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Transition Metal-Catalyzed Formation of Phosphorus−Boron Bonds: A New Route to Phosphinoborane Rings, Chains, and Macromolecules

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Abstract: A novel catalytic dehydrocoupling route for the synthesis of linear, cyclic, and polymeric phosphinoboranes has been developed. The dehydrocoupling of neat $Ph_2PH\cdot BH_3$, which is otherwise very slow below 170 °C, is catalyzed by $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ or $[Rh(1,5\text{-}cod)_2][OTf]$ (0.5−1 mol % Rh) to give the linear compound $Ph_2PH-BH_2-PPh_2-BH_3$ (**1**) at 90 °C, and a mixture of the cyclic trimer $[Ph_2P-BH_2]_3$ (**2a**) and tetramer $[Ph_2P-BH_2]_4$ (**2b**) at 120 °C. In addition, the catalytic potential of other (e.g., Ti, Ru, Rh, Ir, Pd, Pt) complexes toward the dehydrocoupling of $Ph_2PH\cdot BH_3$ was investigated and was in many cases demonstrated. The molecular structures of **1** and **2b**, and of the primary phosphine−borane adduct $PhPH_2\cdot BH_3$, were determined by single-crystal X-ray analysis. The dehydrogenative coupling of $PhPH_2\cdot BH_3$ gave low-molecular-weight poly(phenylphosphinoborane) $[PhPH-BH_2]_n$ (**3**) when performed in toluene (110 °C) with ca. 0.5 mol % $[Rh(1,5\text{-}cod)_2][OTf]$ as catalyst. The absolute weight-average molecular weight was determined by static light scattering (SLS) in THF which showed that $M_w = 5600$. Samples of high-molecular-weight polymer **3** ($M_w = 31\,000$ or $33\,300$ by SLS) were synthesized using neat conditions at 90−130 °C in the presence of $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$, anhydrous $RhCl_3$, or $RhCl_3$ hydrate (ca. 1 mol % Rh). Poly(phosphinoborane) **3** was thereby obtained in ca. 75% yield as an air-stable, off-white solid and was structurally characterized by ^1H, ^{11}B, ^{13}C, and ^{31}P NMR and IR spectroscopy and elemental analysis. The hydrodynamic diameters for polymers **3** in THF were also determined by dynamic light scattering (DLS). Catalytic dehydrocoupling of the alkyl-substituted phosphine−borane adduct $i\text{BuPH}_2\cdot BH_3$ was also investigated and was found to be much slower than that of $PhPH_2\cdot BH_3$. This produced poly(isobutylphosphinoborane) $[i\text{BuPH}-BH_2]_n$ (**4**) under neat conditions at 120 °C in the presence of $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ in 80% yield. Multinuclear NMR spectroscopy and DLS were also used to characterize polymer **4**, and the latter indicated that $M_w =$ ca. 10 000−20 000. Prolonged heating of polymers **3** and **4** at elevated temperatures in the presence of catalyst led to insoluble but solvent-swellable gels possibly due to light interchain cross-linking through P−B bonds. In the absence of rhodium catalyst thermally induced dehydrocoupling of $PhPH_2\cdot BH_3$ and $i\text{BuPH}_2\cdot BH_3$ proceeds very slowly and forms only low-molecular-weight materials with complex NMR spectra and which probably possess a branched structure.

Introduction

Macromolecules based on main group elements are of considerable interest,[1] and the relatively few polymer systems currently known, such as poly(siloxanes) $[R_2Si-O]_n$,[2] polyphosphazenes $[R_2P{=}N]_n$,[3] polysilanes $[R_2Si]_n$,[1,4] polysilynes $[RSi]_n$,[5] and more recent examples which include polystannanes $[R_2Sn]_n$,[6] polyborazylenes $[B_3N_3R_4]_n$,[7] and other boron-based[8] or sulfur-based[9] polymers, illustrate the potential for accessing materials with unusual properties as well as significant applications. The reasons for the interest in such polymers is apparent from simple chemical considerations. Compared to C−C bonds, bonds between main group elements can be stronger and more

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oxidatively stable or provide additional conformational flexibility (e.g., Si−O bonds in $[R_2Si-O]_n$) or can possess interesting electron delocalization effects (e.g., σ-conjugation in $[R_2Si]_n$ and heavier group 14 analogues). In addition to novel properties, versatile reactivity can be accessed (e.g., the substitution of chlorine in $[Cl_2P{=}N]_n$).

The development of new synthetic methods for the formation of homonuclear or heteronuclear bonds between main group elements is of critical importance for the construction of inorganic polymer chains. Transition metal-catalyzed routes, which are of widespread significance in organic chemistry, represent an attractive approach to this problem. Previously, well-characterized transition metal-catalyzed dehydrocoupling reactions to form Si−Si,[4] Ge−Ge,[10] and Sn−Sn[6] as well as P−P,[11] B−Si,[12] and P−Si[13] bonds have been reported.[14]

As part of our continuing program to develop novel extended structures based on main group elements,[15] we are exploring compounds with four-coordinate phosphorus and boron atoms.[16] The attempted synthesis of polymeric materials based on skeletons of alternating phosphorus and boron atoms, poly(phosphinoboranes), received significant attention in the 1950s and 1960s as such materials seemed likely candidates for accessing valuable, high-performance properties such as high-temperature stability and flame retardancy.[17] However, the open literature on phosphinoborane polymer chemistry is very limited, and most of this work is documented in patents and technical reports. The main synthetic methodology studied involved thermally induced dehydrocoupling of phosphine−borane adducts $R_2PH{\cdot}BH_3$ at ca. 200 °C and above, which was often performed in the presence of additives such as amines which were claimed to prevent cyclization.[18] Although in a few cases low yields of "polymeric" materials were claimed, none of the products were convincingly structurally characterized by present day standards and, where reported, the yields and molecular weights were generally very low. Since that time the area of phosphorus−boron polymer chemistry has been neglected.

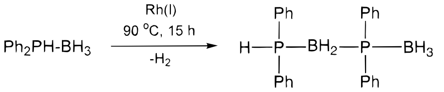
We were initially encouraged to reinvestigate this area by the earlier reports (which in some cases we have subsequently verified) that cyclic structures such as the six-membered rings $[R_2P-BH_2]_3$ show high thermal stability and resistance to oxidation and hydrolysis. Such species were first synthesized by Burg and Wagner in 1953 via dehydrogenative thermolysis of $Me_2PH{\cdot}BH_3$ (150 °C, 40 h) to give a mixture of 90% $[Me_2P-BH_2]_3$ and 9% $[Me_2P-BH_2]_4$.[19] The trimer is reported to be stable up to 300 °C, even in the presence of hydrochloric acid. This suggested that analogous high polymers might, indeed, have useful properties in addition to their intrinsic scientific interest if efficient synthetic routes to these materials could be developed.

We have previously briefly described our preliminary work on the rhodium-catalyzed dehydrocoupling of $Ph_2PH{\cdot}BH_3$ and $PhPH_2{\cdot}BH_3$, as well as the synthesis of the first, well-characterized, high-molecular-weight poly(phosphinoborane), $[PhPH-BH_2]_n$.[20] In this paper we report full details of this chemistry and the extension of our studies to other catalysts for dehydrogenative coupling and to the alkylphosphine−borane adduct *i*$BuPH_2{\cdot}BH_3$. We describe efficient transition metal-catalyzed synthetic routes to a variety of linear, cyclic, and polymeric phosphinoboranes.

Results and Discussion

I. Catalytic Dehydrocoupling of Ph_2PH-BH_3. Synthesis and Characterization of $Ph_2PH-BH_2-PPh_2-BH_3$ (1), $[Ph_2P-BH_2]_3$ (2a), and $[Ph_2P-BH_2]_4$ (2b). For our investigations, we chose $Ph_2PH{\cdot}BH_3$ as starting material. It is cheaper than $Me_2PH{\cdot}BH_3$, readily prepared from commercially available diphenylphosphine and borane−dimethyl sulfide adduct, and stable toward air and hydrolysis.

$Ph_2PH-BH_2-PPh_2-BH_3$ (1). Previous work has shown that neat $Ph_2PH{\cdot}BH_3$ undergoes thermally induced dehydrocoupling at 190−200 °C to yield the cyclic trimer $[Ph_2P-BH_2]_3$ (hereinafter referred to as **2a**).[21] However, on addition of $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ or $[Rh(1,5\text{-}cod)_2][OTf]$ as catalyst (ca. 0.3 mol %) and lowering the temperature to 90 °C, cyclization is prevented and the novel, linear compound $Ph_2PH-BH_2-PPh_2-BH_3$, **1**, is formed (eq 1). Under these conditions, formation of **1** is quantitative and subsequent recrystallization from diethyl ether gives colorless, air-stable crystals in 85% yield.It should be noted that in the absence of the rhodium catalyst no conversion of $Ph_2PH{\cdot}BH_3$ was observed at this temperature (see also Table 1, entry 1).



$$\mathrm{Ph_2PH\text{-}BH_3} \xrightarrow[-\mathrm{H_2}]{\mathrm{Rh(I)},\ 90\ ^{\circ}\mathrm{C},\ 15\ \mathrm{h}} \mathrm{H{-}\underset{Ph}{\overset{Ph}{P}}{-}BH_2{-}\underset{Ph}{\overset{Ph}{P}}{-}BH_3} \qquad (1)$$

