging chemistry of frustrated Lewis pairs provides a new strategy for metal-free hydrogenation which allows hydrogenation to be carried out under mild reaction conditions.[3,4] Various frustrated Lewis pair systems have been designed to effectively hydrogenate unsaturated complexes, such as imines,[4a–g] enamines,[4h] silylenol ethers,[4i] N-heterocyclic compounds,[4j] ynones,[4k] polycyclic aromatic hydrocarbons,[4l] amine-substituted benzenes,[4m] electron-rich alkenes,[4n] and electron-poor alkenes.[4o,p] However, despite such progress, metal-free hydrogenation of unfunctionalized, purely alkyl-substituted olefins under mild reaction conditions still remains an unmet challenge.

Recently, several groups have reported that highly Lewis-acidic borane complexes can react with H$_2$ without Lewis bases under mild reaction conditions.[5–7] For example, Piers et al. reported that antiaromatic pentaarylboroles react with H$_2$ at ambient temperature.[5] Our group as well as Nikonov et al. observed that highly Lewis-acidic hydroborane species such as HBAr$^F_2$ (Ar^F = 2,4,6-tris(trifluoromethyl)phenyl)[6] or HB(C$_6$F$_5$)$_2$[7] can activate D$_2$ to afford the corresponding deuteroboranes at 60°C. These discoveries prompted us to examine if highly Lewis-acidic hydroboranes can be
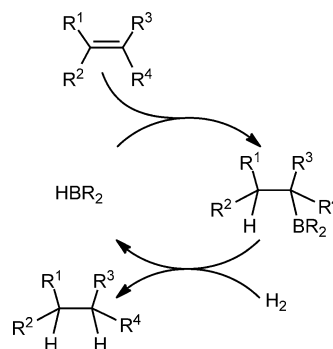
Scheme 1. Working hypothesis for the hydroborane-catalyzed hydrogenation.

employed as catalysts to hydrogenate unfunctionalized olefins. The working hypothesis is illustrated in Scheme 1. First, hydroboration of olefins affords alkyl-substituted organoborane complexes. Subsequently, under H$_2$, the C(alkyl)−B bond of these complexes can undergo hydrogenolysis to yield the hydrogenation product and regenerate the catalyst. We speculated that such hydrogenolysis could occur under comparably mild reaction conditions when highly Lewis-acidic organoboranes are applied.

Cyclohexene was chosen as the standard substrate as its hydrogenation product cyclohexane can be easily identified by ^{1}H NMR spectroscopy. Initially we sought to use HBAr$^F_2$ as the hydrogenation catalyst. However, upon mixing HBAr$^F_2$ and cyclohexene in toluene, no hydroboration took place even at 110°C, possibly because of the large steric bulkiness around the boron center of HBAr$^F_2$.[8] We then examined HB(C$_6$F$_5$)$_2$ as the catalyst for the hydrogenation reaction, as HB(C$_6$F$_5$)$_2$ is known to be a very reactive hydroboration reagent for olefins.[9] When cyclohexene was mixed with 20 mol% of HB(C$_6$F$_5$)$_2$ in C$_6$D$_6$ under 6 bar H$_2$ at 110°C, the hydrogenation product cyclohexane was obtained in 53% yield after 72 hours. After the reaction temperature was increased to 140°C, cyclohexene was quantitatively converted into cyclohexane within 72 hours. For comparison, the less Lewis-acidic 9-borabicyclo[3.3.1]nonane (9-BBN) was also tested as the catalyst, and yielded no hydrogenation product after 72 hours at 140°C.

Using HB(C$_6$F$_5$)$_2$ as the catalyst, we performed the catalytic hydrogenation of a variety of purely alkyl-substituted olefins (Table 1). For most mono-, di-, or trisubstituted olefins, complete hydrogenation can be achieved after 72 hours. For some olefins (entries 2, 6, and 8), a longer

[*] Y. Wang,[+] W. Chen,[+] Z. Lu, Prof. Z. H. Li, Prof. H. Wang
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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201303500.

Table 1: Hydrogenation of olefins catalyzed by $HB(C_6F_5)_2$.[a]

Entry	Olefin	t [h]	Product	Yield [%][b]
1		72		99
2		120		96
3		72		99
4		72		91
5		72		93
6		120		87
7		72		99
8		120		99
9		72		65[c]
10		120		94
11		120		92
12		72		99

[a] Reaction conditions: 20 mol% $HB(C_6F_5)_2$ in C_6D_6 under 6 bar H_2 at 140°C. [b] Yields were determined by ^1H NMR analysis with toluene added as the internal standard. [c] Substantial amount of oligomer was observed.

