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Iron-Catalyzed Dehydropolymerization: A Convenient Route to Poly(phosphinoboranes) with Molecular-Weight Control**

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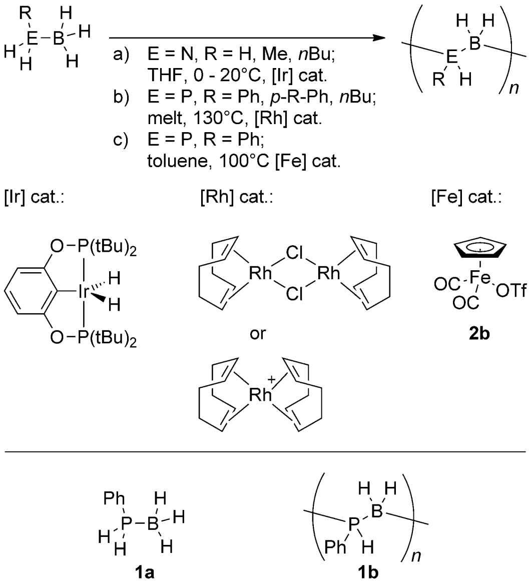
Dedicated to Professor Peter Paetzold on the occasion of his 80th birthday

Abstract: *The catalyst loading is the key to control the molecular weight of the polymer in the iron-catalyzed dehydropolymerization of phosphine–borane adducts. Studies showed that the reaction proceeds through a chain-growth coordination–insertion mechanism.*

Polymers based on main chains that contain *p*-block elements other than carbon are of major current interest as functional soft materials.[1] For example, polysiloxanes $[R_2SiO]_n$ and polyphosphazenes $[R_2PN]_n$ possess remarkable thermophysical properties with a wide range of applications, and polysilanes $[SiR_2]_n$ and polystannanes $[SnR_2]_n$ offer unusual electronic characteristics and photosensitivity.[1] Polymers based on the Group 13 element boron have been developed as easily processable thermal precursors to refractory ceramic fibers and shaped monoliths and are also attracting attention as optoelectronic materials.[2]

Recently, our group and others have explored the catalytic dehydrocoupling of amine–borane adducts ($RNH_2{\cdot}BH_3$) to high-molecular-weight poly(aminoboranes) ($[RNH\text{-}BH_2]_n$), which are boron–nitrogen analogues of polyolefins.[3] These materials are of interest for hydrogen storage, as piezoelectrics, and as precursors to refractory BN-based materials. Developments in this area have been facilitated by the discovery of Ir, Ru, Rh, and Fe catalysts that are highly active in solution at room temperature (Scheme 1). In contrast, although a similar Rh-catalyzed approach using precatalysts $[\{(1,5\text{-cod})Rh(\mu\text{-}Cl)\}_2]$ and $[(1,5\text{-cod})_2Rh]OTf$ (cod = cyclooctadiene) has been developed for the formation of their phosphorus analogues, poly(phosphinoboranes) ($[RPH\text{-}BH_2]_n$) were only accessible by melt reactions at temperatures of ca. 130 °C, giving polydisperse, soluble, branched polymers ($M_n > 10000$) and crosslinked, swellable, but insoluble materials, unless the phosphine–borane adduct is deliberately activated by the presence of electron-withdrawing groups (Scheme 1).[4,5] Although there have been key advances in the mechanistic understanding of P–B bond formation in model examples of these dehydrocoupling reactions,[6] the challenges of using the melt reaction with a precious-metal precatalyst have held back the development of the poly(phosphinoborane) field. Herein we report the discovery of an earth-abundant, iron-based precatalyst for the synthesis of poly(phosphinoboranes) that proceeds in solution and also allows insightful mechanistic investigations and control over the molecular weight for the first time.



Scheme 1. Dehydropolymerization of Group 13/15 adducts with a) [Ir], b) [Rh], and c) [Fe] (pre)catalysts.