1

Two phosphorus environments are detected in the $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) of **1**, centered at δ −3.3 ppm (Ph_2PH group) and δ −17.7 ppm (Ph_2P group). The $^{11}B\{^1H\}$ NMR spectrum also shows two broad lines centered at δ −33.2 ppm (BH_2 group) and δ −37.3 ppm (BH_3 group). In the ^1H NMR

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(18) During this early pioneering stage of research on phosphorus−boron compounds the highest molecular weight polymers were formed by dehydrogenative thermolysis when, e.g., secondary phosphine−borane adducts $R_2PH{\cdot}BH_3$ were heated in the presence of a base, usually a tertiary amine. It was postulated that cyclization is prevented by coordination of the amine to the terminal BH_2 group. For example, thermolysis of $Me_2P-PMe_2{\cdot}BH_3$ or $RMePH{\cdot}BH_3$ (R = Me or Et) at 175−200 °C in the presence of amines was reported to give polymers $[RMeP-BH_2]_n$ with molecular weights of 1800−6000 (where determined): (a) Wagner, R. I.; Caserio, F. F. *J. Inorg. Nucl. Chem.* **1959**, 11, 259. (b) Burg, A. B. *J. Inorg. Nucl. Chem.* **1959**, 11, 258. A patent claims a maximum molecular weight of 13 632 when the thermolysis of $Me_2PH{\cdot}BH_3$ is carried out at 200 °C for 17 h with a difunctional base, but no further product characterization was reported in this particular case: Burg, A. B.; Wagner, R. I. U.S. Patent 3,071,553, 1963. In addition, partially characterized, insoluble materials with three-coordinate phosphorus and boron atoms have been described: Coates, G. E.; Livingstone, J. G. *J. Chem. Soc.* **1961**, 5053.

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Table 1. Dehydrocoupling of $Ph_2PH{\cdot}BH_3$[a]

entry	catalyst	temp (°C)	conversion (%)[b]	product[c]
1	none	90	0	−
2	none	120	<5	**1**
3	none	170	95	**2a**/**2b** (ca. 8:1 ratio)[d]
4	[{Rh(μ-Cl)(1,5-cod)}$_2$]	60	10	**1**
5	[{Rh(μ-Cl)(1,5-cod)}$_2$]	90	100	**1**
6	[{Rh(μ-Cl)(1,5-cod)}$_2$]	120	100	**2a**/**2b** (ca. 2:1 ratio)[d]
7	[{Rh(μ-Cl)(1,5-cod)}$_2$]	120 (4h)	100	**1**/**2a**/**2b**[e]
8	[{Rh(μ-Cl)(1,5-cod)}$_2$]	170	100	**2a**/**2b** (ca. 2:1 ratio)[d]
9	[Rh(1,5-cod)$_2$][OTf]	60	70	**1**
10	[Rh(1,5-cod)$_2$][OTf]	90	100	**1**
11	[Rh(1,5-cod)$_2$][OTf]	120	100	**2a**/**2b** (ca. 2:1 ratio)[d]
12	[Rh(1,5-cod)$_2$][OTf]	120 (4h)	100	**1**/**2a**/**2b**[e]
13	[Rh(PPh$_3$)$_3$Cl]	90	60	**1**
14	[Rh(1,5-cod)(dmpe)][PF$_6$]	90	60	**1**
15	[Rh(CO)(PPh$_3$)$_3$H]	90	20	**1**
16	anhydrous RhCl$_3$	90	90−100	**1**
17	RhCl$_3$ hydrate	90	90−100	**1**
18	[{Cp*Rh(μ-Cl)Cl}$_2$]	90	90−100	**1**
19	[{Ir(μ-Cl)(coe)$_2$}$_2$]	90	25	**1**
20	[Ir(1,5-cod)$_2$][BF$_4$]	120	25	**1**
21	Cp$_2$TiMe$_2$	90	15	**1**
22	Ru$_3$(CO)$_{12}$	90	0	−
23	Ru$_3$(CO)$_{12}$	120	15	**1**
24	[Pd(PPh$_3$)$_4$]	90	0	−
25	[Pt(1,5-cod)$_2$]	90	0	−
26	PdCl$_2$	90	60	**1**
27	PtCl$_2$	90	40	**1**

[a] All reactions were performed without solvent, using ca. 250−350 mg of $Ph_2PH{\cdot}BH_3$ and a catalyst concentration of ca. 0.5−1.5 mol % transition metal, reaction time 14−15 h (unless otherwise noted). [b] Estimated by ^{31}P NMR spectroscopy. [c] Traces of Ph_2PH and $Ph_2P(O)H$ were sometimes detected by ^{31}P NMR spectroscopy. [d] Based on integration of ^{1}H NMR spectra. [e] In the ^{31}P NMR spectra, observation of additional signals of low intensity around δ −5.5 and −7.5 ppm may indicate formation of intermediate species; relative product ratios could not be extracted from the ^{1}H NMR spectra.

spectrum of **1**, particularly noteworthy is the doublet of multiplets at δ 6.71 ppm (PH proton, $J_{HP} = 397$ Hz) and two sets of broad resonances assigned to the two and three BH protons; the latter appears approximately as a 1:1:1:1 quartet. In the EI mass spectrum of **1**, the most intense peak comes from the loss of BH_3 ($m/z = 384$, $[M - BH_3]^+$).

A single-crystal X-ray analysis of compound **1** confirms the chainlike structure of the molecule, and a SHELXTL drawing is shown in Figure 1. The geometry around B1, P1, and P2 is approximately tetrahedral, with bond angles varying from 101.6(12) to 112.7(12)°, 105.18(9) to 113.01(1)°, and 99.0(8) to 117.73(10)°, respectively. All three P−B distances are in the single-bond range (1.90−2.00 Å). The bond distances P1−B2 (1.932(2) Å) and P2−B1 (1.923(2) Å) are comparable to P−B distances found in other simple phosphine−borane adducts such as $Ph_3P{\cdot}BH_3$ (av 1.917 Å),[22] $(C_6H_{11})_2PH{\cdot}BH_3$ (1.919(3) Å),[23] or $PhPH_2{\cdot}BH_3$ (1.924(4) Å, vide infra). The central P1−B1 bond distance (1.944(2) Å) is typical of a phosphorus−boron bond length found in cyclic phosphinoboranes, e.g., $[Ph_2P-BH_2]_3$, **2a**, (av 1.948 Å)[24] or $[Ph_2P-BH_2]_4$, **2b**, (av 1.939(5) Å, vide infra).

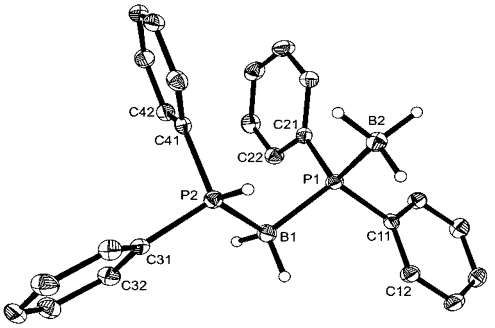
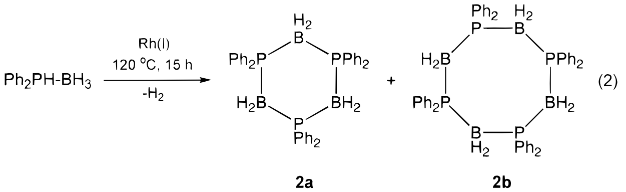


Figure 1. Molecular structure of $Ph_2PH-BH_2-PPh_2-BH_3$ (**1**). Selected bond lengths (Å) and angles (deg): P1−B2 1.932(2), P1−B1 1.944(2), P2−H1P 1.349(19), P2−B1 1.923(2); B2−P1−B1 113.01(11), H1P−P2−B1 112.6(8), P2−B1−P1 109.23(12). Hydrogen atoms attached to phenyl rings are omitted.

Compound **1** is the first well-characterized example of a linear phosphinoborane with four-coordinate boron and phosphorus atoms. In 1989, Imamoto and Oshiki described the preparation of linear phosphinoboranes via nucleophilic substitution reactions at the boron atom. The reaction of $Me_3P{\cdot}BH_2(OSO_2Me)$ with $Ph_2PH{\cdot}BH_3$/NaH was reported to give the four-membered compound $Me_3P-BH_2-PPh_2-BH_3$ as well as six- and eight-membered chains.[25] However, characterization of these species by ^{31}P or ^{11}B NMR spectroscopy or by single-crystal X-ray analysis was not reported.

$[Ph_2P-BH_2]_3$ (2a) and $[Ph_2P-BH_2]_4$ (2b). When neat $Ph_2PH{\cdot}BH_3$ and a catalytic amount of [{Rh(μ-Cl)(1,5-cod)}$_2$] or [Rh(1,5-cod)$_2$][OTf] were heated to 120 °C overnight, the linear compound **1** was completely consumed and a mixture of the cyclic trimer $[Ph_2P-BH_2]_3$ (**2a**) and tetramer $[Ph_2P-BH_2]_4$ (**2b**) was formed (eq 2).



Both the ^{31}P and ^{11}B NMR spectra revealed only single broad resonances centered around δ −18.2 ppm and δ −33.8 ppm, respectively, which are indicative for cyclic phosphinoborane compounds. The ^{1}H NMR spectrum in $CDCl_3$ showed two sets of aromatic protons which were assigned to **2a** and **2b**, respectively (ca. 2:1 ratio). The signal for the BH_2 protons is very broad and is found in the δ 3−1 region of the ^{1}H NMR spectrum.

