



Stauber, A., Jurca, T., Marquardt, C., Seidl, M., Fleischmann, M., Whittell, G., ... Scheer, M. (2016). A Convenient Route to Monoalkyl-Substituted Phosphanylboranes (HRP–BH₂–NMe₃): Prospective Precursors to Poly[(alkylphosphino)boranes]. *European Journal of Inorganic Chemistry*, 2016(17), 2684-2687. DOI: 10.1002/ejic.201600226

Peer reviewed version

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[10.1002/ejic.201600226](https://doi.org/10.1002/ejic.201600226)

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A convenient route to mono-alkyl substituted phosphanylboranes HRP-BH₂-NMe₃, prospective precursors to poly(alkylphosphinoboranes)

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Abstract: A simple method is reported for accessing borylphosphonium iodides [RH₂P-BH₂-NMe₃] (**1a**: R = Me, **1b**: R = Et, **1c**: R = ⁿPr) by the addition of iodoalkanes to PH₂-BH₂-NMe₃. Complexes **1a-c** were characterized by multinuclear NMR spectroscopy, and **1a** and **1b** were characterized by single crystal X-ray diffraction. It was possible to synthesize the Lewis base stabilized organosubstituted phosphanylborane MePH-BH₂-NMe₃ (**2**) from [MePH₂-BH₂-NMe₃] (**1a**). Thermolysis of **2** generated a short and soluble poly(alkylphosphinoborane) polymer (**4**) consisting of at least 40 repeat units as identified by ESI-MS. These results are promising for the future preparation of a wide range of Lewis base stabilized phosphanylboranes, which are of interest as precursors to poly(alkylphosphinoborane) polymers, which are otherwise difficult to access via conventional metal catalyzed methods.

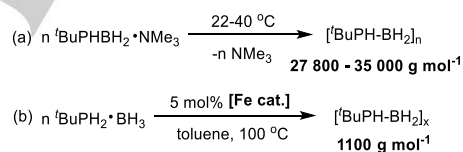
Introduction

Polymers based on main group elements other than carbon are of widespread current interest as a result of their broad range of potential applications.^[1,2] Current synthetic routes to these materials are typically based on polycondensation or ring-opening polymerization pathways.^[3] Metal-catalyzed polycondensation routes that involve a dehydrocoupling process have been of particular significance and have been used for the preparation of polyaminoboranes [NRH-BH₂]_n (R = alkyl, or H),^[4] polyphosphinoboranes [PRH-BH₂]_n (R = aryl).^[5] These materials possess main-chains of alternating group 13 and 15 elements and are formally isoelectronic to polyolefins but possess significantly different properties.^[7,8,9]

High molar mass polyphosphinoboranes are accessible via the Rh- or Fe-catalyzed dehydrocoupling of primary phosphine-boranes RPH₂-BH₃.^[5,10] However, as P-H bonds are essentially non-polar (electronegativity: P = 2.19, H = 2.20),^[8] catalytic dehydrocoupling routes have relied on electron withdrawing aryl groups on phosphorus to promote the reaction, ultimately resulting in a limited substrate scope. For transition metal mediated polymerization to date, the only examples of poly(alkylphosphinoboranes) of modest molar mass have been prepared by the slow dehydrocoupling of ^tBuPH₂-BH₃^[5d] and

FcCH₂PH₂-BH₃^[5f] (Fc = ferrocenyl) at ca.110 – 120 °C in the presence of Rh catalysts in reactions that generally also lead to appreciable chain branching and crosslinking.

