

Hot Paper

Titanium-Catalyzed Polymerization of a Lewis Base-Stabilized Phosphinoborane

Jens Braese,^[a] Felix Lehnfeld,^[a] Vincent T. Annibale,^[b] Tim Oswald,^[c] Rüdiger Beckhaus,^[c] Ian Manners,^[b] and Manfred Scheer*^[a]*Dedicated to Professor P. P. Power on the occasion of his 70th birthday.*

The reaction of the Lewis base-stabilized phosphinoborane monomer tBuHPBH₂NMe₃ (**2a**) with catalytic amounts of bis-(η^5 : η^1 -adamantylidene)pentamethylcyclopentadiene)titanium (**1**) provides a convenient new route to the polyphosphinoborane [tBuPH-BH₂]_n (**3a**). This method offers access to high molar mass materials

under mild conditions and with short reaction times (20 °C, 1 h in toluene). It represents an unprecedented example of a transition metal-mediated polymerization of a Lewis base-stabilized Group 13/15 compound. Preliminary studies of the substrate scope and a potential mechanism are reported.

Introduction

Inorganic polymers, based on main-group elements other than carbon, provide attractive materials with specific uses as elastomers, lithographic resist layers, biomaterials, polyelectrolytes, ceramic precursors and in optoelectronics.^[1] The inorganic monomers for polymerization reactions are comparable to their organic analogues. Ammonia borane H₃N·BH₃ can be regarded as an ethane analogue, and has been studied due to its high hydrogen content and potential use in hydrogen storage materials.^[2] Progress has been made in the regeneration of the dehydrogenated polymeric residue.^[3] In addition to metal-induced dehydropolymerization which has been comprehensively studied,^[4] advances on the dehydrocoupling with earth abundant main group Lewis acid catalysts have also been reported recently.^[5] The heavier homologue H₃P·BH₃ is very labile even at low temperatures, but nonetheless has been

reported to yield a polymer in dehydrocondensation reaction catalyzed by B(C₆F₅)₃.^[6]

Polyphosphinoboranes [RHP-BH₂]_n have been prepared over the past decades as high molar mass materials by rhodium- and iron-catalyzed dehydrocoupling reactions of primary phosphine-boranes.^[7] Recently, a transition metal-free dehydrocoupling for the synthesis of high molar mass polyphosphinoboranes have also been reported.^[8] Catalytic dehydrocoupling routes have relied on the electron-withdrawing effect of aryl groups on the phosphorus atom to promote the reaction since the P–H bonds are essentially nonpolar. The substrate scope for the catalytic dehydrocoupling routes is generally quite limited, and the synthesis of poly(alkylphosphinoboranes)^[7c,e,h] is significantly more challenging than for P-aryl analogues in general.

Following the comparison with the carbon-based analogue, the inorganic BN congener of ethylene would be aminoborane H₂NBH₂, which has been isolated under cryogenic conditions.^[9] The free heavier homologue H₂PBH₂ was not obtained even by matrix-isolation techniques.^[10] The parent phosphinoborane however can be stabilized by Lewis bases to give monomeric compounds such as H₂PBH₂NMe₃.^[11] Moreover, a variety of organic substituted derivatives^[12] and heavier group 15 elements analogues have been synthesized.^[13] Reactions with [Cp₂Ti(btmsa)] (btmsa = bis(trimethylsilyl)acetylene) have shown that H₂PBH₂NMe₃ is an excellent ethylene-like monomer for the stepwise aggregation to form oligomers stabilized in the coordination sphere of titanium centers.^[14] These oligophosphinoborane chains are a result of the loss of the stabilizing NMe₃ group, leading to a head-to-tail aggregation, as well as to an additional P–P coupling via dehydrocoupling through P–H activation. Furthermore, the mild metal-free thermolysis of the derivative tBuHPBH₂NMe₃ leads to a transient free phosphinoborane tBuHPBH₂ via elimination of the Lewis base. Subsequent head-to-tail polymerization results in high molecular mass poly(alkylphosphinoboranes),^[12b] which are difficult to access via catalytic dehydrocoupling reactions due to the weakly polarized P–H bonds (Scheme 1).^[7h,12] Several attempts to use