Recently, iron-catalyzed dehydrocoupling of various amine–borane adducts has been developed,[3e,k,7] and we have shown that poly(aminoboranes) can be formed under ambient conditions in the case of primary amine–borane substrates, such as $MeNH_2{\cdot}BH_3$. In our work, we used the readily accessible iron(II) complex $[Cp(CO)_2FeI]$ (**2a**) as a precatalyst.[3e,7b] While there are few known catalysts that promote both amine–borane and phosphine–borane dehydrocoupling, this species served as a good starting point in our search for a more convenient and improved alternative to the

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previously utilized Rh-based precatalysts.[8] Preliminary experiments showed dehydrocoupling of phenylphosphine–borane adduct (**1a**) to take place in the presence of 10 mol% of **2a**, in toluene at 100°C. Poly(phenylphosphinoborane) (**1b**) was the exclusive product of this reaction and full conversion of monomer **1a** was observed by ^{11}B and ^{31}P NMR spectroscopy after 24 h; the molecular weight of **1b** was however only moderate ($M_n = 18000$, PDI = 2.0; PDI = polydispersity index). Replacement of iodide by the more weakly coordinating trifluoromethanesulfonate gave a more active precatalyst [Cp(CO)$_2$Fe(OTf)] (OTf = OSO$_2$CF$_3$, **2b**).[9] Thus, when **1a** was heated with only 1 mol% of **2b** (toluene, 100°C, 24 h), quantitative conversion to high-molecular-weight **1b** was observed ($M_n = 59000$, PDI = 1.6).[10] The ^{31}P NMR spectrum of polymer **1b**, which was isolated by precipitation into cold pentane, showed a doublet at $\delta(^{31}\text{P}) = -49$ ppm ($^1J_{\text{PH}} = 349$ Hz), and the ^{11}B NMR spectrum showed a broad singlet at $\delta(^{11}\text{B}) = -35$ ppm, similar to previous reports (Figure 1).[4b]

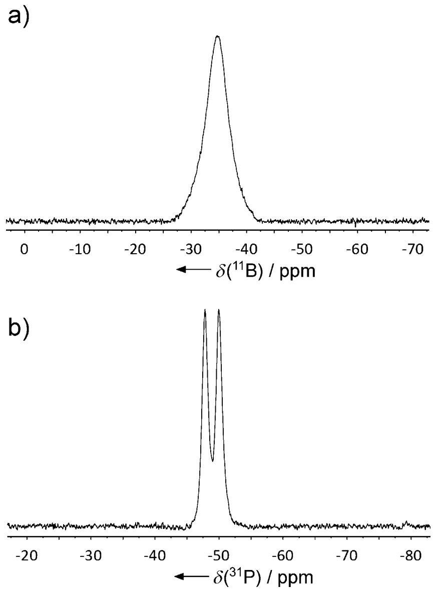
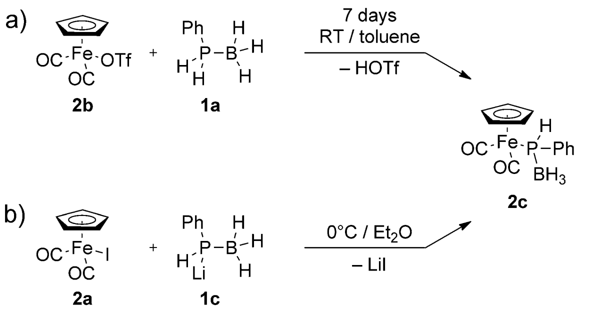


Figure 1. a) ^{11}B (128 MHz, 298 K, CDCl$_3$) and b) ^{31}P NMR spectrum (162 MHz, 298 K, CDCl$_3$) of **1b**, isolated from the reaction of **1a** with 1 mol% of **2b**.