The mixture of **2a**/**2b** can partially be separated upon addition of diethyl ether. It is thus possible to isolate small amounts of pure tetramer **2b**, which is less soluble in diethyl ether than the trimer **2a**. Compound **2b** is a colorless, air-stable solid which is very soluble in $CHCl_3$, THF, and toluene, less soluble in diethyl ether, and almost insoluble in hexanes. Again, virtually no conversion of $Ph_2PH{\cdot}BH_3$ was observed over 14 h at 120 °C in a blank experiment (Table 1, entry 2).

As mentioned above, the synthesis of **2a** was described earlier, from the uncatalyzed pyrolysis of $Ph_2PH{\cdot}BH_3$, and the compound was characterized by IR, elemental, and molecular weight analysis,[21] and later by single-crystal X-ray analysis.[24] To our

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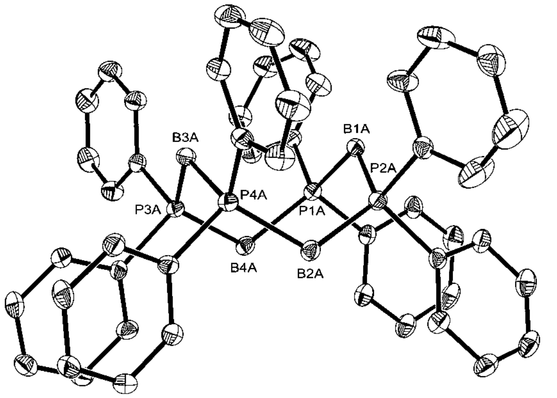

Figure 2. Molecular structure of $[Ph_2P{-}BH_2]_4$ (**2b**). Of the two independent molecules in the asymmetric unit, only one is shown. Selected bond lengths (Å) and angles (deg): P1A−B1A 1.951(5), P2A−B1A 1.942(5), P2A−B2A 1.937(5), P4A−B2A 1.932(5), P4A−B3A 1.940(5), P3A−B3A 1.931(5), P3A−B4A 1.939(5), P1A−B4A 1.945(5); B4A−P1A−B1A 120.6(2), B2A−P2A−B1A 121.6(2), B3A−P3A−B4A 120.2(2), B2A−P4A−B3A 119.6(2), P2A−B1A−P1A 113.3(3), P4A−B2A−P2A 115.8(3), P3A−B3A−P4A 113.7(2), P3A−B4A−P1A 113.8(3). Hydrogen atoms are omitted.

knowledge, NMR data for **2a** have not so far been reported in the literature. To compare spectroscopic data of the new tetramer **2b** with the trimer **2a**, a sample of compound **2a** was prepared from neat $Ph_2PH{\cdot}BH_3$ at 170 °C (15 h, uncatalyzed, see also Table 1, entry 3).

Multinuclear NMR studies of **2a** and **2b** revealed that there are virtually no differences in the ^{31}P and ^{11}B spectra and only subtle but distinctive differences in the ^{1}H and ^{13}C spectra. Mass spectroscopic investigations of **2a** and **2b** were carried out in order to obtain information about the molecular mass (and thus the ring size) of the compounds. In the EI mass spectrum of trimeric **2a** the peak with the highest molecular mass is observed at $m/z = 592$ and corresponds to the $[M - 2H]^+$ ion. The EI mass spectrum for **2b** clearly indicates formation of a tetramer, with the base peak corresponding to the $[M - 4H]^+$ ion ($m/z = 788$).

The eight-membered cyclic structure of **2b** was conclusively proved by an X-ray diffraction study on a single crystal grown from a toluene solution at room temperature (Figure 2). The ring adopts the boat−boat conformation. The P−B single-bond distances range from 1.922(5) to 1.962(5) Å, with an average distance of 1.939(5) Å. The B−P−B and P−B−P bond angles fall in the range 119.5(2)−121.6(2)° (av 120.4(2)°) and 113.3(3)−115.8(3)° (av 114.2(3)°), respectively, and differ slightly from the tetrahedral values.

Only one example of the eight-membered ring family has been previously crystallographically characterized. In 1962, the preliminary low-accuracy X-ray structure of $[Me_2P{-}BH_2]_4$ was reported and revealed a puckered ring with very long P−B distances (2.08(5) Å) and average B−P−B and P−B−P bond angles of 125(1)° and 104(2)°, respectively.[26] The six-membered ring $[Ph_2P{-}BH_2]_3$, **2a**, has a chair conformation in the solid state, a mean P−B bond length of 1.948 Å, and mean bond angles of 114.3° (B−P−B) and 112.6° (P−B−P).[24] For further comparison, the isoelectronic octaphenylcyclotetraphosphazene $[Ph_2PN]_4$ consists of an eight-membered ring in the twist−boat conformation with ring angles of 119.8° at phosphorus and 127.8° at nitrogen.[27]

Catalyst Activities for the Dehydrocoupling of $Ph_2PH{\cdot}BH_3$. To our knowledge, the reactions described above represent the first examples of transition metal-catalyzed formation of phosphorus−boron bonds. We have therefore surveyed and compared a variety of transition metal complexes as catalysts for the dehydrocoupling of $Ph_2PH{\cdot}BH_3$, and the results are recorded in Table 1. The reactions were performed over 14−15 h without solvent, and 0.5−1.5 mol % of the transition metal complex was used.

We found that neat $Ph_2PH{\cdot}BH_3$ is stable at 120 °C (entries 1 and 2) and slowly forms a mixture of **2a**/**2b** (ca. 8:1 ratio) when heated at 170 °C for 15 h (entry 3) in the absence of catalysts.

The most efficient dehydrocoupling catalysts we found were $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ and $[Rh(1,5\text{-}cod)_2][OTf]$, for which full conversion of $Ph_2PH{\cdot}BH_3$ to **1** was observed at 90 °C (entries 5 and 10) and to **2a**/**2b** (ca. 2:1 ratio) at 120 °C (entries 6 and 11). At 60 °C, only 10% of $Ph_2PH{\cdot}BH_3$ was converted to **1** in the presence of $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ (entry 4), but approximately 70% conversion was found for $[Rh(1,5\text{-}cod)_2][OTf]$ (entry 9). If the dehydrocoupling at 120 °C is performed for 4 h instead of 15 h, $Ph_2PH{\cdot}BH_3$ is still completely consumed, but mixtures of **1** and **2a**/**2b** result in both cases (entries 7 and 12). Phosphine ligands at rhodium appear to reduce the catalytic activity, as was found for Wilkinson's catalyst, $[Rh(1,5\text{-}cod)(dmpe)][PF_6]$ and $[Rh(CO)(PPh_3)_3H]$, presumably due to the lower lability of these complexes (entries 13−15). Efficient catalytic activity was also observed with Rh(III) complexes. Thus, 90−100% conversion was found when anhydrous $RhCl_3$, $RhCl_3$ hydrate, or $[\{Cp^*Rh(\mu\text{-}Cl)Cl\}_2]$ was tested at 90 °C (entries 16−18). It is possible, however, that Rh(III) is initially reduced to a low-valent form. Interestingly, the iridium complexes $[\{Ir(\mu\text{-}Cl)(coe)_2\}_2]$ and $[Ir(1,5\text{-}cod)_2][BF_4]$ are less efficient dehydrocoupling catalysts in comparison to the rhodium analogues (entries 19 and 20).

Cp_2TiMe_2, which catalyzes the heterodehydrocoupling of phosphines with silanes,[13b] shows only moderate activity, as does $Ru_3(CO)_{12}$ (entries 21−23). Among the palladium and platinum compounds tested, no catalysis was observed for the d^{10} complexes $[Pd(PPh_3)_4]$ and $[Pt(1,5\text{-}cod)_2]$ (entries 24 and 25), but dehydrocoupling occurs with $PdCl_2$ or $PtCl_2$ as catalysts (entries 26 and 27).

In summary, P−B bond formation via the dehydrocoupling of $Ph_2PH{\cdot}BH_3$ is clearly promoted by certain transition metal complexes, especially $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ or $[Rh(1,5\text{-}cod)_2][OTf]$. Another interesting result is that no evidence for homodehydrocoupling (i.e., P−P or B−B bond formation) was detected for any of the reactions. The mechanism of these reactions is unclear at present. The most likely possibility, however, appears to be a sequence of oxidative addition/reductive elimination and/or σ-bond metathesis reactions involving P−H, B−H, M−P, M−B, and M−H bonds.[28,29]

II. Synthesis and Characterization of Poly(phenylphosphinoborane), $[PhPH{-}BH_2]_n$ (3), and Poly(isobutylphosphinoborane), $[iBuPH{-}BH_2]_n$ (4). An important goal on undertaking this work was the synthesis of high-molecular-weight

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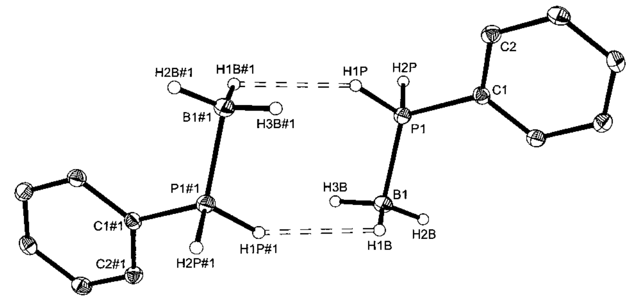


Figure 3. Molecular structure of $PhPH_2{\cdot}BH_3$ and its symmetry-related molecule (symmetry code #1: $1 - x$, $1 - y$, $1 - z$), showing weak intermolecular H···H interactions. Selected bond lengths (Å) and angles (deg): P1−B1 1.924(4), P1−H1P 1.33(4), P1−H2P 1.33(4), B1−H1B 1.12(4), B1−H2B 1.10(4), B1−H3B 1.12(4); H1P−P1−B1 112.9(18), H2P−P1−B1 114.0(16), H1B−B1−P1 106(2), H2B−B1−P1 105(2), H3B−B1−P1 103(2).

phosphinoborane polymers. Encouraged by the rhodium-catalyzed dehydrocoupling of $Ph_2PH{\cdot}BH_3$, and based on our view that the prospective polymer $[Ph_2P{-}BH_2]_n$ might be insoluble and that the anticipated steric congestion at phosphorus could disfavor polymer formation, we moved on to explore the dehydrocoupling of the analogous primary phosphine−borane adduct $PhPH_2{\cdot}BH_3$, as well as the previously unknown alkyl-substituted adduct $i\mathrm{BuPH_2{\cdot}BH_3}$.