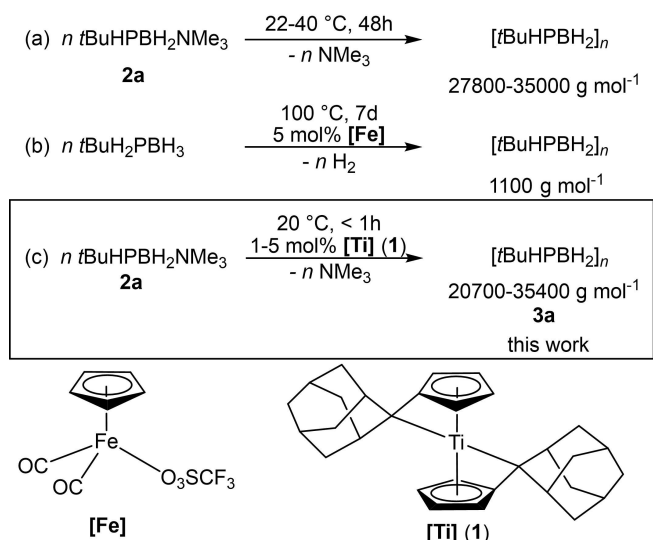
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Scheme 1. Comparison of different routes to poly(*tert*-butylphosphinoboranes). a) metal-free thermolysis, b) dehydrocoupling using [Fe] = [Cp(CO)₂Fe(OSO₂CF₃)], c) this work, using [Ti] = [(η^5 : η^1 -C₅H₄C₁₀H₁₄)₂Ti] (1).

transition metal complexes to initiate a polymerization reaction have not been successful,^[15] thus a transition metal-mediated polymerization of Lewis base-stabilized phosphinoboranes is unknown so far. Consequently, the quest for a general metal-mediated polymerization of Lewis base-stabilized pnictogenylboranes at low temperature to yield high molecular mass polymers without crosslinks was still an open synthetic challenge. Moreover, some of the heavier homologues H₂EBH₂·NMe₃ (E = As, Sb) are not suitable for thermolysis given the weakness of the E–B bond within the monomer,^[12] therefore lowering the activation barrier for E–B bond formation via addition of a transition metal catalyst might lead to new polymeric materials. We chose a bis(η^5 : η^1 -pentafulvene)-titanium precatalyst due to its similarities to titanocene fragments and the high reactivity of the pentafulvene ligand. Bis(η^5 : η^1 -pentafulvene)titanium has been found to participate in haptotropic shifts accompanied by different E–H bond activations under mild conditions or in insertion reactions of polar multiple bonded substrates.^[16] Compared with the previously studied oligomerization of Lewis base-stabilized phosphinoborane by [Cp₂Ti(btmsa)],^[14] the investigation of the influence of a bis(η^5 : η^1 -pentafulvene)titanium precatalyst on the resulting polymer came into the focus of our research. This might influence the molecular mass or polydispersity of the resulting polymers and can also be compared with the uncatalyzed thermally-driven polymerization.^[12b]

Results and Discussion

Preliminary polymerization reactions of *t*BuHPBH₂NMe₃ (**2a**), in the presence of 5 mol% of the sterically encumbered bis(η^5 : η^1 -adamantylidenepentafulvene)titanium (**1**)^[17] were conducted in toluene at room temperature (20 °C). Surprisingly, full conversion to the polymer [tBuPH-BH₂]_{*n*} (**3a**) and the release of free

NMe₃ were observed within 30 min., as detected by ¹H, ¹¹B, and ³¹P NMR spectroscopy (Scheme 1c).

