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Communication

Transition metal-catalyzed dehydrocoupling of group 13-group 15 Lewis acid–base adducts

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Abstract

Transition metal-catalyzed dehydrocoupling is a relatively new method for main group element–element bond formation, providing a facile alternative to salt metathesis processes. Lewis acid–base adducts of Groups 13 and 15 can undergo dehydrocoupling with both early and late transition metals and complexes thereof to yield rings, chains and macromolecules based on a framework of alternating B–N or B–P atoms. Evidence is also provided for Group 13 hydrides acting as poisons towards heterogeneous dehydrocoupling catalysts.
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1. Introduction

In general, elimination reactions such as salt metathesis have been the workhorse of synthetic main group chemistry since the early 20th century. However, in contrast to their prevalent use in organic chemistry, the application of transition metal catalysts for the preparation of homonuclear or heteronuclear bonds between p-block elements is still in its relative infancy. The first reports in the dehydrocoupling area emerged from the groups of Sneddon and Harrod in the mid-1980s and involved the generation of B–B [1] and Si–Si [2] bonds, respectively. In particular, the latter example where primary silanes formed polysilanes using Group 4 metallocene catalysts was particularly interesting in comparison to the hazardous Wurtz coupling process by which polysilanes were traditionally prepared. Since these early studies, a variety of other bonds have been successfully formed by metal-catalyzed dehydrocoupling underscoring the growing importance of this reaction [3].

Our group has investigated the dehydrocoupling of phosphine- and amine–borane adducts and found that they generally dehydrocouple in the presence of late transition metal (e.g. Rh) catalysts to yield chains, rings and high molecular weight polymers based on a Group 13/15 framework [4,5]. Recent studies into the mechanism of these reactions have revealed that for the case of phosphine–borane adducts, the process appears to be homogeneous while that for amine–borane adducts is heterogeneous [6]. We have also reported the use of the room temperature dehydrocoupling of amine–borane adducts as a means of delivering a stoichiometric quantity of dihydrogen to molecules containing unsaturated organic bonds, such as cyclohexene [7]. Furthermore, there is considerable interest in using $H_3N \cdot BH_3$ as a hydrogen storage material as it possesses a high density of H_2 per molecule and is an air-stable, commercially available solid [8].

In this communication, we discuss some of our recent studies in the area of Group 13/15 dehydrocoupling with

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a particular emphasis on scope and applications of the reaction.

2. Results and discussion

2.1. Rhodium-catalyzed dehydrocoupling of fluorinated phosphine–borane adducts

Previously, we have reported that $Ph_2PH \cdot BH_3$ reacts with Rh catalysts (typically $[Rh(\mu\text{-}Cl)(1,5\text{-}cod)]_2$) to generate either the linear dimer $Ph_2PH\text{–}BH_2\text{–}PPh_2\text{–}BH_3$ at 90 °C or a mixture of the cyclic trimer $[Ph_2P\text{–}BH_2]_3$ and tetramer $[Ph_2P\text{–}BH_2]_4$ at 120 °C [4b]. In contrast, the dehydrocoupling of $^tBu_2PH \cdot BH_3$ using the same catalysts requires temperatures as high as 160 °C to yield the linear dimer $^tBu_2PH\text{–}BH_2\text{–}P^tBu_2\text{–}BH_3$ [9]. Similarly, we have found that $PhPH_2 \cdot BH_3$ undergoes catalytic dehydrocoupling at 90–130 °C for 6 h to generate high molecular weight poly(phenylphosphinoborane) while $^iBuPH_2 \cdot BH_3$ requires heating in the presence of catalyst to 120 °C for 15 h in order to produce the polymer [4b,4c]. This difference in reaction temperature can be attributed to the presence of electron donating substituents on the phosphorus atom of $^tBu_2PH \cdot BH_3$ and $^iBuPH_2 \cdot BH_3$ which likely decreases the polarity and reactivity of the P–H bond relative to $Ph_2PH \cdot BH_3$ and $PhPH_2 \cdot BH_3$. Thus, we investigated the effect of fluoroaryl substituents on phosphorus in the anticipation that they would have a strong (−)-inductive effect and render the P–H linkage more polar and reactive towards $B^{\delta+}\text{–}H^{\delta-}$ bonds. This would potentially lead to lower dehydrocoupling reaction temperatures and allow these interesting P–B systems to be prepared under milder conditions.