Single-Crystal X-ray Structure of $PhPH_2{\cdot}BH_3$. Primary phosphine−borane adducts are an interesting but poorly studied class of organophosphorus compounds. These species tend to be unstable and decompose over time or upon heating. To further investigate the nature of the bonding in this class of compounds, we decided to examine the molecular structure of $PhPH_2{\cdot}BH_3$ in detail and undertook a single-crystal X-ray study on a crystal obtained by sublimation at room temperature. To our knowledge this represents the first X-ray structure of a primary phosphine−borane adduct. A SHELXTL plot is depicted in Figure 3.

The $PhPH_2{\cdot}BH_3$ molecule has a staggered geometry with a P−B bond length of 1.924(4) Å. The hydrogen atoms at phosphorus and boron were located and refined (P1−H1P, 1.33(4) Å; P1−H2P, 1.33(4) Å; B1−H1B, 1.12(4) Å; B1−H2B, 1.10(4) Å; B1−H3B, 1.12(4) Å). The closest intermolecular contacts were found between two molecules which create a centrosymmetric dimer and were determined to be 2.47(6) Å for H1P···H1B ($1 - x$, $1 - y$, $1 - z$) and H1B···H1P ($1 - x$, $1 - y$, $1 - z$) (Figure 3). However, these distances are underestimated due to the systematic error in determining hydrogen positions in X-ray structures. When a value of 1.21 Å is used for B−H bonds (the bond length established by neutron diffraction)[30] and 1.40 Å for P−H bonds (determined by microwave spectroscopy),[31] the H···H distances are found to be 2.375 Å, slightly shorter than the sum of the van der Waals radii for two hydrogen atoms (2.4 Å). This may suggest a weak attractive $\mathrm{P{-}H^{\delta+}\cdots{}^{\delta-}H{-}B}$ interaction as a result of the oppositely charged hydrogen atoms. Furthermore, the P−H···H angle (148(3)°) is more linear and the B−H···H angle (111(3)°) is more bent which is also observed for most compounds comprising an $\mathrm{N{-}H^{\delta+}\cdots{}^{\delta-}H{-}B}$ arrangement.[30]

Due to the packing of the molecules, all other H···H distances are considerably longer than 2.4 Å. Nevertheless, these H···H interactions should be borne in mind when some of the properties of $[PhPH{-}BH_2]_n$ are discussed (vide infra).

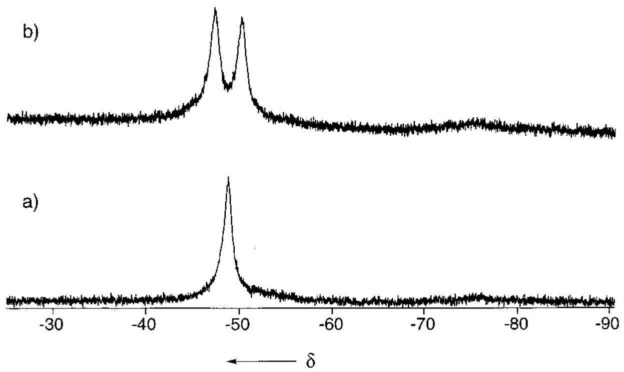
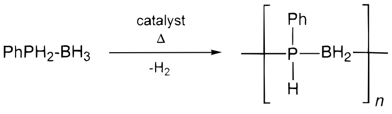


Figure 4. ^{31}P NMR spectrum of $[PhPH{-}BH_2]_n$ (**3**) in $CDCl_3$ (121 MHz): (a) ^1H-decoupled; (b) ^1H-coupled, $J_{PH} = 360$ Hz.

Synthesis and Characterization of Poly(phenylphosphinoborane), $[PhPH{-}BH_2]_n$ (3). Early work on the pyrolysis of $PhPH_2{\cdot}BH_3$ by Korshak et al. in 1963 suggested that low-molecular-weight polymers of possible formula $[PhPH{-}BH_2]_n$ could exist. For instance, heating of $PhPH_2{\cdot}BH_3$ at temperatures between 100 and 150 °C for a period of 13 h was reported to give a benzene-soluble polymer with an average composition unit $PhPH{-}BH_2$, as determined by elemental analysis, and a molecular weight (M_n) of 2150, which was determined ebullioscopically. Longer heating and elevated temperatures (up to 250 °C) led to the formation of insoluble material, without significant molecular weight increase of the benzene-soluble fraction (maximum $M_n = 2630$).[32] We have reinvestigated the dehydrocoupling chemistry of $PhPH_2{\cdot}BH_3$. Strong motivation came from the expectation that the rhodium catalysts would promote P−B coupling in much the same way as for $Ph_2PH{\cdot}BH_3$ but beyond dimers, trimers, or tetramers.

When $PhPH_2{\cdot}BH_3$ is refluxed in toluene overnight in the presence of approximately 0.5 mol % of $[Rh(1,5\text{-}cod)_2][OTf]$, dehydrogenative coupling was indeed observed (eq 3). After precipitation into hexanes an off-white product was isolated and subsequently identified as poly(phenylphosphinoborane) (**3**).



$$\mathrm{PhPH_2{-}BH_3} \xrightarrow[-\mathrm{H_2}]{\text{catalyst}\ \Delta} \left[\overset{\mathrm{Ph}}{\underset{\mathrm{H}}{\mathrm{P}}}{-}\mathrm{BH_2}\right]_n \tag{3}$$

3

The ^{31}P NMR spectrum of **3** in $CDCl_3$ shows a broad signal at δ −48.9 ppm ($\nu_{1/2}$ ca. 135 Hz) which is in close proximity to the $PhPH_2{\cdot}BH_3$ signal (δ −47 ppm). The singlet splits into a doublet with $J_{PH} \approx 360$ Hz in the ^1H-coupled spectrum and is thus characteristic of a single hydrogen substituent at phosphorus (Figure 4). The ^1H NMR spectrum of **3** is also consistent with the assigned structure (Figure 5): it contains broad peaks 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 centered around δ 4.25 ppm for the PH group ($J_{PH} \approx 360$ Hz), somewhat upfield of that in $PhPH_2{\cdot}BH_3$ (δ 5.51 ppm). The ^{11}B NMR spectrum of **3** shows a single broad resonance at δ −34.7 ppm, which is characteristic for a four-coordinate boron center attached to two phosphorus atoms.[33] The ^{13}C NMR resonances for **3** appear in the expected region; however, the ipso-carbon of the phenyl ring could not be detected. In the IR spectrum of **3**, strong absorptions were observed around 2421 and 2381

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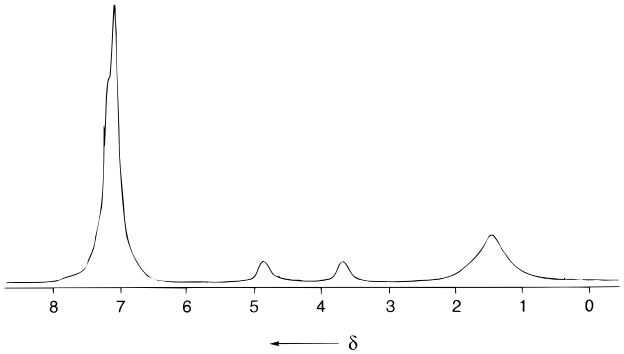


Figure 5. ^{1}H NMR spectrum of $[PhPH{-}BH_2]_n$ (**3**) in $CDCl_3$ (300 MHz).

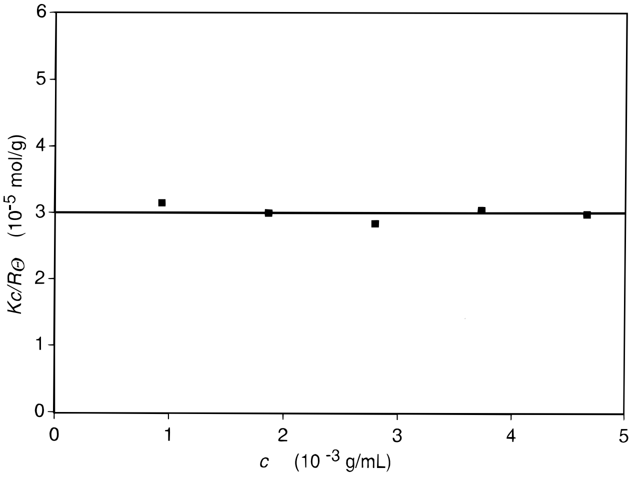


Figure 6. Low-angle laser light scattering plot for high-molecular-weight $[PhPH{-}BH_2]_n$ (**3**) in THF at 22 °C (K = optical constant, c = concentration, R_θ = Rayleigh ratio). The absolute molecular weight M_w is determined as the inverse of the intercept on the y axis (M_w = 33 300).

cm^{-1}, which is the region typical for both the P−H and B−H stretching vibrations; exact assignments could not be made with certainty. An elemental analysis for C and H afforded data consistent with the formula $[PhPH{-}BH_2]_n$.