The ability to perform the dehydropolymerization in solution rather than in molten monomer provided an opportunity to further probe the mechanism of the Fe-catalyzed process. A key question is whether the catalyst is homogeneous or heterogeneous. In our previous study on the Fe-catalyzed dehydrocoupling of amine–borane Me$_2$NH·BH$_3$, the reaction with precatalyst **2a** proceeded through a homogeneous mechanism, whereas the Fe$^{\text{I}}$ dimers [Cp$_2$(CO)$_2$Fe$_2$(μ-CO)$_2$] and [Cp$_2$(CO)(CH$_3$CN)Fe$_2$(μ-CO)$_2$] gave rise to very small Fe nanoparticles, which were potent heterogeneous catalysts.[7b] We found that treatment of **1a** with these nanoparticles did not result in detectable catalytic dehydrocoupling at ambient temperature or upon heating (100°C, toluene, 24 h).[11] This observation is in marked contrast to the smooth dehydropolymerization of **1a** upon treatment with 1 mol% of **2b** under identical conditions, under which the typical darkening of the reaction solution that accompanies the Fe nanoparticle formation was not observed. These observations suggest that the dehydropolymerization of **1a** mediated by precatalyst **2b** is a homogeneous process, an assertion further supported by the lack of poisoning detected with a substoichiometric amount of PMe$_3$.[11]

In a typical dehydropolymerization of **1a** (1 mol% of **2b**, 100°C, toluene), a color change from red (corresponding to **2b**) to yellow was observed early in the reaction. We also studied the reaction of **1a** with **2b** on a stoichiometric scale (1:1 ratio) under ambient conditions (Scheme 2a). Although very slow, a clean conversion to the corresponding iron phosphidoborane species **2c** was detected by ^{11}B and ^{31}P NMR spectroscopy.[11] This species was isolated as a yellow solid and the structure was confirmed by multinuclear NMR spectroscopy, single-crystal X-ray diffraction (Figure 2), and an independent synthesis starting from **2a** and LiPhPH·BH$_3$ (**1c**; Scheme 2b).[11] The analogous iron(diphenylphosphido)borane complex **2d** has been reported before by our group[7] and also by Wagner and co-workers.[12]



Scheme 2. Synthesis of **2c** by the reaction of a) **1a** with **2b**, and b) **1c** with **2a**.

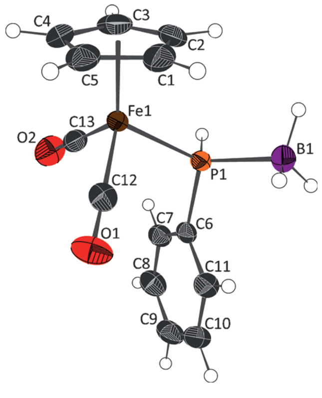


Figure 2. Molecular structure of **2c** in the crystal. Thermal ellipsoids drawn at 75% probability level. Selected bond distances: Fe-P: 225.39(1) pm, P-B: 195.14(1) pm (color code: grey: carbon, white: hydrogen, purple: boron, brown: iron, red: oxygen, orange: phosphorus).

When species **2c** rather than **2b** was used as a precatalyst under identical conditions (1 mol %, 100 °C, toluene, 24 h), **1b** was obtained with similar molecular weight ($M_n = 80000$; PDI = 1.6). This result suggests that initiation with **2b** involves triflate dissociation followed by P−H bond activation and [Fe]−P bond formation. The previous observation of facile CO substitution in the diphenylphosphido analogue of **2c**[13] at ambient temperature suggests that this is likely to be followed by CO dissociation, substrate coordination, and the formation of the P−B bond. This process is mechanistically similar to that demonstrated by Weller and co-workers in model reactions of secondary phosphine–borane adducts at Rh centers.[6a,b] To further probe the postulated CO dissociation step following the initial formation of **2c**, we turned to DFT investigations. The relative energy differences for the loss of one CO ligand from **2c** and the complexation of **1a** in a μ-H σ borane fashion to the Fe center were calculated at the M06-2X/6-311+G(d,p)(C, H, B, O, P), SDD(Fe) level of theory (Figure 3).[11]

