matrix least squares with SHELXL-97.[14] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 125050 and CCDC 125051. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambrige CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Rhodium-Catalyzed Formation of Phosphorus–Boron Bonds: Synthesis of the First High Molecular Weight Poly(phosphinoborane)**

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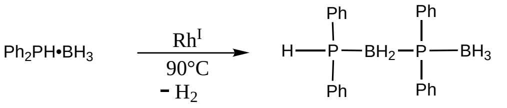
Virtually all currently known and commercially available polymers are based on extended catenated structures containing mainly carbon atoms together with a few other elements such as oxygen and nitrogen. In contrast, the development of extended structures based on atoms of other elements has been much less successful, and their synthesis still represents a substantial challenge.[1, 2] Nevertheless, the relatively few inorganic polymers such as poly(siloxanes) (silicones) $[R_2Si{-}O]_n$, polyphosphazenes $[R_2P{=}N]_n$, polysilanes $[R_2Si]_n$, and more recently poly(silynes), poly(stannanes), sulfur-containing polymers, poly(metallocenes), and other metallopolymers illustrate the potential for accessing materials with fascinating and unexpected properties as well as significant applications.[1–5] As part of a continuing program to develop novel extended chain structures based on main group elements we have explored compounds with skeletons comprising four-coordinate phosphorus and boron atoms. We were encouraged by previous reports that known cyclic compounds such as the six-membered ring $[Me_2P{-}BH_2]_3$ show considerable thermal and hydrolytic stability.[6]

Thermally induced dehydrocoupling of phosphane–borane adducts $R_2PH \cdot BH_3$ at elevated temperatures (150–200 °C) has been previously used to prepare cyclic phosphinoborane species (mainly six-membered rings of the type $[R_2P{-}BH_2]_3$).[6] In addition, in a few cases low yields of "polymeric" materials have been claimed, but none have been convincingly structurally characterized (by present day standards) and, where reported, the molecular weights were very low.[7, 8] We have reinvestigated this "dehydrocoupling chemistry" (coupling with elimination of hydrogen) with the idea that if lower temperatures could be used and more efficient coupling reactions identified, then linear, high polymeric structures might indeed result.[9, 10]

The phosphane–borane adduct $Ph_2PH \cdot BH_3$ undergoes dehydrocoupling at 180–190 °C to exclusively and quantitatively yield the cyclic trimer $[Ph_2P{-}BH_2]_3$.[11] However, on addition of about 0.3 mol % of a Rh^I catalyst such as [Rh(1,5-cod)$_2$][OTf] or [{Rh(μ-Cl)(1,5-cod)}$_2$] (1,5-cod = cycloocta-1,5-diene) dehydrocoupling of the neat adduct is observed at 90 °C over 14 h to form a white, crystalline, air-stable product [Eq. (1)]. A ^{31}P NMR spectrum of the new compound showed the presence of two different phosphorus environments ($\delta = -3.3$ and -17.7). Additional characterization by ^{11}B and ^1H NMR spectroscopy, mass spectrometry, and single-crystal X-ray diffraction (Figure 1) identified the product as the novel linear dimer **1**.[12, 13] Notably, the P–B bonds in **1** (1.92–1.94 Å) are long compared to carbon–carbon bonds (ca. 1.54 Å) and have lengths typical of single bonds between four-coordinate phosphorus and boron centers.



$$\mathrm{Ph_2PH{\cdot}BH_3} \xrightarrow[\substack{90^\circ C \\ -\,H_2}]{Rh^I} \mathrm{H{-}P(Ph)_2{-}BH_2{-}P(Ph)_2{-}BH_3} \qquad (1)$$

1

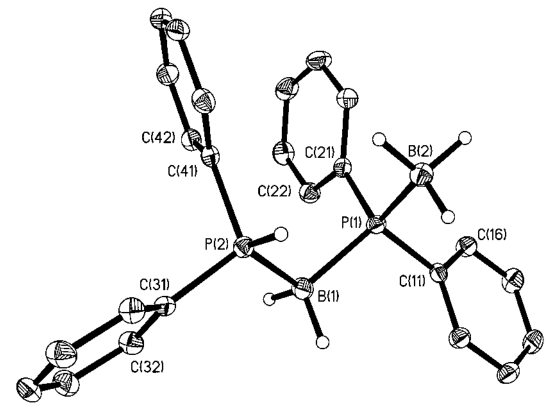


Figure 1. Molecular structure of **1** (thermal ellipsoids at the 30 % probability level). Selected bond lengths [Å] and angles [°]: P(1)–B(2) 1.932(2), P(1)–B(1) 1.944(2), P(2)–H(1P) 1.349(19), P(2)–B(1) 1.923(2); B(2)-P(1)-B(1) 113.01(11), H(1P)-P(2)-B(1) 112.6(8), P(2)-B(1)-P(1) 109.23(12).