The molecular weight of **3** was determined by static light scattering (SLS) in THF. However, the absolute weight-average molecular weight (M_w) of **3** prepared by this solution method was found to be relatively low (M_w = 5600), corresponding to a weight-average degree of polymerization (DP_w) of 46.

To obtain higher molecular weights by increasing the extent of reaction, $PhPH_2{\cdot}BH_3$ and a rhodium catalyst were heated in the absence of solvent at slightly more elevated temperatures. 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. The reaction mixture gradually became viscous at 90 °C and was completely solid after 3 h at 130 °C. Vigorous gas evolution (H_2) was observed when the temperature was raised to 130 °C. Dissolution of the product in THF and subsequent precipitation into hexanes gave polymer **3** (ca. 75% yield) which was spectroscopically identical to that prepared in toluene. However, in this case the high-molecular-weight nature of **3** was confirmed by SLS, which afforded an absolute value of M_w = 33 300, corresponding to DP_w = 273 (Figure 6).

To ensure reproducibility, another polymerization of $PhPH_2{\cdot}BH_3$ was performed using the same conditions as described above and the poly(phosphinoborane) **3** subsequently analyzed by SLS. The material thus obtained was found to have a molecular weight of M_w = 31 000 (DP_w = 254), which is a comparable value.

The SLS studies on solutions of polymers **3** in THF also revealed that the second virial coefficient A_2, which is obtained from the slope of the line in Figure 6, equals zero. This indicates that THF is a poor solvent for $[PhPH{-}BH_2]_n$ at 22 °C and that the polymer is on the verge of precipitation (θ conditions). Indeed, our attempts to analyze the molecular weight distribution of samples of **3** by gel permeation chromatography (GPC) using styragel columns and THF as eluent were unsuccessful and reproducible values for M_w and M_n could not be obtained. An explanation for this might be the formation of aggregates and/or adsorption of the polymer chains to the GPC columns which is likely as THF is a θ solvent at 34 °C.

Prior to the SLS studies we also carried out dynamic light scattering (DLS) experiments on THF solutions of **3**. DLS is capable of obtaining the distribution of sizes in a polymer solution and provides a measurement of the hydrodynamic diameter (D_h) of the polymer. A freshly prepared sample of high-molecular-weight **3** (with M_w = 33 300) in THF showed a bimodal size distribution with approximate peak values of $D_h \approx 10$ nm and $D_h \approx 30$ nm. After 24 h, however, the size distribution obtained by DLS revealed only a single broad peak with a hydrodynamic diameter $D_h \approx 10$ nm. The same size distribution was obtained when the polymer solution was remeasured after 3 days. We believe that the two peaks observed in the freshly prepared solutions arise from the presence of single polymer chains ($D_h \approx 10$ nm) and larger aggregates ($D_h \approx 30$ nm). The aggregates may be partially held together by interactions between the polymer chains, possibly of the type $P{-}H^{\delta+}{\cdots}{}^{\delta-}H{-}B$, as was observed to some extent in the X-ray structure of $PhPH_2{\cdot}BH_3$ (vide supra). However, these aggregates break up over a period of 24 h and produce mainly single polymer chains. At that point the SLS measurement was performed on the polymer solution, and this afforded high-quality data at five different concentrations (Figure 6).

Similar behavior as a function of time was noted by DLS for other samples of **3**. Furthermore, a small D_h value (ca. 1 nm) was measured for the sample of polymer **3** prepared by catalytic dehydrocoupling in solution which is consistent with the relatively low-molecular-weight subsequently determined by SLS (M_w = 5600).

Poly(phenylphosphinoborane) (**3**) is air- and moisture-stable in the solid state. It is soluble in THF and chlorinated hydrocarbons, moderately soluble in toluene and benzene, and insoluble in aliphatic hydrocarbons such as hexanes or in hydrophilic solvents such as methanol or water. Prolonged storage of polymer **3** in THF solution in air results in slow decomposition, which is indicated by a number of additional resonances in the ^{31}P and ^{1}H NMR spectra. This process may involve peroxide-mediated oxidation of the P−H or B−H groups.

When the reaction mixture for the preparation of high-molecular-weight **3** was heated for 5 h rather than 3 h at 130 °C, the final product was insoluble in CH_2Cl_2 or THF, but it swelled significantly in these solvents to form a colorless gel. However, the ^{31}P and ^{1}H NMR spectra of this material (immersed and swollen in $CDCl_3$) were similar to those obtained for $CDCl_3$-soluble polymer **3**. As branching positions could not be detected in the ^{31}P and ^{11}B NMR spectra, we assume that polymer **3** either becomes weakly cross-linked (through additional interchain P−B coupling) or increases in molecular weight above the solubility limit when heated for prolonged

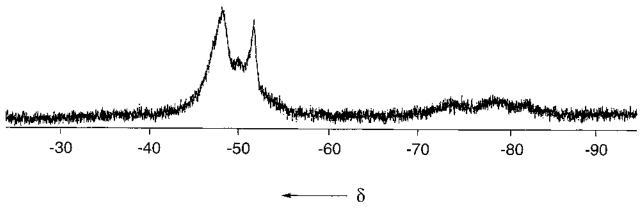


Figure 7. $^{31}P\{^1H\}$ NMR spectrum (in $CDCl_3$) of the material obtained from the uncatalyzed thermolysis of $PhPH_2{\cdot}BH_3$ (121 MHz).

periods above 130 °C in the presence of catalyst. If the material is indeed cross-linked, it is not surprising that branching points could not be detected; even in the case of the low-molecular-weight sample of **3** ($M_w = 5600$) we were unable to observe Ph_2PH- or BH_3- end groups in the NMR spectra.

A final result of interest regarding the dehydrogenative coupling of $PhPH_2{\cdot}BH_3$ concerns the catalytic performances of the different rhodium complexes. We found that catalytic amounts of [{Rh(μ-Cl)(1,5-cod)}$_2$], anhydrous $RhCl_3$, or even $RhCl_3$ hydrate (ca. 1 mol % rhodium, 3 h at 90 °C and 3 h at 130 °C) gave high polymeric **3** of comparable molecular weight, which was confirmed by DLS experiments in THF ($D_h \approx 10$ nm, after 2 days). Under the same polymerization conditions, the Rh(I) salt [Rh(1,5-cod)$_2$][OTf] gave a polymer **3** for which a significantly smaller hydrodynamic diameter ($D_h \approx 5$ nm, after 1 day) was found. This suggests that the molecular weight is significantly lower in this case and, although an absolute value for M_w was not determined, a value of M_w between 10000 and 20 000 is suggested by the DLS data.

Investigation of the Uncatalyzed Dehydrocoupling of $PhPH_2{\cdot}BH_3$. To confirm the catalytic effect of the added rhodium complexes, neat $PhPH_2{\cdot}BH_3$ was reacted under the conditions for the synthesis of high-molecular-weight **3** (3 h at 90 °C and 3 h at 130 °C) but without added catalyst. A colorless semisolid was thus obtained which was then dissolved in THF and precipitated into hexanes. Finally, a colorless solid was isolated in 27% yield. The ^{31}P NMR spectrum of the product from the uncatalyzed thermolysis of $PhPH_2{\cdot}BH_3$ is shown in Figure 7. A comparison of this spectrum with that recorded for **3** (Figure 4) indicated that the two materials possessed different structures.

The $^{31}P\{^1H\}$ NMR spectrum in Figure 7 shows the signal of polymer **3** (ca. δ −49 ppm), but another main peak around δ −52 ppm is also present. In the ^1H NMR spectrum a number of poorly resolved signals are found in the PH region, in contrast to the distinct, well-defined doublet at δ 4.25 ppm for **3** (Figure 5). This suggests the presence of low-molecular-weight oligomers (and perhaps cyclics or branched species) in the uncatalyzed thermolysis of $PhPH_2{\cdot}BH_3$. Also, hydrodynamic diameters obtained by DLS measurements in THF solution clearly revealed the low-molecular-weight nature of the material ($D_h \approx 1$ nm), consistent with the previous work by Korshak and co-workers, where molecular weights M_n of ca. 2000 were reported.[32]

Synthesis and Characterization of Poly(isobutylphosphinoborane), [iBuPH−BH$_2$]$_n$ (4). To study the reactivity and the polymerization behavior of primary phosphine−borane adducts containing an alkyl group at phosphorus, we investigated the dehydrocoupling of iBuPH$_2{\cdot}$BH$_3$, which we prepared in quantitative yield from the free phosphine and $Me_2S{\cdot}BH_3$ in THF solution. The resulting colorless liquid was fully characterized by multinuclear NMR and mass spectrometry.

Dehydropolymerization of neat iBuPH$_2{\cdot}$BH$_3$ using [{Rh(μ-Cl)(1,5-cod)}$_2$] as the catalyst produced [iBuPH−BH$_2$]$_n$ (**4**) (eq 4). However, the reaction time was much longer (13 h at 120 °C) compared to the case for the aryl-substituted polymer **3**. Polymer **4** was isolated as a tacky solid after precipitation into a mixture of 2-propanol/water (1:1) from THF.