The *para*-substituted phosphine–borane adducts (p-$CF_3C_6H_4)_2PH \cdot BH_3$ (**1**) and (p-$CF_3C_6H_4)PH_2 \cdot BH_3$ (**2**) were synthesized in four steps from PCl_3 by using a protec-

tion–deprotection sequence and their dehydrocoupling reactivity investigated [10]. In the case of **1**, it was found that it underwent catalytic dehydrocoupling at 60 °C to afford the linear dimer (p-$CF_3C_6H_4)_2PH\text{–}BH_2\text{-}(p$-$CF_3C_6H_4)_2P\text{–}BH_3$ (**3**) while at 100 °C the cyclic trimer $[(p$-$CF_3C_6H_4)_2P\text{–}BH_2]_3$ (**4a**) and tetramer $[(p$-$CF_3C_6H_4)_2P\text{–}BH_2]_4$ (**4b**) were isolated (Scheme 1).

The ring systems **4a** and **4b** are likely produced by chain extension from **3** to form the linear trimer and tetramer, facilitated by the elevated temperature, followed by back-biting reactions. A blank reaction conducted by heating **1** to 100 °C for 15 h resulted in no conversion to either **3** or **4a** and **4b**, verifying the crucial role of the catalyst in the process. Interestingly, the reaction temperatures are significantly lower than those required for the dehydrocoupling of $Ph_2PH \cdot BH_3$ [4b] and $^tBu_2PH \cdot BH_3$ [9] reflecting the relative increased acidity and reactivity of the P–H functionality in **1**.

We then turned our attention to the catalytic dehydrocoupling of **2** in the hopes that a high molecular weight fluorinated polyphosphinoborane would be synthesized. Indeed, treatment of neat **2** with $[Rh(\mu\text{-}Cl)(1,5\text{-}cod)]_2$ at 60 °C for 9 h resulted in the evolution of H_2 gas and the mixture becoming increasingly viscous. Precipitation from THF into pentane afforded polymer $[(p$-$CF_3C_6H_4)PH\text{–}BH_2]_n$ (**5**) as air- and moisture-stable light brown fibers (Scheme 2) [10].

Scheme 2.

Scheme 1.
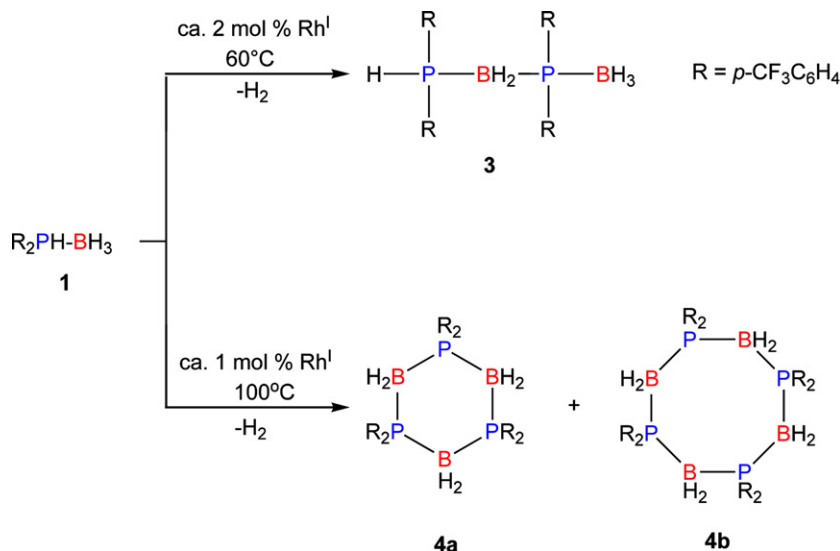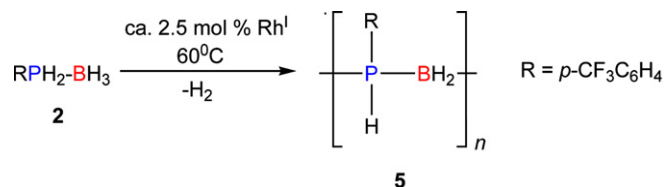
The high molecular weight of the material was confirmed by gel permeation chromatography ($M_w = 56,170$, PDI = 1.67). In the absence of catalyst, no reaction was detected at 60 °C under the same conditions. In addition, the dehydrocoupling temperature of 60 °C for the conversion of **2** to **5** in the presence of a Rh catalyst is much lower than that previously reported for the dehydrocoupling of PhPH$_2$ · BH$_3$ and ^{i}BuPH$_2$ · BH$_3$ [4b,4c]. This further demonstrates the significant influence of changing the substituent at phosphorus in the phosphine–borane adduct on the reaction conditions. In particular, this result is important as a high molecular weight polyphosphinoborane **5** can now be accessed at a relatively low temperature.