Encouraged by this result 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 in the case

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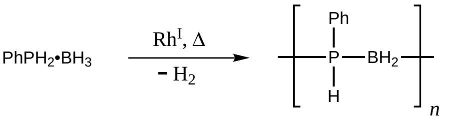
described above [Eq. (1)] could disfavor polymer formation, we moved on to explore the dehydrocoupling of the analogous primary phosphane–borane adduct $PhPH_2 \cdot BH_3$.[14] In this case, dehydrocoupling occurred in solution in refluxing toluene (110 °C, 14 h, ca. 0.3 mol% $[Rh(1,5\text{-cod})_2][OTf]$). An off-white polymeric product was isolated by precipitation into hexanes and was subsequently identified as poly(phenylphosphinoborane) [**2**; Eq. (2)].



$$PhPH_2 \cdot BH_3 \xrightarrow[-\,H_2]{Rh^I,\,\Delta} \left[\overset{\displaystyle Ph}{\underset{\displaystyle H}{P}} - BH_2 \right]_n \qquad (2)$$

2

Thus, the ^{31}P NMR spectrum of **2** showed a broad singlet at $\delta \approx -48.9$, which split into a doublet ($J_{PH} = 360$ Hz) in the ^1H-coupled spectrum and is characteristic of a single hydrogen substituent at phosphorus (Figure 2). The ^1H NMR spectrum of **2** was also consistent with the assigned structure: It contains broad peaks for the phenyl group ($\delta = 6.65-7.90$) and the BH_2 protons ($\delta = 0.65-2.20$) as well as a broad doublet at $\delta = 4.25$ ($J_{PH} = 360$ Hz) for the PH group. The ^{11}B NMR spectrum of **2** showed a single broad resonance at $\delta = -34.7$, which is characteristic for a four-coordinate boron center attached to two phosphorus atoms.[15] Further characterization of **2**, which is air- and moisture-stable, was achieved by ^{13}C NMR and IR spectroscopy as well as elemental analysis, which also afforded data consistent with the assigned structure.

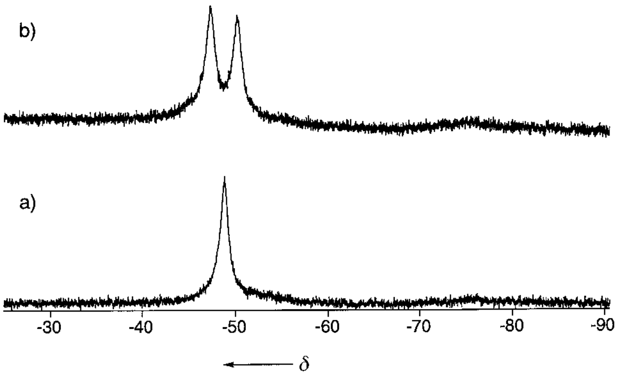


Figure 2. ^{31}P NMR spectra of polymer **2** (121 MHz) in $CDCl_3$: a) ^1H-decoupled; b) ^1H-coupled, $J_{PH} = 360$ Hz.

The absolute weight average molecular weight (M_w) of **2** prepared by this solution method was determined by static light scattering in THF and was found to be relatively low ($M_w = 5600$), corresponding to a weight average degree of polymerization (DP_w) of 46.[16] To obtain higher molecular weights by increasing the extent of reaction, $PhPH_2 \cdot BH_3$ and a Rh^I catalyst were heated in the absence of solvent at slightly elevated temperatures (3 h at 90 °C and 3 h at 130 °C). This yielded a polymeric product **2** which was spectroscopically identical to that prepared in toluene. However, in this case the high molecular weight nature of **2** was confirmed by static light scattering, which afforded an absolute value of $M_w = 31000$, corresponding to $DP_w = 254$ (Figure 3).[16]

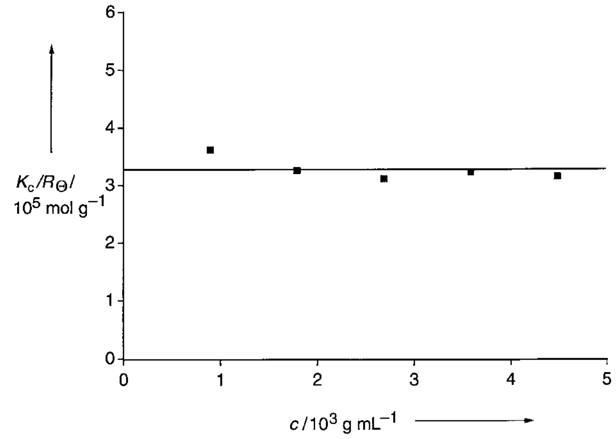


Figure 3. Low-angle laser light scattering plot for **2** in THF at 22 °C (K = optical constant, c = concentration, R_Θ = Rayleigh ratio). The absolute molecular weight M_w is determined as the inverse of the intercept on the y axis.[17]