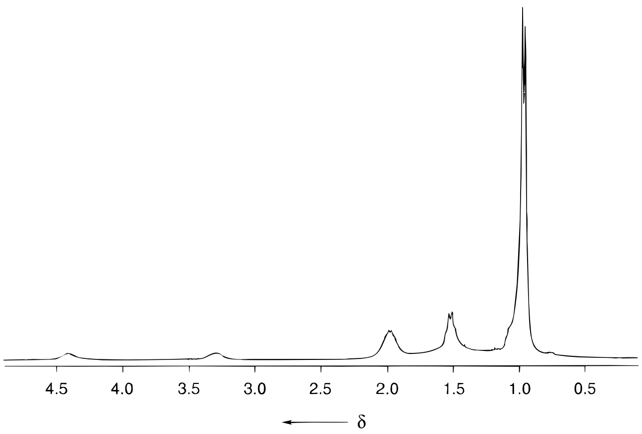
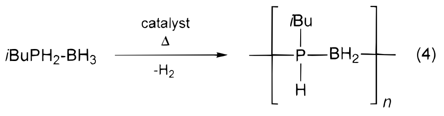


Figure 8. ^1H NMR spectrum of [iBuPH−BH$_2$]$_n$ (**4**) in $CDCl_3$ (300 MHz).



$$i\text{BuPH}_2\text{-BH}_3 \xrightarrow[\text{-H}_2]{\text{catalyst}\;\Delta} \left[\begin{array}{c} i\text{Bu} \\ | \\ -\text{P}-\text{BH}_2- \\ | \\ \text{H} \end{array}\right]_n \qquad (4)$$

4

The $^{31}P\{^1H\}$ NMR spectrum of **4** showed a very broad signal around δ −69 ppm ($\nu_{1/2}$ ca. 300 Hz), in contrast to the relatively sharp δ −48.9 ppm resonance ($\nu_{1/2}$ ca. 135 Hz) obtained for [PhPH−BH$_2$]$_n$ (**3**). It is shifted upfield with respect to the monomer (δ −59.6 ppm). Due to the broadness of the ^{31}P NMR signal, no clear splitting was observed when the proton-coupled spectrum was recorded. The ^1H NMR spectrum of **4** (Figure 8), on the other hand, was very well resolved and showed a broad doublet at δ 3.86 ppm ($J_{HP} = 335$ Hz) for the PH proton, which is also shifted upfield compared to the singlet at δ 4.46 ppm for the initial adduct. The BH_2 signal appears just above the baseline and overlaps with the range of the CH, CH_2, and CH_3 resonances of the isobutyl group. The ^{11}B NMR signal of **4** is a single broad peak around δ −36 ppm. The signals in the ^{13}C NMR spectrum appear at δ 30.2 (CH, $J_{CP} = 29$ Hz), 25.6 (CH_3), and 23.7 (CH_2) ppm.

In the IR spectrum of **4**, a broad, unresolved absorption around 2421 cm^{-1} presumably arises from overlapping ν(P−H) and ν(B−H) bands. Poly(isobutylphosphinoborane) (**4**) is stable to both oxygen and moisture and is soluble in THF, chlorinated solvents, toluene, and even hexanes but is insoluble in water and methanol.

Conclusive evidence for the polymeric character of **4** was obtained from DLS experiments in THF solution. As in the case of **3**, a bimodal size distribution was observed for a freshly prepared sample of **4** in THF (D_h values ca. 7 and 25 nm). After 2 days the distribution became monomodal (peak value of $D_h \approx 7$ nm). This behavior is qualitatively similar to that for poly(phenylphosphinoborane) **3** and suggests the presence of larger aggregates in freshly prepared solutions of **4** which break up over time. However, the hydrodynamic diameters of polymer **4** are slightly smaller than those measured for high polymeric **3**. Making the approximation that polymers **3** and **4** exhibit similar hydrodynamic behavior in THF, the DLS data for **4** suggest a molecular weight of 10 000−20 000.

As was found for polymer **3**, prolonged heating of iBuPH$_2{\cdot}$BH$_3$ (72 h at 90 °C and 6 h at 130 °C) also afforded an insoluble polymer **4** which was found to swell significantly upon addition of THF or CH_2Cl_2. NMR spectra of a $CDCl_3$-swollen polymer sample were similar to those of soluble polymer **4**. Light P−B cross-linking or a higher molecular weight above the solubility limit are possible explanations for the swelling behavior of these materials.

Investigation of the Uncatalyzed Dehydrocoupling of *i*BuPH$_2$·BH$_3$. A control experiment without catalyst was run using neat *i*BuPH$_2$·BH$_3$ adduct and the same time−temperature profile as for the synthesis of polymer **4**. Numerous signals in the ^{31}P NMR spectrum of the colorless viscous product were present in the range of δ −60 to −96 ppm which indicated formation of different phosphinoborane species. Accordingly, the ^{1}H NMR spectrum displays several peaks in the PH region as well as in the isobutyl region. The ^{11}B NMR spectrum contains two broad, overlapping resonances as the main signals. However, DLS studies in THF showed that the products possess a very low molecular weight ($D_h < 1$ nm). It appears likely that the product has a branched, oligomeric structure similar to that formed in the case of PhPH$_2$·BH$_3$.

In comparison to the dehydrocoupling of PhPH$_2$·BH$_3$, more drastic reaction conditions are necessary to polymerize *i*BuPH$_2$·BH$_3$. For example, if *i*BuPH$_2$·BH$_3$ is reacted for 3 h at 90 °C/3 h at 130 °C in the presence of [{Rh(μ-Cl)(1,5-cod)}$_2$], the conditions used to generate high-molecular-weight **3**, unreacted monomer is still present. The dehydrocoupling of *i*BuPH$_2$·BH$_3$ is even more sluggish in the absence of rhodium catalyst.

Summary

Novel and facile transition metal-catalyzed P−B bond formation reactions have been discovered and the first well-characterized, high-molecular-weight poly(phosphinoboranes) **3** and **4** have been isolated as air- and moisture-stable solids. Future work will focus on detailed studies of the physical properties of poly(phosphinoboranes), which can be regarded as analogues of poly(α-olefins) with a phosphorus−boron backbone. This should be very revealing from a fundamental perspective, and useful properties such as flame retardancy and oxidative stability may emerge. Substantial differences in physical properties would be anticipated as the skeletal P−B bonds (typically > 1.92 Å) are much longer than C−C single bonds (1.54 Å). Opportunities also exist for the facile structural modification of poly(phosphinoboranes) such as **3** and **4** and analogues via exploitation of the P−H functionality using hydrophosphination chemistry or deprotonation/electrophilic addition reaction sequences.[34] The dehydrocoupling mechanism is also of considerable interest; the catalytic chemistry may involve M−P and/or M−B bonds, and studies in this area are in progress.[28,29,35a] The extension of the synthetic methodology to other skeletons based on alternating atomic sequences of Group 13 and Group 15 elements may also be possible by analogous chemistry, and such materials would be of potential interest as precursors to III/V semiconductor materials.[35b]

Experimental Section

General Procedures and Materials. All reactions were performed under an atmosphere of dinitrogen using dry solvents. Workup of all phosphinoborane compounds was carried out in air. Ph$_2$PH, PhPH$_2$, [Rh(1,5-cod)$_2$][OTf] (1,5-cod = 1,5-cyclooctadiene), [Rh(1,5-cod)(dmpe)][PF$_6$] (dmpe = 1,2-bis(dimethylphosphino)ethane), [Rh(CO)(PPh$_3$)$_3$H], [Ir(1,5-cod)$_2$][BF$_4$], Ru$_3$(CO)$_{12}$, [Pd(PPh$_3$)$_4$], PdCl$_2$, PtCl$_2$ (Strem Chemicals), RhCl$_3$, RhCl$_3$ hydrate (Pressure Chemical Co.), and [Rh(PPh$_3$)$_3$Cl], Me$_2$S·BH$_3$ (Aldrich) were purchased and used as received. *i*BuPH$_2$ was obtained from Cytec Canada Inc. PhPH$_2$·BH$_3$,[36] [{Rh(μ-Cl)(1,5-cod)}$_2$],[37] [{Cp*Rh(μ-Cl)Cl}$_2$],[38] [{Ir(μ-Cl)(coe)$_2$}$_2$] (coe = cyclooctene),[39] Cp$_2$TiMe$_2$,[40] and [Pt(1,5-cod)$_2$][41] were prepared following literature procedures. Ph$_2$PH·BH$_3$ was prepared using a procedure analogous to that used for PhPH$_2$·BH$_3$.[36]

Equipment. NMR spectra were recorded on a Varian Gemini 300 MHz or Unity 400/500 MHz spectrometer. Chemical shifts are referenced to solvent peaks or internal TMS (^{1}H, ^{13}C), or external BF$_3$·Et$_2$O (^{11}B) or H$_3$PO$_4$ (^{31}P). Mass spectra were obtained with a VG 70-250S mass spectrometer operating in electron impact (EI) mode. Infrared spectra were taken on a Nicolet Magna 550 FT-IR instrument as Nujol mulls between KBr plates. Elemental analyses were performed by Quantitative Technologies, Inc., Whitehouse, NJ. Absolute molecular weights of polymer **3** in THF were determined by static light scattering (SLS) performed on a Chromatix KMX-6 instrument at a wavelength of 632.8 nm and a scattering angle of 6−7°. Measurements were carried out at 22 °C using a metal cell 4.93 mm in length. Each solution was filtered three times through a MILEX filter with an average pore size of 0.2 μm before injection into the cell. The refractive index increment, d*n*/d*c*, of the solutions of polymer **3** in THF was obtained by using a Chromatix KMX-16 differential refractometer operating at a wavelength of 632.8 nm and determined to be 0.24 mL/g. The instrument was calibrated with NaCl solutions. Dynamic light scattering (DLS) experiments were carried out on a wide-angle laser light scattering photometer from Brookhaven Instruments Corp. A Lexel Excel 3000 argon ion laser with a wavelength of 514.5 nm was used as the light source. The concentration of the solutions was ca. 7 mg/mL, using commercially available THF (ACS grade) as solvent. The solutions were filtered through disposable 0.2 μm filters from Millipore into glass scattering cells with a diameter of 12.3 mm. The cells were placed into the BI-200SM goniometer and set in a vat of thermostated toluene which matched the index of refraction of the glass cells. All samples were measured at a scattering angle of 90°. The scattered light was detected by a photomultiplier interfaced to the BI-2030AT digital correlator with 136 channels and the correlation function measured in real time. The instrument was controlled by a 486AT computer, and the data were analyzed by using software supplied by Brookhaven.