Compound **3a** was isolated by precipitation through addition of a saturated solution of **3a** in toluene to vigorously stirred acetonitrile as described for similar polymers by our group.^[12b] The ³¹P{¹H} NMR spectrum of **3a** showed a set of three broad signals at $\delta = -19$, -22 and -24 ppm, similar to the triad-assigned resonances for the atactic polymer reported previously obtained by the thermally induced elimination of NMe₃.^[12b] In the ³¹P NMR spectrum of the product, further broadening and splitting into poorly defined doublets was observed. A very broad signal at $\delta = -38$ ppm was found in the ¹¹B{¹H} NMR spectrum. The total conversion of the monomer **2a** occurs much faster and at lower temperatures than the metal-free polymerization reaction (48 h at 40 °C), however the molecular weight of polymer **3a** prepared using **1** as a catalyst was lower as determined by GPC using THF with 0.1 wt.% [nBu₄N]Br as the eluant ($M_n = 5,500$ g mol⁻¹, $M_w = 11,000$ g mol⁻¹, PDI = 2.0, PDI = polydispersity index). By lowering the catalyst loading to 1 mol% of **1**, the conversion of *t*BuHPBH₂NMe₃ (**2a**) proceeds quantitatively at 20 °C within 60 min to give a higher molar mass polymer than when 5 mol% catalyst loading was used ($M_n = 20,700$ g mol⁻¹, $M_w = 45,000$ g mol⁻¹, PDI = 2.2). Product samples arising from this method were analyzed by DLS at concentrations of 2 mg/mL in CH₂Cl₂. The value of R_h of 4.95 nm corresponds to a molar mass of 35400 g mol⁻¹ for monodisperse polystyrene samples in THF,^[18] supporting the presence of a higher molecular weight polymer obtained at lower catalyst concentrations. Lowering the catalyst loadings further, presumably leads to a competitive reaction between the catalyzed polymerization and the metal-free polymerization reaction, as reaction times progressively approach those of the uncatalyzed reaction. Upon mixing of the catalyst with the monomer, we observe an immediate change in color from turquoise-blue of the titanium complex **1** to orange-red, which is believed to be related to the formation of the active catalytic species. Regardless of several attempts, no respective product could be isolated.

To evaluate the influence of the titanium complex on the polymerization reaction, we conducted the experiments at different temperatures. With 5 mol% of **1** at 40 °C, the same temperature as previously used for metal-free polymerization, the observed molar mass of the polymer was still significantly lower ($M_n = 3900$ g mol⁻¹, PDI = 2.3). At 0 °C, no conversion of the monomer **2a** is observed without the addition of the Ti complex. The addition of 5 mol% of **1** at 0 °C gives a slow polymerization reaction with full conversion to the polymer **3a** within 20 h, providing strong evidence of the impact of the metal complex on the polymerization reaction. Monitoring the reaction between *t*BuHPBH₂NMe₃ (**2a**) and 5 mol% of the bis(η^5 : η^1 -pentafulvene)titanium complex (**1**) at 0 °C by ¹H and ³¹P{¹H} NMR spectroscopy showed the consumption of the monomer (**2a**) and the release of an equivalent amount of free NMe₃ as well as the formation of the polymer [tBuPH-BH₂]_{*n*} (**3a**) over the course of 20 h (Figures 1 and 2). Figure 1 shows the decline of the relatively sharp signal of the monomer at $\delta = -67.6$ ppm in the ³¹P{¹H} NMR spectra and the growth of the

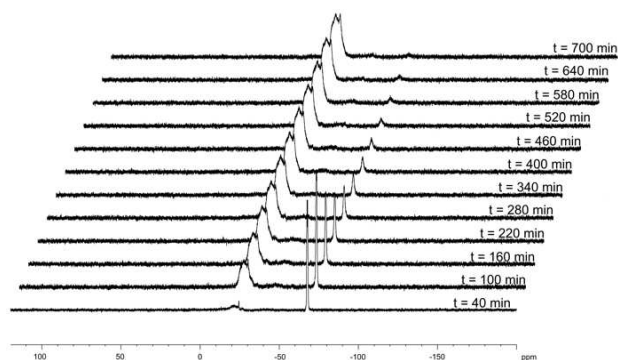


Figure 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the reaction of **2a** with 5 mol% $[(\eta^5:\eta^1\text{-C}_5\text{H}_4\text{C}_{10}\text{H}_{14})_2\text{Ti}]$ (**1**) at 0°C in C_6D_6 . $\delta = -67.6$ ppm: $t\text{BuHP-BH}_2\text{NMe}_3$, $\delta = -16.0\text{--}32.0$ ppm: $[t\text{BuHP-BH}_2]_n$.