Recently we reported that pnictogenylboranes ER₂-BH₂-NMe₃ (R = alkyl, aryl, or H) are valuable starting materials for the formation of oligomeric (E = As, P)^[11,12] and in some cases, polymeric materials (E = P).^[12] Simple thermal treatment of the phosphanylboranes PR₂-BH₂-NMe₃ (R = H, alkyl, aryl) either in dilute solution or in the absence of solvent led to the elimination of trimethylamine, and subsequent polymerization of intermediate [PR₂-BH₂] to yield oligo- and polyphosphinoboranes [PRH-BH₂]_n. In particular, gentle thermolysis (22 – 40 °C) of ^tBuPH-BH₂-NMe₃ afforded poly(alkylphosphinoborane) [^tBuPH-BH₂]_n with high molar mass (M_n = 27 800 – 35 000 g mol⁻¹) and reasonably low PDI (1.6 – 1.9) characteristic of a mainly linear material (Scheme 1a). Attempts to synthesize [^tBuPH-BH₂]_n by the established Cp(CO)₂Fe(OSO₂CF₃) catalyzed dehydrocoupling of ^tBuPH₂-BH₃ resulted in short chain oligomers with masses of no more than 1100 g mol⁻¹ (Scheme 1b).^[12]



Scheme 1. Comparison of routes to oligo- and poly(^tbutyl)phosphinoboranes. Fe cat. = Cp(CO)₂Fe(OSO₂CF₃).

Primary phosphines (RPH₂) can often be highly reactive and also highly volatile (e.g. boiling point: MePH₂ = -13.0 °C, EtPH₂ = 25 °C).^[13] Their derivatives of primary phosphine-boranes (RPH₂-BH₃), the common precursor to polyphosphinoboranes [RPH-BH₂]_n via catalytic dehydrocoupling, often share similar characteristics, and in addition, can be prone to degradation and release of the respective phosphines upon handling. Further development of precursors to poly(alkylphosphinoboranes) which circumvent the use of highly reactive and/or volatile precursors, and facilitate the access to polymers currently inaccessible by common metal catalyzed routes, is of fundamental interest. Herein, we describe an expansion of substrate scope and synthetic strategy for Lewis base stabilized phosphanylboranes with alkyl substituents on phosphorus, and their thermally induced coupling.

Results and Discussion

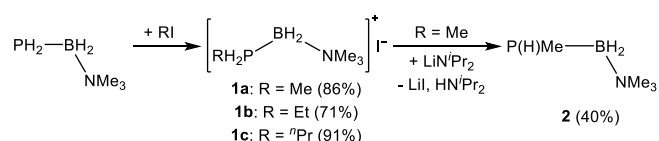
To build on previously reported R¹R²P-BH₂-NMe₃ (R¹ = R² = H; R¹ = R² = Ph, R¹ = ^tBu, R² = H), we targeted the synthesis of MePH-BH₂-NMe₃ (**2**). For stibanes, the substitution of a hydrogen

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by a methyl group could easily be realized in a one-step reaction by addition of MeI and 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU).^[14] The use of an analogous procedure with phosphinoborane, however, did not result in methyl substitution at phosphorous, but rather formed [DBU·Me] instead. In contrast, the addition of one equivalent of iodoalkane RI (R = Me, Et, ⁿPr) to PH₂-BH₂-NMe₃ resulted in the formation of the corresponding alkylated phosphonium iodides [RPH₂-BH₂-NMe₃]⁺I⁻ (**1a**: R = Me, **1b**: R = Et, **1c**: R = ⁿPr; Scheme 2) in good to excellent yields (71–91%), without the formation of byproducts. Interestingly **1c** is a colorless liquid whereas **1a** and **1b** are white crystalline solids at room temperature. The products were characterized by multinuclear NMR spectroscopy (Table 1), and for **1a** and **1b**, by single crystal X-ray diffraction (Figure 1).^[15]



Scheme 2. Synthesis of the phosphonium iodides **1a-c** and the Lewis base stabilized phosphanylborane **2**.