Static Light Scattering. Static light scattering (SLS) experiments in the low-angle regime were used to determine the weight-average molecular weight, M_w. The M_w was obtained from the Rayleigh−Debye relationship in the limit of low scattering angle,

$$Kc/R_\theta = 1/M_w + 2A_2c$$

where c is the concentration of the polymer, R_θ is the measured Rayleigh ratio, A_2 is the second virial coefficient, and K is an optical constant defined as

$$K = [4\pi^2 n^2/N_0\lambda_0^{\,4}](\mathrm{d}n/\mathrm{d}c)^2$$

where n is the refractive index of the solvent, λ_0 is the wavelength of the laser light in a vacuum, N_0 is Avogadro's number, and d*n*/d*c* is the refractive index increment of the polymer in THF. Refractive index increment measurements were carried out at five different concentrations in THF at 22 °C.

Dynamic Light Scattering. In dynamic light scattering (DLS) the experimentally determined intensity autocorrelation function $G^{(2)}(\tau)$ is related to the autocorrelation function representative of the motions of

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Table 2. Crystallographic Data and Structure Refinement

	1	**2b**	$PhPH_2{\cdot}BH_3$
formula	$C_{24}H_{26}B_2P_2$	$C_{48}H_{48}B_4P_4$	$C_6H_{10}BP$
formula weight	398.01	791.98	123.92
temperature, K	150.0(1)	150.0(1)	100.0(1)
crystal system	orthorhombic	triclinic	monoclinic
space group	*P*2(1)2(1)2(1)	$P\bar{1}$	*P*2(1)/*c*
a, Å	10.247(2)	12.4731(8)	5.7037(2)
b, Å	13.616(3)	17.7114(11)	7.4676(4)
c, Å	15.684(3)	21.70110(10)	16.9791(6)
α, deg	90	87.409(3)	90
β, deg	90	73.293(3)	97.455(3)
γ, deg	90	69.386(2)	90
volume, $Å^3$	2188.3(7)	4289.4(4)	717.08(5)
Z	4	4	4
density, g cm^{-3}	1.208	1.226	1.148
absorp coeff, mm^{-1}	0.206	0.210	0.274
F(000)	840	1664	264
crystal size, mm	0.28 × 0.17 × 0.12	0.17 × 0.13 × 0.08	0.30 × 0.30 × 0.30
θ range, deg	4.18−26.36	4.09−25.03	4.54−26.33
index ranges	$-12 \le h \le 12$, $-17 \le k \le 16$, $-19 \le l \le 19$	$0 \le h \le 14$, $-19 \le k \le 21$, $-24 \le l \le 25$	$0 \le h \le 7$, $0 \le k \le 9$, $-21 \le l \le 20$
reflns collected	16 513	33 054	6287
independ reflns	4455 ($R_{int} = 0.061$)	14 871 ($R_{int} = 0.121$)	1440 ($R_{int} = 0.059$)
GoF on F^2	1.059	0.926	1.211
$R1^a$ ($I > 2\sigma(I)$)	0.0342	0.0604	0.0564
$wR2^b$ (all data)	0.0820	0.1556	0.1447
peak/hole, e $Å^{-3}$	0.283/−0.200	0.293/−0.325	0.486/−0.298

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

the particles $G^{(1)}(\tau)$,

$$G^{(2)}(\tau) = I_\theta^{\,2}\left[1 + \left|\frac{G^{(1)}(\tau)}{G^{(1)}(0)}\right|^2\right] = I_\theta^{\,2}[1 + e^{-2Dq^2\tau}]$$

where the normalized intensity autocorrelation function which is determined experimentally can be expressed as an exponential with a decay of Γ,

$$g^{(1)}(\tau) = G^{(1)}(\tau)/G^{(1)}(0) = A\ \mathrm{e}^{-\Gamma\tau}$$

Real systems can rarely be described by a single decay, and therefore CONTIN, a program supplied by Brookhaven, was used deconvolute the autocorrelation function and determine the decay from which the effective diffusion coefficient, D_z, can be calculated:

$$\Gamma_1/q^2 = D_z$$

where q is the magnitude of the scattering vector, $q = (4\pi n/\lambda_0)\sin(\Theta/2)$.

From the diffusion coefficient the effective hydrodynamic diameter, D_H, can be determined from the Stokes−Einstein relation,

$$D_H = kT/3\pi\eta D_z$$

where η is the solvent viscosity.

X-ray Structural Characterization. Crystal data and details of the data collection are provided in Table 2. Diffraction data were collected on a Nonius Kappa-CCD using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). A combination of 1° ϕ and ω (with κ offsets) scans were used collect sufficient data. The data frames were integrated and scaled using the Denzo-SMN package.[42] The structures were solved and refined with the SHELXTL-PC V5.1 software package.[43] Refinement was by full-matrix least squares on F^2 using all data (negative intensities included). Molecular structures are presented with ellipsoids at a 30% probability level. In all structures hydrogens bonded to carbon atoms were included in calculated positions and treated as riding atoms. Hydrogens attached to B1 and P2 in compound **1** as well as B1 and P1 in $PhPH_2{\cdot}BH_3$ were refined with isotropic thermal parameters, while in **2b** the positions of the hydrogens bonded to boron atoms were refined with thermal parameters tied to the parent boron atoms. Crystallographic data were deposited in the Cambridge Crystallographic Data Centre with codes CCDC-114009 (**1**), CCDC-140990 (**2b**), and CCDC-140991 ($PhPH_2{\cdot}BH_3$).

$Ph_2PH{-}BH_2{-}PPh_2{-}BH_3$ (1). Neat $Ph_2PH{\cdot}BH_3$ (0.63 g, 3.12 mmol) and [Rh(1,5-cod)$_2$][OTf] (ca. 4 mg, 0.3 mol %) were stirred at 90 °C for 15 h. The reaction mixture became liquid upon heating and solidified when cooled to room temperature. Recrystallization from diethyl ether (10 mL) gave colorless crystals of **1** which were also suitable for single-crystal X-ray analysis. Yield: 0.53 g (85%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.68{-}7.17$ (m, aromatic), 6.71 (dm, $J_{HP} = 397$ Hz, PH), 3.1−1.5 (br, BH_2), 1.6−0.4 (br q, BH_3). $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$): $\delta = -33.2$ (br, BH_2), −37.3 (br, BH_3). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = -3.3$ (br, Ph_2PH), −17.7 (br, Ph_2P). ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = -3.3$ (br d, $J_{PH} = 397$ Hz, Ph_2PH), −17.7 (br, Ph_2P). MS (EI, 70 eV): *m*/*z* (relative intensity) 395 (16) [$M^+ - 3H$], 384 (100) [$M^+ - BH_3$].

Dehydrocoupling of $Ph_2PH{\cdot}BH_3$. Neat $Ph_2PH{\cdot}BH_3$ (0.27 g, 1.35 mmol) and [{Rh(μ-Cl)(1,5-cod)}$_2$] (4 mg, ca. 1 mol % rhodium) were heated at 120 °C for 15 h, and the resulting solid material was analyzed without further purification or removal of the catalyst. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.51$ (m, aromatic), 7.34 (m, aromatic), 7.23 (m, aromatic), 7.14 (m, aromatic), 7.03 (m, aromatic), 6.90 (m, aromatic), 3.4−1.2 (br, BH_2). $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$): $\delta = -33.8$ (br). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 132.7$, 132.6, 129.3, 128.5, 127.9, 127.4. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = -18.2$ (br). MS (EI, 70 eV): *m*/*z* (relative intensity) 788 (30) [$M_4^+ - 4H$], 592 (16) [$M_3^+ - 2H$], 409 (100) [$M_3^+ - PPh_2$].

Characterization of $[Ph_2P{-}BH_2]_3$ (2a). Compound **2a** was prepared by a procedure similar to the reported procedure: neat $Ph_2PH{\cdot}BH_3$ (0.48 g, 2.40 mmol) was heated at 170 °C overnight (15 h) to give a colorless solid. Diethyl ether (10 mL) was then added and the suspension filtered. Crystals of pure **2a** were grown from the filtrate at room temperature. Yield: 0.38 g (80%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.51$ (m, aromatic), 7.23 (m, aromatic), 7.14 (m, aromatic), 2.8−1.2 (br, BH_2). $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$): $\delta = -32.9$ (br, $\nu_{1/2}$ ca. 230 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 132.7$ (C_{ortho}), 129.3 (C_{para}), 127.9 (C_{meta}), C_{ipso} not observed. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = -17.9$ (br, $\nu_{1/2}$ ca. 220 Hz). MS (EI, 70 eV): *m*/*z* (relative intensity) 409 (100) [$M^+ - PPh_2$], 592 (15) [$M^+ - 2H$].