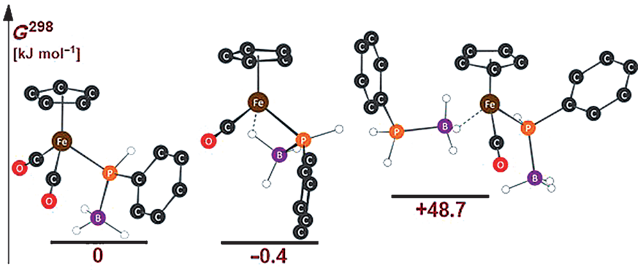
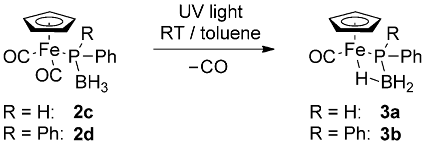


Figure 3. Calculated relative Gibbs free energies (in kJ mol^{-1}) of **2c** (left), for CO dissociation forming **3a** (center), and subsequent coordination of **1a** to **3a** (right) at the M06-2X/6-311+G(d,p) (C, H, B, O, P), SDD(Fe) level of theory (relative Gibbs free energies given for: $C_{19}H_{24}B_2FeO_2P_2$; all H atoms except P-H and B-H omitted for clarity; color code: grey: carbon, white: hydrogen, purple: boron, brown: iron, red: oxygen, orange: phosphorus).

The dissociation of one CO ligand from **2c** was found to be quasi thermoneutral. The calculations suggested that the phosphidoborane moiety acts as a bidentate ligand, with the BH_3 group involved in an agostic interaction with the metal center, thereby promoting CO loss through chelation. Binding of **1a** to the resulting monocarbonyl complex, as a σ-borane complex, was slightly endergonic ($\Delta G^{298} = +48.7$ kJ mol^{-1}).[14] However, taking into consideration the large excess of monomer **1a** present in solution under catalytic conditions, this is still reasonable (indeed, analogous σ-borane complexes, such as $[Cp(Me_3P)_2Ru(\eta^1\text{-}H_3B{\cdot}PMe_3)]^+$, have been reported for ruthenium).[15] Moreover, we were able to obtain key evidence for the stability of the monocarbonyl complex **3a** by ^{11}B and ^{31}P NMR spectroscopy and by the synthesis and isolation of the analogous diphenyl derivative **3b** from **2d**, through photolysis of a solution of **2d** in toluene at room temperature (Scheme 3).[11] Compound **3b** was isolated as a red solid and was characterized by ^{1}H, ^{11}B, and ^{31}P NMR spectroscopy as well as single-crystal X-ray diffraction, which showed the presence of a 3-center-2-electron [Fe]-H-B agostic interaction (Figure 4).[11]



Scheme 3. Photolysis of **2c,d** to give the corresponding monocarbonyl derivatives **3a,b**.

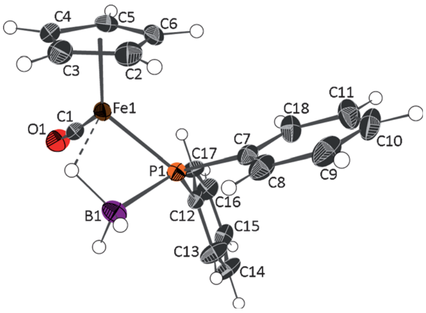
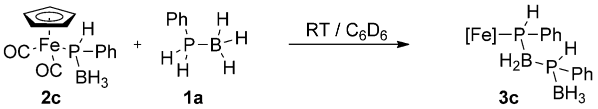


Figure 4. Molecular structure of **3b** in the crystal. Thermal ellipsoids drawn at 75 % probability level. Selected bond distances: Fe-P: 218.08(5) pm, Fe-H: 128.64(252) pm, B-H:. 108.77(238) pm, 110.40-(254) pm (color code: grey: carbon, white: hydrogen, purple: boron, brown: iron, red: oxygen, orange: phosphorus).