broad signal for the polymer at about $\delta = -20$ ppm. The decline of the signals corresponding to the stabilizing Lewis base NMe_3 in $t\text{BuHPBH}_2\text{NMe}_3$ and the appearance of free NMe_3 in the ^1H NMR spectra over time provided insight into the kinetics of the polymerization reaction. The natural logarithm of the monomer concentration versus time can be fitted linearly, suggesting first order reaction with respect to the monomer concentration with a reaction rate constant $k = 0.00318\text{ s}^{-1}$ at 0°C (Figure 2). While less precise due to the lower sensitivity of ^{31}P NMR spectroscopy, also the monomer consumption according to the ^{31}P spectra was used to get further insight into the kinetics. It also indicates a first order reaction as one of the rate-determining steps with a reaction rate constant of $k = 0.0045\text{ s}^{-1}$ at 0°C . (cf. Supporting Information, Figures S44 and S45).

The resulting polymers were also studied by ESI-MS in the positive ion mode with CH_2Cl_2 as solvent (Figure 3). The maximum m/z observed is around 4000 Da for all samples, showing the limitation for molecular weight determination in such polyphosphinoboranes by ESI-MS. ESI-MS from the metal-free polymer showed m/z up to 2000, while GPC analysis shows a M_n up to 35000 g mol^{-1} .^[12b] These limitations are also known for polyaminoboranes.^[4d,19] The ESI mass spectrum of **3a** shows a degree of polymerization up to 47 ($\sim 4800\text{ g mol}^{-1}$). Three product distributions with different end groups were identified, two major distributions corresponding to linear material $[\text{H}(t\text{BuHPBH}_2)_n\text{NMe}_3]^+$ and $[\text{Me}_3\text{NBH}_2(t\text{BuHPBH}_2)_n\text{NMe}_3]^+$ and a minor distribution which best matches $[\text{H}(t\text{BuHPBH}_2)_n\text{PH}_2t\text{Bu}]^+$ (Figure 3). The identification of the end groups was further supported by the simulated mass peaks, which reveal a very close similarity between the simulated and the measured mass data.

However, it is worth being aware of some limitations of ESI-MS in end group analysis: a) The end groups observed could arise due to fragmentation under the conditions in the MS instrument. This offers a potential explanation for the observation of polymers, which have formally lost a P- or B-containing moiety, as these can be cleaved off as small molecular ions during the ionization. Respective molecular ion peaks could be observed, further supporting this formation. b) The end group