Thin films of **5** were prepared by spin-coating a toluene solution of the polymer onto a Si substrate and their use as resists in electron beam lithography (EBL) were explored. The EBL was performed on the films by treatment with a converted thermionic scanning electron microscope (SEM) using the direct write method. After development of the films by sonication in THF, the films were analyzed by SEM and atomic force microscopy and revealed that they indeed acted as negative-tone resists towards EBL [10]. The portions of the film that were treated with the electron beam remained on the surface of the substrate in the form of micron-scale bars. The elemental composition of the bars was confirmed by time-of-flight secondary ion mass spectrometry, as boron and fluorine maps clearly showed that the elements were concentrated within the bars. Future work with these patterned thin films of **5** is directed towards conversion to patterned boron phosphide ceramics via pyrolysis studies.

## 2.2. Poisoning of heterogeneous dehydrocoupling catalysts by group 13 hydrides

We have previously observed that some phosphine–borane adducts (Ph$_2$PR · BH$_3$, R = H, Ph) undergo metal-assisted dissociation in the presence of colloidal Rh catalysts [6]. We investigated the generality of this reaction and consequently prepared a series of amine and phosphine adducts with various Group 13 hydride acceptors. The same metal-catalyzed dissociation process was found to occur, with the degree of dissociation increasing down Group 13 (e.g. GaH$_3$ > AlH$_3$ > BH$_3$). Subsequent treatment of these solutions *in situ* with Me$_2$NH · BH$_3$ did not result in dehydrocoupling to afford the cyclic dimer [Me$_2$N–BH$_2$]$_2$ in most cases implying catalyst poisoning

had occurred [11]. It seemed likely that the σ donor amine or phosphine fragments were the cause of this catalyst deactivation as strong donor ligands are well-known poisons of heterogeneous catalysts [12]. However, unlike the case with phosphines such as PMe$_3$, treatment of colloidal Rh with a variety of amines (e.g. NEt$_3$, Me$_2$NH, pyridine) did not result in suppression of catalytic activity towards the dehydrocoupling of Me$_2$NH · BH$_3$. This suggested that the Group 13 hydride species "XH$_3$" (X = B, Al, Ga) might be responsible for the catalyst poisoning.

In order to test this hypothesis, colloidal Rh metal was reacted with an excess of BH$_3$ · THF resulting in the immediate evolution of H$_2$ gas. Upon subsequent treatment of this solution with Me$_2$NH · BH$_3$, no evidence of any dehydrocoupling activity was observed by ^{11}B NMR spectroscopy (Scheme 3) [11].

Thus it seemed that the "BH$_3$" fragment was reacting with the colloidal Rh causing catalyst deactivation. The surface of the catalyst was analyzed by X-ray photoelectron spectroscopy (XPS) before and after reaction with BH$_3$ · THF. The XPS spectrum of the colloids performed prior to treatment with BH$_3$ · THF showed essentially no boron content as indicated by the lack of a B(1s) peak. However, the colloids after treatment with BH$_3$ · THF did show a B(1s) peak at 193.4 eV indicating it is likely an oxide species (B$_2$O$_3$ = 192–193.5 eV) [13]. The presence of a passivating layer of boron on the surface of the Rh colloid was also verified by the indication of a significantly lower boron concentration after sputtering the surface of the colloid with an Ar$^+$ beam.

The scope of this poisoning reaction was found to be extensive as analogous poisoning effects were found in the cases of colloidal Rh treated with other species containing B–H bonds such as [HB–NH]$_3$, or Ga–H bonds such as those present in GaH$_3$ · OEt$_2$ as well as colloidal Rh that was generated from Rh(I) and Rh(III) salts using borane or borohydrides as reductants [11]. Also, identical results were obtained for other Rh catalysts including Rh stabilized on Al$_2$O$_3$ and Rh black, along with additional metals such as Ru and Pd. In contrast, analogous poisoning effects were not detected for the catalytic hydrogenation of cyclohexene using Rh/Al$_2$O$_3$ or the Pd-catalyzed Suzuki cross-coupling of PhB(OH)$_2$ and PhI. Overall, although this poisoning behaviour is not a universal phenomenon, the results strongly imply that catalyst poisoning/surface passivation effects need to be carefully considered in catalytic reactions in which heterogeneous transition metal catalysts are prepared
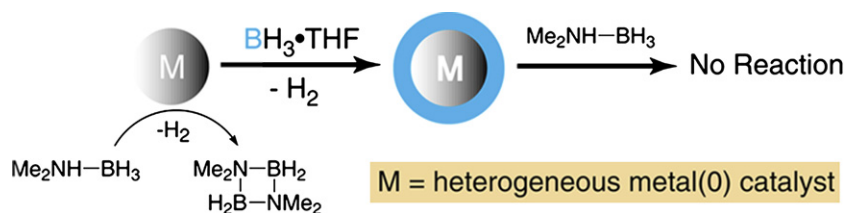
Scheme 3.

using the commonly applied borane or borohydride reduction procedures.