Table 1. NMR spectroscopic data for the phosphonium iodides **1a-c** in CD₃CN at 300 K.

	chemical shift (ppm) and coupling constant (Hz)				
	¹ H			³¹ P	¹¹ B
	PH ₂ (¹ J _{PH})	BH ₂ (¹ J _{BH})	N(CH ₃) ₃	PH ₂ (¹ J _{PB})	BH ₂
1a	5.24 (415)	2.19 (112)	2.85	-79.7 (68)	-10.8
1b	5.28 (408)	2.20 (111)	2.86	-62.6 (68)	-11.7
1c	5.26 (407)	2.20 (110)	2.85	-69.3 (68)	-11.5

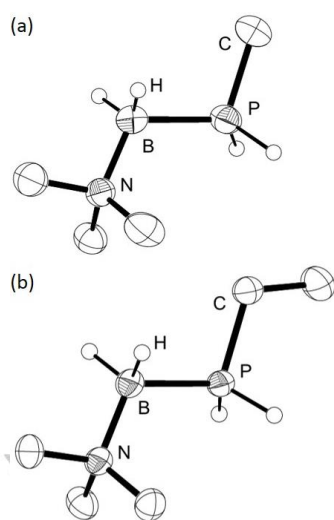


Figure 1. Solid state structures of the cations of **1a** (top) and **1b** (bottom) with hydrogen atoms bound to carbon atoms omitted for clarity and ellipsoids drawn at the 50% probability level. Selected bond lengths [Å] and angles [°] **1a**: P–B 1.943(4), P–C 1.792(4), N–B 1.586(4), C–P–B 107.8(2), P–B–N 116.7(2); **1b**: P–B 1.952(4), P–C 1.810(3), N–B 1.581(5), C–P–B 108.24(18), P–B–N 114.6(3).

To validate the feasibility of borylphosphonium iodides (**1a-c**) as precursors for the preparation of monoalkylsubstituted phosphanylboranes of the type RPH–BH₂-NMe₃, the methylated derivative **1a** was further studied. After reacting **1a** with lithium diisopropylamide (Scheme 2) the volatiles were removed at reduced pressure and the residue was extracted with toluene. Subsequent removal of the solvent yielded a colorless oil, which contained phosphanylborane **2** as the main component. Unreacted PH₂-BH₂-NMe₃, the byproduct PMe₂-BH₂-NMe₃, and poorly defined species tentatively attributed to polyphosphinoboranes could be identified as side products by NMR spectroscopy (ca. 15% total side products by NMR). Washing the residual oil with hexanes, afforded **2** as a clear oil in a modest yield of 40% (due to product loss from workup). Like previously reported PH₂-BH₂-NMe₃,^[16] compound **2** is a clear colorless liquid at room temperature, but has a much lower melting point, which is below -80 °C. The ¹¹B NMR spectrum of **2** revealed a doublet of triplets at δ = -3.3 ppm due to the coupling of the boron nucleus with a phosphorus atom (¹J_{PB} = 48 Hz) and the two bound protons (¹J_{BH} = 105 Hz) (Figure 2). The ³¹P NMR spectrum revealed a doublet of quartets at δ = -150.7 ppm (¹J_{PB} = 48 Hz, ¹J_{PH} = 206 Hz) (Figure 2). These resonances are similar to those observed for previously reported analogues PH₂-BH₂-NMe₃ (³¹P δ = -215.5, ¹J_{PB} = 31 Hz, ¹J_{PH} = 189 Hz; ¹¹B δ = -6.7, ¹J_{BP} = 30 Hz, ¹J_{BH} = 107 Hz)^[16] and ^tBuPH–BH₂-NMe₃ (³¹P δ = -67.7, ¹J_{PB} = 48 Hz, ¹J_{PH} = 197 Hz; ¹¹B δ = -6.0, ¹J_{BP} = 48 Hz, ¹J_{BH} = 104 Hz).^[12] The difference in the ³¹P resonances arises from the varying substituents, however, the splitting patterns, and coupling remain similar. A similar procedure was utilized for the deprotonation of **1b** and **1c**, respectively, however, isolation of the pure analogous Lewis base stabilized phosphanylboranes has thus far been unsuccessful.