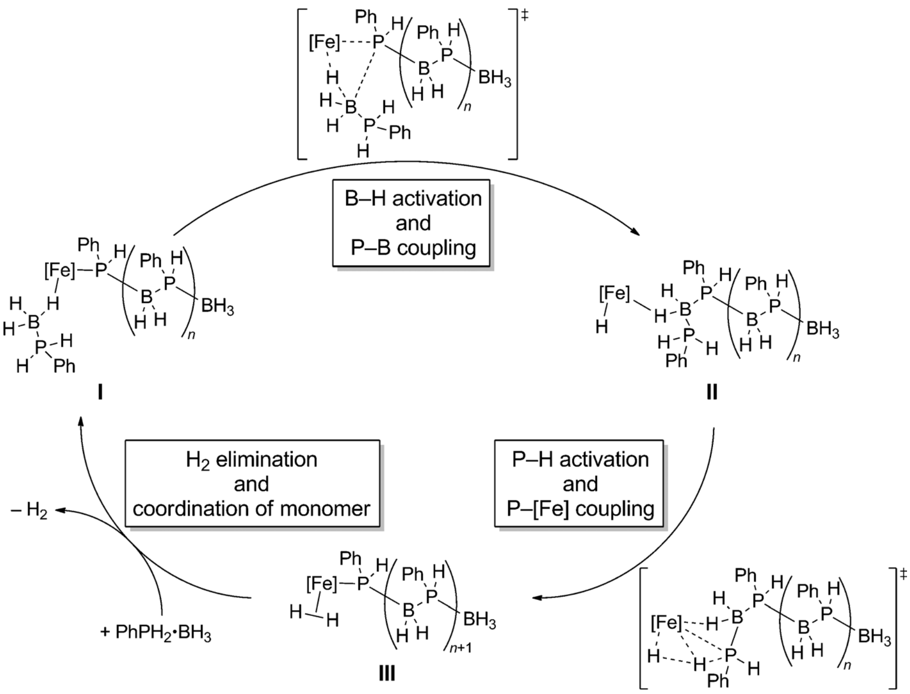
In order to provide evidence for the P−B bond-forming step that follows CO dissociation and substrate binding, **2c** was reacted with **1a** in a stoichiometric manner (1:1 ratio). The reaction proved to be extremely slow at ambient conditions, but, after four weeks, the ^{11}B and ^{31}P NMR spectra showed new signals, which we tentatively assigned to the iron-bound phosphinoborane dimer **3c** (Scheme 4, Figure S6).[16] This assignment is further supported by the observation of metal-bound P−B species by ESI-MS.[11]



Scheme 4. Reaction of **2c** with **1a** to give a metal-bound phosphine–borane dimer complex (**3c**; [Fe] = $Cp(CO)_xFe$).

Another key mechanistic consideration is whether the polymerization proceeds through a step-growth or a chain-growth mechanism.[17] To probe this issue, the molecular weight of **1b** in a typical reaction of **1a** with 5 mol % **2b** was analyzed at a low conversion (6 h/≈35 %). High-molecular-weight polymer ($M_n = 40000$, PDI = 1.7) was detected, indicating a chain-growth mechanism. Significantly, for a chain-growth polymerization, the molecular weight should decrease with increased catalyst loading. This tendency offers convenient control over molecular weight and the use of 0.1, 1, 5 or 10 mol % precatalyst **2b** gave a smooth decrease of both M_n and M_w under otherwise identical conditions (24 h, 100 °C, toluene; Figure 5). In addition, allowing the reaction of **1a** with 5 mol% of **2b** to continue for another 24 h led to no further increase in molecular weight, which suggests that the polymer cannot condense further.