2.3. [Cp₂Ti]: A highly active, homogeneous, early transition metal catalyst for the dehydrocoupling of amine–borane adducts

Previously, we have shown that the Ti(IV) catalyst Cp_2TiMe_2 is inactive towards the dehydrocoupling of both phosphine- and amine–borane adducts [4b,5]. For example, treatment of $Me_2NH \cdot BH_3$ with a catalytic amount of Cp_2TiMe_2 at 25 °C for 160 h resulted in no reaction by ^{11}B NMR spectroscopy [5]. Corey and co-workers have described [Cp₂M] catalysts (M = Group 4 metal), generated *in situ* by reaction of the appropriate Cp_2MCl_2 with two equivalents of [n]BuLi, which act as catalysts for the dehydrocoupling of secondary silanes to afford oligomers [14]. This report prompted our interest in whether or not catalysts of this type could be extended to Group 13/15 adducts.

Treatment of $Me_2NH \cdot BH_3$ with [Cp₂Ti] at 20 °C (generated as above) resulted in immediate bubbling, release of H_2 gas and conversion to $[Me_2N–BH_2]_2$ in 4 h [15]. In comparison, the Rh-catalyzed reaction takes 16 h. under the same conditions [5] indicating the relatively high activity of the Ti-based system. Other more sterically encumbered adducts were also found to rapidly dehydrocouple in the presence of [Cp₂Ti]. For example, $^iPr_2NH \cdot BH_3$ afforded $^iPr_2N = BH_2$ in just 1 h [15] whereas the reaction takes 96 h if Rh catalysts are employed (Scheme 4) [5].

We have previously reported that in the case of the dehydrocoupling of amine–borane adducts, the active Rh(0) catalyst is likely heterogeneous in nature [6]. As the [Cp₂Ti] reactions are black, we were interested as to whether or not this process proceeded by a homogeneous or heterogeneous mechanism. The observation that no dehydrocoupling occurs between $Me_2NH \cdot BH_3$ and catalytic amounts of both bulk and colloidal Ti metal suggested that the reaction mechanism might be homogeneous. This hypothesis was tested using a variety of standard methods which are used to discern between homogeneous and heterogeneous catalysts.

Firstly, the [Cp₂Ti]-catalyzed dehydrocoupling of $Me_2N-H \cdot BH_3$ was initiated in the presence of a large excess of Hg which acts as an effective poison towards heterogeneous catalysts by either surface adsorption or the formation of an amalgam [16]. No suppression of catalytic activity was observed indicating that the reaction may indeed be homo-

geneous. This was further corroborated by the differing % conversion vs. time plots for the Rh- and Ti-catalyzed dehydrocoupling reactions. In the case of the former, the graph showed a sigmoidal-shaped curve characteristic of a heterogeneous process with an induction period prior to generation of colloidal Rh metal [6], while in the latter the reaction proceeds immediately after [Cp₂Ti] addition with an approximately linear conversion vs. time kinetic profile [15]. Finally, the most convincing piece of evidence was obtained through filtration studies [12]. In the case of Rh, filtration of the dehydrocoupling reaction mixture removes the heterogeneous catalyst and thus no reaction of any additional equivalents of $Me_2NH \cdot BH_3$ is observed [6]. However, in the case of [Cp₂Ti], filtration through 200 nm porous filters did not result in any change in catalyst activity confirming that it is highly likely that the catalytic dehydrocoupling of amine–borane adducts by [Cp₂Ti] is homogeneous [15]. Studies are now under way to explore the generality and utility of this highly active Ti catalyst.

3. Conclusions

In summary, we have shown that phosphine–borane adducts which possess fluorinated aryl groups on phosphorus render the P–H bond highly polar and thus, catalytically dehydrocouple at relatively mild reaction temperatures to yield chains, rings or high molecular weight polymers. Group 13 hydrides were unexpectedly found to act as effective poisons towards heterogeneous catalysts, which are typically active towards the dehydrocoupling of amine–borane adducts, by the formation of a passivating boron layer on the surface of the colloid. Lastly, [Cp₂Ti] generated *in situ* is a homogeneous early transition metal catalyst that exhibits greater catalytic activity than it's heterogeneous Rh counterpart towards the dehydrocoupling of amine–borane adducts.
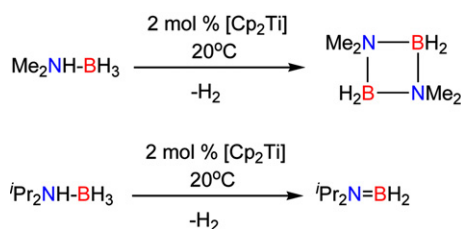
4. Experimental

For full experimental details, please see the appropriate references.

Scheme 4.

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