In contrast to the situation for $Ph_2PH \cdot BH_3$, the dehydrocoupling of $PhPH_2 \cdot BH_3$ proceeds at a similar temperature in the absence of added catalyst. However, the rate is substantially slower and the observed molecular weights were considerably lower, which indicates that P–B chain formation is much less efficient than in the catalyzed process.[14]

In summary, novel and facile transition metal catalyzed P–B bond formation reactions have been discovered and the first, well-characterized, high molecular weight poly(phosphinoborane) (**2**) has been isolated as an air and moisture stable solid. Future work will focus on the further development of this new area of inorganic high polymer chemistry and on the dehydrocoupling mechanism. In addition, detailed studies of the physical properties of polymers such as **2**, which can be regarded as an analogue of polystyrene with a phosphorus–boron backbone, should be very revealing from a fundamental perspective, and useful properties such as flame retardancy and oxidative stability may emerge.

Experimental Section

Reactions were performed under nitrogen using dry solvents. Workup of **2** was carried out in air. Light scattering experiments were carried out in THF at 22 °C and were performed as described in detail elsewhere.[17] The refractive index increment (dn/dc) for **2** was determined to be 0.24 mL g^{-1}. Low-angle laser light scattering experiments were performed on solutions in THF that had been left undisturbed for 24 h.

Synthesis of **1**: Neat $Ph_2PH \cdot BH_3$ (0.625 g, 3.12 mmol) and $[Rh(1,5\text{-cod})_2][OTf]$ (ca. 4 mg, 0.3 mol%) were heated at 90 °C for 14 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 air-stable **1**. Yield 0.530 g (85%). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.68-7.17$ (m, 20H, aromatic), 6.71 (dm, 1H, $J_{PH} = 397$ Hz, PH), 2.24 (br, 2H, BH_2), 1.01 (brq, 3H, $J_{BH} = 75$ Hz, 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); MS (EI, 70 eV): m/z (%): 395 (16) $[M^+ - 3H]$, 384 (100) $[M^+ - BH_3]$.

Synthesis of low molecular weight **2**: In a typical experiment $PhPH_2 \cdot BH_3$ (1.025 g, 8.27 mmol) and $[Rh(1,5\text{-cod})_2][OTf]$ (ca. 10 mg, 0.3 mol%) were dissolved in toluene (15 mL), and the resulting solution was refluxed for 14 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 **2** was washed with hexanes, decanted, and dried in vacuo. Yield 0.678 g (67%). Static light scattering (THF): $M_w = 5600$, $DP_w = 46$; the second virial coefficient A_2 was found to be zero. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 6.65-7.90$ (br, Ph), 4.25 (br d, $J_{PH} = 360$ Hz, PH), 0.65–2.20 (br, BH$_2$); ^{11}B{^{1}H} NMR (160 MHz, CDCl$_3$): $\delta = -34.7$ (br s); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): $\delta = 132.5$ (br, *o*-Ph), 129.3 (br, *p*-Ph), 128.2 (br, *m*-Ph); ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$) $\delta = -48.9$ (br s); ^{31}P NMR (121 MHz, CDCl$_3$): $\delta = -48.9$ (br d, $J_{PH} = 360$ Hz); IR (nujol): $\tilde{\nu}$(B–H) = 2417, 2378 cm^{-1}, $\tilde{\nu}$(P–H) = 2213 cm^{-1}; elemental analysis calcd for C_6H_8BP: C 59.1, H 6.6; found: C 58.9, H 6.5.

Synthesis of high molecular weight **2**: In a typical experiment, neat $PhPH_2 \cdot BH_3$ (1.22 g, 9.84 mmol) and [Rh(μ-Cl)(1,5-cod)]$_2$ (ca. 15 mg, 0.3 mol%) were heated for 3 h at 90 °C and for a further 3 h at 130 °C. After cooling to room temperature, the yellow solid was dissolved in CH_2Cl_2 (15 mL), and the solution was filtered and precipitated into hexanes (250 mL). The off-white polymeric product was washed with hexanes, decanted, and dried under vacuum at 50 °C for 48 h. Yield 0.90 g (75%). The ^{1}H, ^{11}B, and ^{31}P NMR and IR spectra are as described above. Static light scattering (THF): $M_w = 31000$, $DP_w = 254$.; the second virial coefficient A_2 was found to be zero.

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