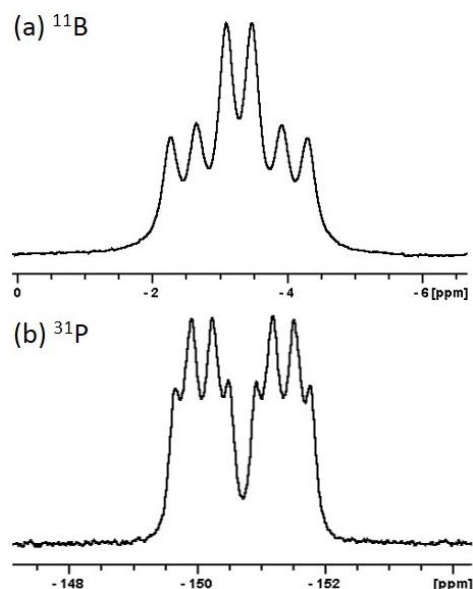
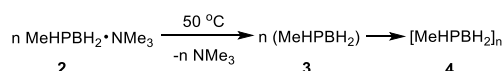


Figure 2. ¹¹B (top) and ³¹P (bottom) NMR spectra of phosphanylborane **2** (T = 300 K; C₆D₆).

Thermolysis of **2** was conducted at 50 °C, both in the absence of solvent and in toluene solution for 20 h (Scheme 3). Both methods (neat and solution) were effective for the consumption of **2**, and corresponding formation of **4**, which is soluble in organic solvents like toluene and thf. However, the solution approach led to less complex NMR spectra (^1H , ^{11}B , ^{31}P). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4** obtained from thermolysis experiments in toluene featured a set of two broad signals at $\delta = -75$, -87 ppm, which showed further broadening in the ^1H coupled ^{31}P NMR spectrum. These chemical shifts were in the expected region based on previous reports on polyphosphinoborane $[\text{R}^1\text{R}^2\text{P}-\text{BH}_2]_n$ oligomers.^[5] They were also consistent with the expected downfield shift upon interaction of the P atom of protected phosphanylboranes with a B center; $\text{PH}_2-\text{BH}_2\cdot\text{NMe}_3$ ^{31}P $\delta = -215.5$ vs $\text{BH}_3\cdot\text{H}_2\text{P}-\text{BH}_2\cdot\text{NMe}_3$ ^{31}P $\delta = -116.0$.^[15] The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum featured a set of very broad signals at ca. $\delta = -35$ and -9 ppm, respectively, which showed further broadening in the ^1H coupled ^{11}B NMR spectrum. Again, these were consistent with reported chemical shifts for internal BH_2 groups in phosphinoborane polymers and oligomers; $[\text{H}_2\text{P}-\text{BH}_2]_n$ ^{11}B $\delta = -32$ ppm, $[\text{PhHP}-\text{BH}_2]_n$ ^{11}B $\delta = -34.7$ ppm.^[5a,b,h,i] The signal at $\delta = -9$ was tentatively assigned to the NMe_3 -coordinated BH_2 end groups (cf. NMe_3 -capped terminal BH_2 group in $\text{PH}_2-\text{BH}_2\cdot\text{NMe}_3$ at $\delta(^{11}\text{B}) = -6.7$ ppm).^[15] The multiple signals observed in both the ^{31}P and ^{11}B NMR spectra were attributed to the presence of oligomeric species of differing lengths.



Scheme 3. Polymerization of Lewis base stabilized phosphanylborane (**2**).

Electrospray Ionization (ESI) MS of THF solutions of **4** were indicative of oligomeric products with a mass in the range of 2400 Da (Figure 3). A distinct fragmentation pattern of 60 Da was observed; representative of a single unit of $[\text{MeHP}-\text{BH}_2]$. This confirmed the formation of short polymers of at least 40 repeating units, with fragmentation patterns indicative of both THF and NMe_3 end-capping. Further characterization was attempted by dynamic light scattering (DLS) however this was suggestive of aggregate formation as particles within the measurable size range (1 nm – 5 μm) were detected. Neither DLS, ESI-MS, nor NMR were conclusive for the presence of any high-molecular weight, soluble polymers. We propose that polymerization of **2** is triggered by initial thermolysis leading to elimination of NMe_3 to form the unprotected monomeric phosphinoborane intermediate **3**. The resulting absence of the Lewis base electronically destabilizes **3**, promoting a head-to-tail addition polymerization sequence which ultimately affords **4**.^[17]