Based on our findings in this work as well as previous studies of dehydrocoupling mechanisms and model species,[6] we propose a chain-growth coordination-type mechanism (Scheme 5).[18] The first proposed step after monomer coordination to iron (in **I**) is the activation of the B–H bond and the formation of a new P–B bond by insertion into the [Fe]–P bond. We postulate an intermediate (**II**), in which the polymer chain is bound to the iron center through the BH_2 group. In a second step, P–H activation is proposed to form H_2 and a species with a new [Fe]–P bond (**III**). Finally, elimination of coordinated H_2 can open up the vacant coordination site for binding further monomer.



Scheme 5. Postulated catalytic cycle for the chain-growth coordination polymerization of **1a** by the iron catalyst derived from **2c** (scheme showing one insertion event).

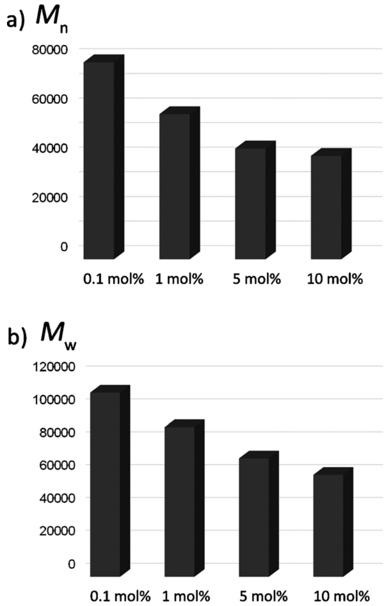


Figure 5. Dependence of the molecular weight of **1b** (*y* axis: a) M_n, b) M_w) derived from the reaction of **1a** with different catalyst loadings of **2b** (*x* axis).

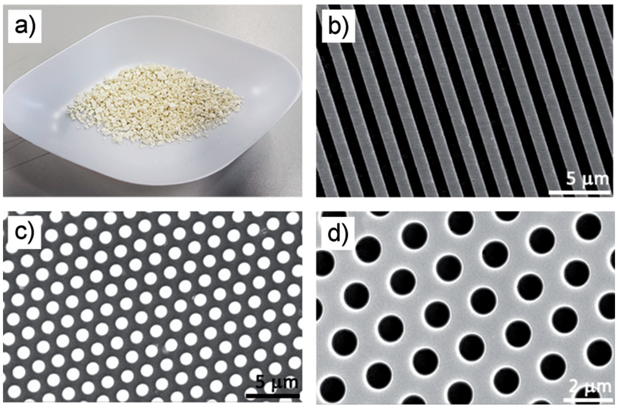


Figure 6. a) Isolated **1b**, and b–d) SEM images of micropatterns fabricated from **1b** on silicon wafers by soft-lithography.

Poly(phosphinoboranes) are of interest as inorganic soft materials with unusual and useful properties. Preliminary evidence for their use as precursors to the luminescent semiconductor boron phosphide[4d] and as electron-beam resists for lithography[4e] have been reported. With the ability to now readily synthesize colorless, essentially metal-free, high-molecular-weight poly(phenylphosphinoborane) (Figure 6a) using precatalyst **2b**, we were able to show that the resulting material was easily patterned on silicon wafers using soft lithographic techniques.[11] Micrometer-scale patterns with excellent definition were imaged by scanning electron microscopy (SEM; Figure 6b–d).[11] The facile synthesis and fabrication of this material should enable future studies of properties and applications.

In summary, we report the first earth-abundant, iron-based (pre)catalyst for the synthesis of poly(phosphinoborane) **1b** in solution. The molecular weight of **1b** can be controlled by varying the catalyst loading. The catalysis appears to be homogenous in nature and to occur through a chain-growth coordination–polymerization mechanism. These discoveries should facilitate the future development of the field of poly(phosphinoboranes).

Keywords: dehydrocoupling · dehydropolymerization · iron catalysis · phosphine–borane adducts · poly(phosphinoboranes)

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[11] See the Supporting Information for further details.

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[18] Comprehensive DFT calculations support this mechanism. See Section 3 in the Supporting Information for further details.

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