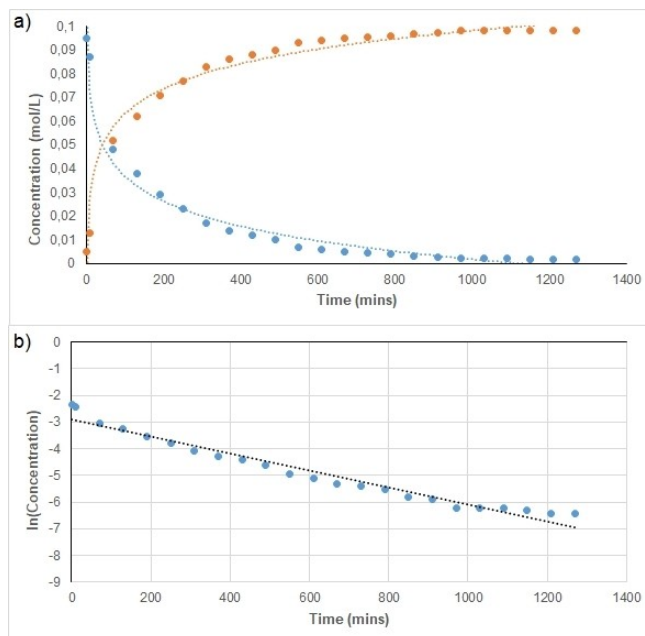


Figure 2. a) Plot of the consumption of monomer **2a** (blue)/release of free NMe_3 (orange) over the time using 5 mol% $[(\eta^5:\eta^1\text{-C}_5\text{H}_4\text{C}_{10}\text{H}_{14})_2\text{Ti}]$ (**1**) at 0°C . b) Natural logarithm of the monomer (**2a**) concentration; linear fit for a first order reaction with reaction rate constant of $k = 0.00318\text{ s}^{-1}$ at 0°C .

in the bulk samples might be different since only oligomers are being observed. c) The ionization method that is biased towards species that ionize easily also may not reflect the true quantities of different polymer populations. Furthermore, it is worth noting that in contrast to previously published results for catalyst-free polymerizations, the observed end groups differ. Whereas here three different end groups were observed, for the catalyst-free pathway predominantly the pattern marked red in Figure 3 was observed. Therefore an influence of the catalyst on the possible end groups can be expected, although no final statement can be given based on the observed data. All mass distributions showed repeat units of $m/z = 102$ Da corresponding to the $[t\text{BuHPBH}_2]$ formula unit.

Having established the capabilities of **1** as catalyst for the polymerization of $t\text{BuHPBH}_2\text{NMe}_3$ (**2a**), the scope of substrates and the polymerization pathway were investigated. The steric hindrance of the monomer, the electron density on the phosphorus atom as well as the solubility of the resulting polymer have been previously reported as key factors for the formation of polyphosphinoboranes.^[7h,12] A series of different pnictogenylboranes $\text{RR}'\text{EBH}_2\text{NMe}_3$ was therefore synthesized following adjusted procedures of our group^[12–13] and then reacted with 5 mol% of **1** in toluene at 20°C . Due to the steric shielding of the metal center in **1**, investigating the influence of the steric demand on the phosphorus atom was crucial. Therefore, the scope of substrates was expanded to phosphinoboranes which have revealed polymerization under thermal conditions in the past.^[12] Investigation of the reactivity of the sterically less demanding phosphinoboranes $\text{H}_2\text{PBH}_2\text{NMe}_3$ (**2b**) and $\text{MeHPBH}_2\text{NMe}_3$ (**2c**) towards **1** lead to no indication for polymerization in either case. The parent phosphinoborane **2b**