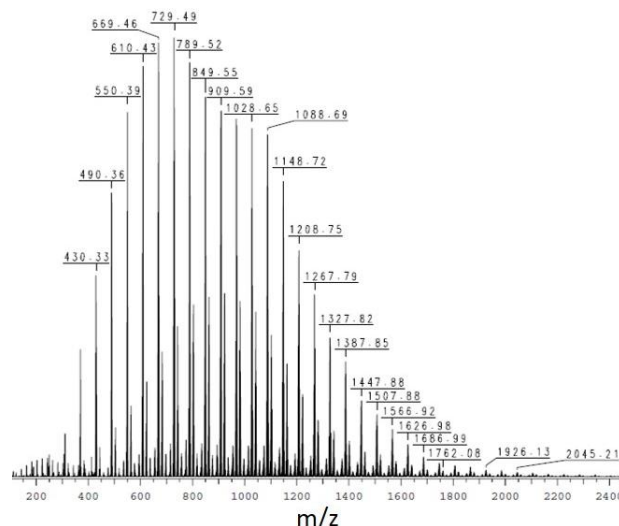


Figure 3. ESI – mass spectrum of **4** in THF.

Conclusions

In summary, we have demonstrated a simple method for accessing borylphosphonium iodides (**1a-c**) by addition of iodoalkanes to $\text{PH}_2-\text{BH}_2\cdot\text{NMe}_3$. For $[\text{MePH}_2-\text{BH}_2\cdot\text{NMe}_3]$ (**1a**) it was possible to generate $\text{MePH}-\text{BH}_2\cdot\text{NMe}_3$ (**2**). Gentle thermolysis of **2** afforded the soluble poly(alkylphosphinoborane) **4** (at least 40 repeat units as identified by ESI-MS). However, due to aggregation as a result of solubility problems, the formation of high molar mass materials could not be confirmed. These results offer promise for the future preparation of a greater range of poly(alkylphosphinoboranes), which are otherwise difficult to access via conventional metal catalyzed means. Expansion of the range of available Lewis base stabilized phosphanylboranes, their thermally induced polymerization reactions, and the elucidation of the reaction mechanism by which they operate are currently under investigation.

Acknowledgements

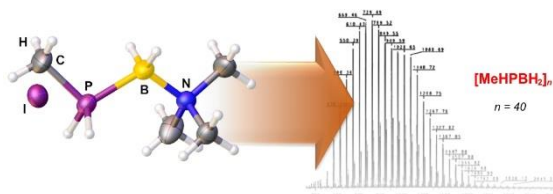
The German group thanks the DFG for comprehensive support. The SIPs COST action CM1302 is gratefully acknowledged. I.M. thanks the EPSRC and Alexander von Humboldt Foundation for support. T.J. thanks EPSRC for funding and the EU for a Marie Curie Fellowship. The authors thank Dr. P. Gates (University of Bristol) for MS data.

Keywords: phosphorus • boron • phosphanylborane • poly(phosphinoboranes) • inorganic polymers

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SHORT COMMUNICATION



A novel route for the synthesis of monoalkylsubstituted Lewis base stabilized phosphinoboranes via borylphosphonium precursors is presented. Mild thermolysis of the Lewis base stabilized methylphosphinoborane generated the corresponding polymer consisting of at least 40 repeat units, which exemplifies the applicability of this method.

Key Topic* phosphinoboranes;
inorganic polymers

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A convenient route to mono-alkyl substituted phosphanylboranes HRP-BH₂-NMe₃, prospective precursors to poly(alkylphosphinoboranes)