Figure 1. Pseudo-first-order plots of the reaction between **1** and H_2 (6 bar) at various temperatures.
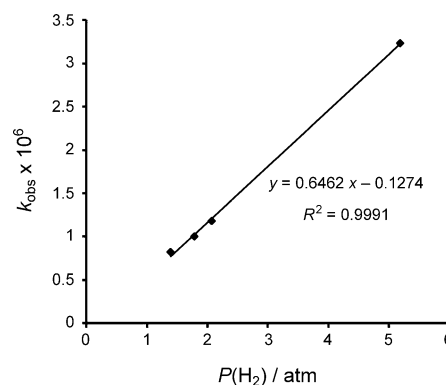
Figure 2. Plot of k_{obs} against H_2 pressure at 90°C.

reaction time is required to gain high product yield. It is noteworthy that the tetrasubstituted olefin tetramethylethylene can be quantitatively converted into 2,3-dimethylbutane, a reaction which is even challenging for some transition-metal-based hydrogenation catalysts.[10] The olefins bearing phenyl substituents (entry 9–12) were also subjected to hydrogenation and yields within the 65–99% range can be obtained.

While monitoring the hydrogenation of cyclohexene by ^1H NMR spectroscopy, we observed the signals of the hydroboration product $CyB(C_6F_5)_2$ (**1**) throughout the reaction process until the completion of the reaction. This observation indicates that the hydrogenolysis of the C(alkyl)−B bond is the rate-determining step in the catalytic process. As there has been no mechanism study on such hydrogenolysis reaction, we synthesized the intermediate **1**[11] and started to investigate its reaction with H_2 through kinetic analysis and theoretical studies.

The reaction between **1** and H_2 was monitored by ^1H NMR spectroscopy.[12,13] The rate of disappearance of **1** under 10-fold excess of H_2 (6 bar) followed pseudo-first-order kinetics (Figure 1). A linear dependence of the observed rate constant k_{obs} on the pressure of H_2 between 1.4 and 5.2 bar at 90°C established a first-order dependence on H_2 pressure (Figure 2). These data were consistent with an overall second-order rate law for the hydrogenolysis reaction. Kinetic mea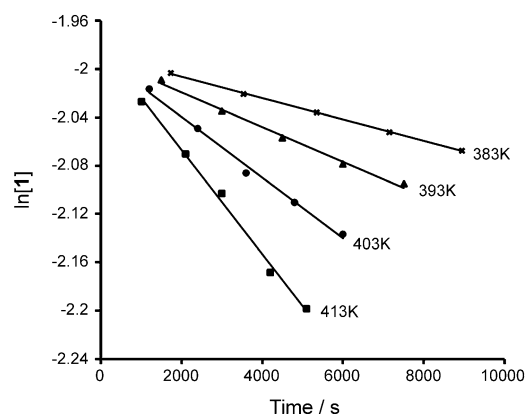surements were carried out between 110 and 140°C to allow the determination of activation parameters. An Eyring plot provided the values $\Delta H^{\ddagger} = 15.8(6)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -40.9(15)$ cal mol^{-1} K^{-1}.[14] The low value of $\Delta S^{\ddagger}$ implies that the loss of translational entropy contributed substantially to the overall activation energy.

