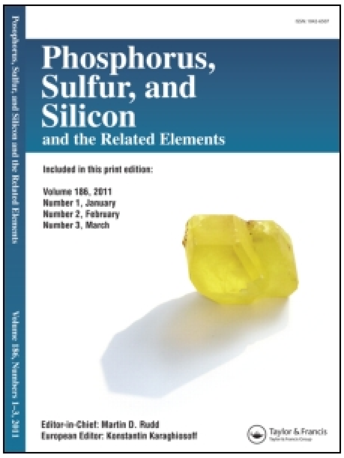

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Transition Metal-Catalyzed Formation of Phosphorus-Boron Bonds: a New Route to Phosphinoborane Rings, Chains and the First High Polymers

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A novel catalytic route for the formation of phosphorus-boron bonds has been developed. The dehydrogenative coupling of the phosphine-borane adducts $Ph_2PH{\cdot}BH_3$ and $PhPH_2{\cdot}BH_3$ is efficiently catalyzed by transition metal-complexes such as $[Rh(1,5\text{-cod})_2][OTf]$ or $[\{Rh(\mu\text{-Cl})(1,5\text{-cod})\}_2]$ to give the linear compound $HPPh_2\text{-}BH_2\text{-}PPh_2\text{-}BH_3$ (**1**), the cyclic phosphinoboranes $[Ph_2P\text{-}BH_2]_3$(2a) and $[Ph_2P\text{-}BH_2]_4$ (2b), and the first high molecular weight poly(phosphinoborane) $[PhPH\text{-}BH_2]_n$ (3).

Keywords: boron; catalysis; phosphorus; polymers; rings

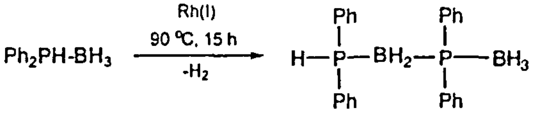
INTRODUCTION

The development of new catalytic methods for the formation of main group element-element bonds other than carbon represents a significant synthetic challenge. However, in recent years, new catalytic routes for the synthesis of extended inorganic structures have been developed. For example, transition metal-catalyzed dehydrocoupling reactions to form Si-Si, Ge-Ge and Sn-Sn bonds have been reported.[1]

The thermally induced dehydrocouling of phosphine-borane adducts to form P-B bonds has long been known as a method for the preparation of phosphinoborane rings, mainly of the type $[R_2P\text{-}BH_2]_3$. The recently discovered rhodium-catalyzed dehydrocoupling of secondary and primary phosphine-borane adducts provides a powerful tool for the extension of phosphinoborane chemistry far beyond the previously known cyclic structures.[2][3] Some recent findings are summarized below.

RESULTS AND DISCUSSION

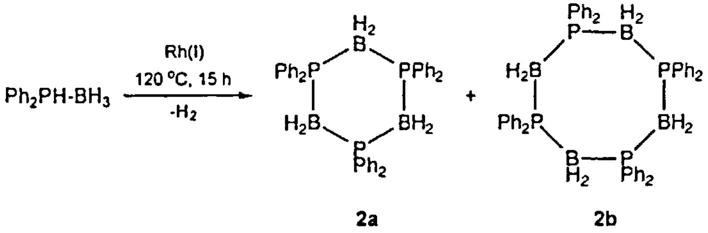
The phosphine-borane adduct $Ph_2PH\cdot BH_3$ undergoes dehydrocoupling at 190-200 °C to yield the cyclic trimer $[Ph_2P\text{-}BH_2]_3$.[4] However, on addition of $[Rh(1,5\text{-cod})_2][OTf]$ or $[\{Rh(\mu\text{-Cl})(1,5\text{-cod})\}_2]$ as catalyst (ca. 0.3 mol % rhodium) and lowering the temperature to 90 °C, cyclization is prevented and the novel, linear compound $HPPh_2$-BH_2-PPh_2-BH_3 (1) is obtained in quantitative yield. Interestingly, no conversion of $Ph_2PH{\cdot}BH_3$ was observed at this temperature without added catalyst.