$[Ph_2P{-}BH_2]_4$ (2b). To a mixture of **2a**/**2b** was added ca. 10 mL of diethyl ether, and the mixture was stirred for 1 h until all of the material was dissolved or finely suspended in the solution. The suspension was filtered and colorless compound **2b** collected and dried under vacuum. Yield: ca. 20%. Single crystals for X-ray analysis were obtained from a toluene solution at room temperature over a period of several days. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.34$ (m, aromatic), 7.03 (m, aromatic), 6.90 (m, aromatic), 3.4−1.3 (br, BH_2). $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$): $\delta = -31.2$ (br, $\nu_{1/2}$ ca. 290 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 132.6$ (C_{ortho}), 128.5 (C_{para}), 127.4 (C_{meta}), C_{ipso} not observed. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = -19.1$ (br, $\nu_{1/2}$ ca. 170 Hz). MS (EI, 70 eV): *m*/*z* (relative intensity) 788 (100) [$M^+ - 4H$].

Synthesis of Low-Molecular-Weight $[PhPH{-}BH_2]_n$ (3). $PhPH_2{\cdot}BH_3$ (1.03 g, 8.31 mmol) and [Rh(1,5-cod)$_2$][OTf] (ca. 10 mg, 0.3 mol %) were dissolved in toluene (15 mL), and the resulting solution was refluxed for 15 h. The reaction mixture was then concentrated under vacuum to ca. 5 mL, filtered, and precipitated into 120 mL of hexanes. The off-white polymeric product **3** was washed with hexanes, decanted, and dried in vacuo. Yield: 0.68 g (67%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.90{-}6.65$ (br, aromatic), 4.25 (br d, $J_{HP} = 360$ Hz, PH), 2.20−0.65 (br, BH_2). $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$): $\delta = -34.7$ (br, $\nu_{1/2}$ ca. 800 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 132.5$ (C_{ortho}), 129.3 (C_{para}), 128.2 (C_{meta}), C_{ipso} not observed. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = -48.9$ (br, $\nu_{1/2}$ ca. 135 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = -48.9$ (br d, $J_{PH} = 360$ Hz). IR (Nujol):

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ν(B−H) and ν(P−H) = 2421 (vs) and 2381 (vs) cm^{-1}. Anal. Calcd for C_6H_8BP: C, 59.1; H, 6.6. Found: C, 58.9; H, 6.5. Static light scattering (THF): $M_w = 5600$, DP$_w = 46$, $A_2 = 0$.

Synthesis of High-Molecular-Weight [PhPH−BH$_2$]$_n$ (3). Neat $PhPH_2{\cdot}BH_3$ (4.10 g, 33.1 mmol) and [{Rh(μ-Cl)(1,5-cod)}$_2$] (ca. 50 mg, 0.6 mol % rhodium) were stirred for 3 h at 90 °C and then for 3 h at 130 °C. When the temperature reached 130 °C, vigorous gas elimination was observed, and after 3 h the contents of the flask were completely solid. After cooling to room temperature, the dark yellow material was dissolved in THF (40 mL), filtered, and precipitated into hexanes (700 mL). The off-white polymeric product was washed with hexanes, decanted, and dried under vacuum at 50 °C for 48 h. Yield: 3.03 g (75%).

The ^{1}H, ^{11}B, ^{13}C, and ^{31}P NMR and IR spectra are as described above. Static light scattering (THF): $M_w = 33\,300$, DP$_w = 273$, $A_2 = 0$.

A second polymerizaton was conducted following the same procedure: 1.22 g of $PhPH_2{\cdot}BH_3$. (9.84 mmol) and ca. 15 mg of [{Rh(μ-Cl)(1,5-cod)}$_2$] (0.6 mol % rhodium) gave polymer **3** in 75% yield (0.90 g). Static light scattering (THF): $M_w = 31\,000$, DP$_w = 254$, $A_2 = 0$.

Synthesis of Cross-Linked [PhPH−BH$_2$]$_n$ (3). Heating of neat $PhPH_2{\cdot}BH_3$ (0.53 g, 4.28 mmol) and [{Rh(μ-Cl)(1,5-cod)}$_2$] (ca. 11 mg, 1.0 mol % rhodium) for 3 h at 90 °C and then for 5 h at 130 °C resulted in an insoluble material. However, the solid was found to swell in THF and chlorinated solvents. ^{1}H, ^{11}B, and ^{31}P NMR spectra of the $CDCl_3$-swollen gel were identical with those of the $CDCl_3$-soluble polymer **3**.

Uncatalyzed Dehydrocoupling of PhPH$_2$·BH$_3$. Neat $PhPH_2{\cdot}BH_3$ (0.49 g, 3.95 mmol) was stirred for 3 h at 90 °C and then for 3 h at 130 °C. The resulting semisolid was dissolved in THF (3 mL), precipitated into hexanes (100 mL), filtered, and dried under vacuum overnight at 50 °C to give a colorless powder. Yield: 0.13 g (27%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90−6.40 (br, Ph), 6.20−3.30 (many broad signals, PH), 2.30−0.65 (br, BH_2). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$): δ = −34.0 (br). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ = −48.3 (br), −50.0 (br), −51.8 (br).

Synthesis of *i*BuPH$_2$·BH$_3$. To a solution of *i*BuPH$_2$ (4.59 g, 50.9 mmol) in THF (40 mL) was added dropwise $Me_2S{\cdot}BH_3$ (5.1 mL, 1.05 equiv) at −25 °C. After stirring of the solution at room temperature for 15 h, all volatiles were removed under vacuum, and spectroscopically pure *i*BuPH$_2$·BH$_3$ was obtained in quantitative yield as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.46 (dm, J_{HP} = 362 Hz), 1.93 (m, CH), 1.71 (m, CH_2), 0.99 (d, J_{HH} = 6.7 Hz, CH_3), 1.1 to −0.1 (br q, BH_3). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$): δ = −42.3 (br d, J_{BP} = 37 Hz). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 26.1 (d, J_{CP} = 5.4 Hz, CH), 25.5 (d, J_{CP} = 34.3 Hz, CH_2), 23.0 (d, J_{CP} = 8.0 Hz, CH_3). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = −59.6 (m, J_{PB} = 37 Hz). MS (EI, 70 eV): *m*/*z* (relative intensity) 90 (46) [$M^+ - BH_3$], 41 (100) [C_3H_5].

Synthesis of [*i*BuPH−BH$_2$]$_n$ (4). Neat *i*BuPH$_2$·BH$_3$ (0.45 g, 4.33 mmol) and [{Rh(μ-Cl)(1,5-cod)}$_2$] (ca. 11 mg, 1.0 mol % rhodium) were stirred for 13 h at 120 °C. After cooling to room temperature, the sticky product was dissolved in THF (3 mL) and precipitated into 2-propanol/water (40 mL/40 mL). The solution was decanted and the product redissolved in CH_2Cl_2 (3 mL). Removal of the volatiles under vacuum (50 °C/24 h) left a light yellow sticky solid. Yield: 0.35 g (80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.86 (br d, J_{HP} = 335 Hz, PH), 1.98 (m, CH), 1.51 (m, CH_2), 0.95 (d, J_{HH} = 5.5 Hz, CH_3), 2.0−0.8 (br, BH_2). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$): δ = −36.3 (br, $\nu_{1/2}$ ca. 630 Hz).l ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 30.2 (d, J_{CP} = 29 Hz, CH), 25.6 (CH_3), 23.7 (CH_2). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = −69.2 (br, $\nu_{1/2}$ ca. 300 Hz). IR (Nujol): ν(B−H) and ν(P−H) = 2421 (vs) cm^{-1}. Anal. Calcd for $C_4H_{12}BP$: C, 47.1; H, 11.9. Found: C, 46.9; H, 11.3.

Synthesis of Cross-Linked [*i*BuPH−BH$_2$]$_n$ (4). Neat *i*BuPH$_2$·BH$_3$ (0.44 g, 4.23 mmol) and [{Rh(μ-Cl)(1,5-cod)}$_2$] (ca. 10 mg, 1.0 mol % rhodium) were stirred for 72 h at 90 °C and then for 6 h at 130 °C. The product was found to be insoluble in common organic solvents. Subsequent ^{1}H, ^{11}B, and ^{31}P NMR spectroscopic analyses of the product as a $CDCl_3$-swollen gel afforded data similar to those for $CDCl_3$-soluble polymer **4**.

Uncatalyzed Dehydrocoupling of *i*BuPH$_2$·BH$_3$. Heating of neat *i*BuPH$_2$·BH$_3$ (0.41 g, 3.94 mmol) for 13 h at 120 °C resulted in a colorless, viscous oil which was analyzed without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.7−3.3 (many signals, PH and PH_2), 2.0−1.7 (br, CH), 1.5−1.2 (br, CH_2), 1.1−0.9 (br, CH_3), 2.0−0.1 (br, BH_2 and BH_3). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$): δ = −31.6 (br), −34.5 (br), −42.3 (m, *i*BuPH$_2$·BH$_3$). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = −59.6 (m, *i*BuPH$_2$·BH$_3$), −61.2 (br), −62.7 (br), −65.2 (br), −69.5 (br), −87.2 (br), −95.7 (br).

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Supporting Information Available: ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of the phenyl region of **2a** and **2b**, a low-angle laser light scattering plot for low-molecular-weight [PhPH−BH$_2$]$_n$ (**3**) in THF (M_w = 5600), and a ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of the material obtained from the uncatalyzed thermolysis of $PhPH_2{\cdot}BH_3$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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