The mechanism of the hydrogenolysis of **1** was further investigated by DFT(M06-2X) calculations.[15] Our studies revealed that the reaction is slightly exothermic ($\Delta E = -4.4$ kcal mol^{-1}) and the hydrogenolysis of **1** takes place through only one four-centered transition state without prior coordination of H_2 (Figure 3a). The calculated activation enthalpy ($\Delta H^{\ddagger} = 19.3$ kcal mol^{-1}) and activation entropy ($\Delta S^{\ddagger} = -32.6$ cal mol^{-1} K^{-1}) are comparable with the experimental values. In the transition state, the H−H bond is significantly elongated to 1.06 Å. Both H atoms are closely bonded to the B atom with a B−H$_\alpha$ distance of 1.28 Å and B-H$_\beta$ distance of 1.25 Å. The B−C bond length is 1.78 Å, thus elongated by 0.22 Å when compared with $CyB(C_6F_5)_2$. A long C−H$_\beta$ interaction (1.46 Å) was also observed. The orientation of the reactants in the transition state closely resembles those of σ-bond metathesis involving early-transition-metal or lanthanide complexes.[16] As organoboranes lack both d and f orbitals, it would be interesting to find out how the orbitals of **1** interact with those of H_2 in the transition state. Thus the NBO analysis of the transition state was performed
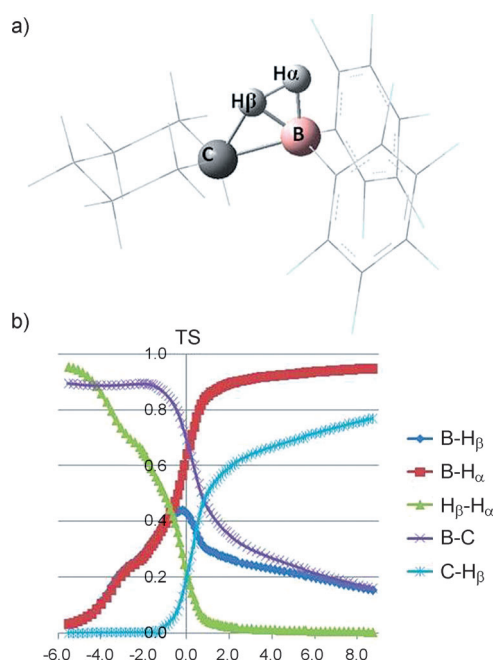
a)

b)

TS

Figure 3. a) Geometry of the transition state. b) Evolution of the Wiberg bond orders of the five bonds along the IRC.
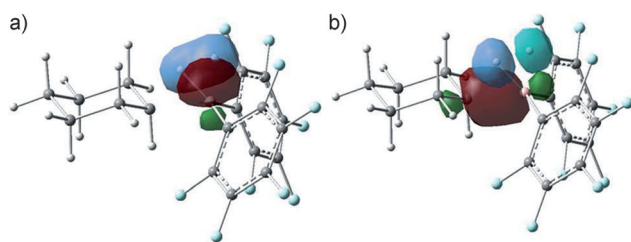
a)   b)

Figure 4. a) The empty 2p orbital of boron (LP*$_B$) and the natural bond orbital between H$_\alpha$ and H$_\beta$ ($\sigma_{H\text{-}H}$). b) The natural bond orbital between carbon and boron ($\sigma_{C\text{-}B}$) and the natural anti-bond orbital between H$_\alpha$ and H$_\beta$ ($\sigma^*_{H\text{-}H}$).

(Figure 4).[17] It was revealed that charge transfer occurs from the σ-bonding orbital of H$_2$ to the empty p orbital of the boron atom of **1**. At the same time, electron charge also transfers from the occupied σ-bonding orbital of C(alkyl)-B to the H$_2$ σ*-antibonding orbital. It is noteworthy that the amounts of the electron charge transfer in these two ways are not equal. The charge transfer from H$_2$ to **1** (0.81 e$^-$) plays a more dominant role than the charge transfer from **1** to H$_2$ (0.25 e$^-$). This suggests that a low-lying empty p orbital of the organoboranes is crucial for a viable σ-bond metathesis, and is in agreement with our experimental observation that the less Lewis-acidic hydroborane 9-BBN cannot catalyze the hydrogenation under similar reaction conditions. To gain a more complete view of the process of the σ-bond metathesis, we analyzed the bond orders of some important bonds along the intrinsic reaction coordinate (IRC; Figure 3b).[18,19] It was discovered that the cleavage of the H—H bond precedes the cleavage of the B—C bond. In contrast, the formation of the B—H bond takes place ahead of the formation of the new C—H bond. These results indicate that the process of σ-bond

metathesis occurs in an asynchronous manner, thus avoiding the otherwise symmetry forbidden [2$_\sigma$ + 2$_\sigma$] pathway.

In conclusion, we have developed an efficient method for metal-free hydrogenation of unfunctionalized olefins by employing HB(C$_6$F$_5$)$_2$ as the catalyst. The reaction proceeds under low pressure and a comparatively mild temperature. The key step in the catalytic reaction is believed to involve a novel borane-mediated σ-bond metathesis, which was investigated both experimentally and theoretically for the first time. Efforts to activate small molecules by highly Lewis acidic organoboranes through σ-bond metathesis are currently underway.

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[12] Activation of H_2 by the mixture of **1** and amines has been reported; see Ref. [11a].

[13] No cyclohexene, the possible retro-hydroboration product, was observed.

[14] See the Supporting Information.

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[19] The potential energy curve obtained from IRC calculations indicates that there is no additional transition state along the reaction path except the one reported (see the Supporting Information for the potential energy curve).