1

The ^{31}P NMR spectrum of **1** shows two broad signals at δ -3.3 ppm (Ph_2PH group) and δ -17.7 ppm (Ph_2P group). Likewise, the ^{11}B NMR spectrum shows two different environments, centered at δ -33.2 ppm (BH_2 group) and δ -37.3 ppm (BH_3 group). Further characterization by ^1H NMR spectroscopy, mass spectrometry and single crystal X-ray diffraction confirmed the proposed linear structure with a P-B-P-B backbone.

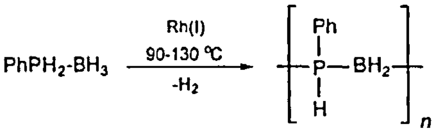
When neat $Ph_2PH{\cdot}BH_3$ and rhodium catalyst were heated to 120 °C overnight, the linear compound **1** was completely consumed and a mixture of cyclic trimer $[Ph_2P$-$BH_2]_3$ (**2a**) and tetramer $[Ph_2P$-$BH_2]_4$ (**2b**) was formed (ca. 2:1 ratio).



Since the ^{31}P and ^{11}B NMR chemical shifts of **2a** and **2b** are nearly identical, only single broad resonances were observed in the NMR spectra, centered around δ -18.2 ppm and δ -33.8 ppm, respectively. The ^{1}H NMR spectrum, however, showed two distinct sets of protons in the phenyl region, which were subsequently assigned to **2a** and **2b**, respectively. The characterization of the phosphinoborane rings was completed by mass spectrometry and, in the case of **2b**, by single crystal X-ray analysis. The molecular structure of **2b** revealed an eight-membered ring in a boat-boat conformation with approximately tetrahedrally coordinated P and B atoms and an average P-B bond length of 1.939(5) Å. It is noteworthy, again, that virtually no conversion of $Ph_2PH{\cdot}BH_3$ occurs at 120 °C in the absence of rhodium catalyst.

We have then investigated the dehydrocoupling of the corresponding primary phosphine-borane adduct $PhPH_2{\cdot}BH_3$, using the same rhodium catalysts. Previous work had suggested that low-molecular weight polymers of the formula $[PhPH\text{-}BH_2]_n$ could exist, when $PhPH_2{\cdot}BH_3$ is heated at 100-250 °C for several hours without any added catalyst.[5]

Neat $PhPH_2{\cdot}BH_3$ and a catalytic amount of $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ (ca. 0.6 mol % rhodium) were heated at 90 °C for 3 h and then at 130 °C for 3 h; vigorous gas evolution (H_2) was observed. Dissolution of the product in THF and subsequent precipitation into hexanes gave poly(phenylphosphinoborane) (**3**) in 75 % yield as an off-white powder.



3

The ^{31}P NMR spectrum of **3** showed a broad singlet at δ -48.9 ppm, which split into a doublet (J_{PH} = 360 Hz) in the ^1H coupled spectrum and is characteristic of a single hydrogen substituent at phosphorus. The ^1H NMR spectrum contains broad signals for the phenyl group (δ 7.90-6.65 ppm) and the BH_2 protons (δ 2.20-0.65 ppm) as well as a broad doublet (J_{PH} = 360 Hz) at δ 4.25 ppm for the PH group. The ^{11}B NMR spectrum of **3** showed a single broad resonance at δ -34.7 ppm, which is characteristic for a four-coordinate boron center attached to two phosphorus atoms. The absolute weight average molecular weight (M_w) of **3** was determined by static light scattering (SLS) in THF and was found to be M_w = 33300, which corresponds to a weight-average degree of polymerization (DP_w) of 273. Poly(phenylphosphinoborane) (3) is air- and moisture-stable in the solid state. It is readily soluble in THF and chlorinated hydrocarbons, moderately soluble in toluene, and insoluble in hexanes, methanol or water.

In summary, novel and facile transition metal-catalyzed P-B bond forming reactions have been discovered and the first well characterized, high molecular weight poly(phosphinoborane) (3) has been synthesized. Future work will focus on the properties and the structural modification of the poly(phosphinoboranes), and the investigation of the dehydrocoupling mechanism.[6]

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