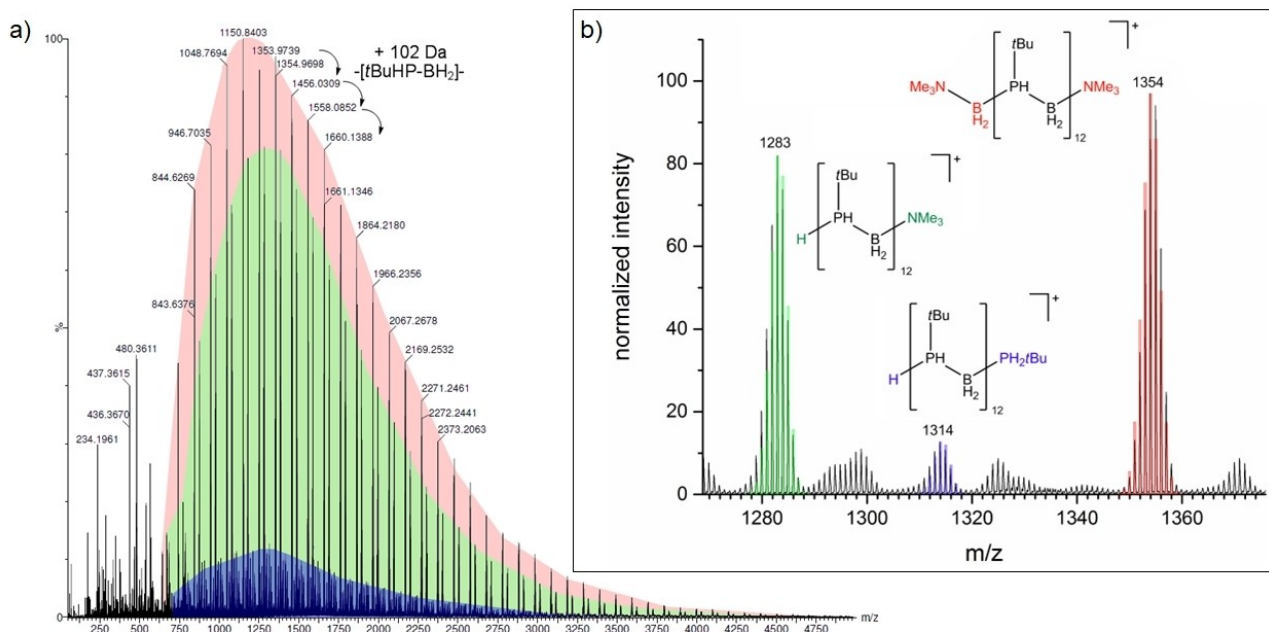


Figure 3. ESI-MS of polyphosphinoborane (**3a**) from reaction with 5 mol % [$(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{C}_{10}\text{H}_{14}\text{Ti})$] (**1**) at 0 °C; showing three different possible end groups, as indicated by underlying simulated mass peaks in green, blue and red (b) and their distribution (a) Mass differences of 102 Da correspond to the $t\text{BuHP-BH}_2$ repeat unit.

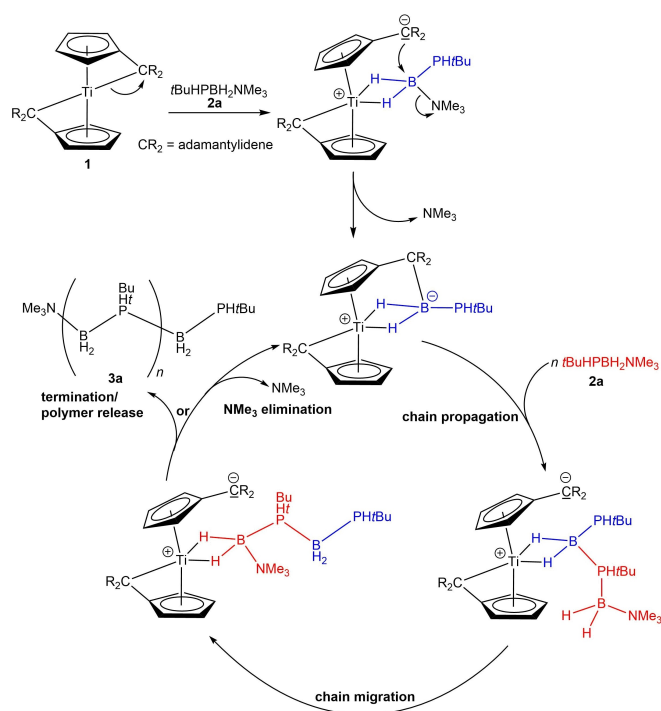
revealed different behavior with the formation of paramagnetic coordination complexes that could not be conclusively identified, but no polymerization reaction was observed. Neither increasing the steric demand on the phosphorus atom compared to **2a** by introducing an additional Me group, as in $t\text{BuMePBH}_2\text{NMe}_3$ (**2f**), nor lowering the electron density on the phosphorus atom by incorporating Ph substituents, as in $\text{Ph}_2\text{PBH}_2\text{NMe}_3$ (**2g**), led to polymer formation as neither compound showed any reactivity towards **1**. Nevertheless, preliminary studies showed that the reaction of analogous substrates with larger primary alkyl substituents $\text{RHPBH}_2\text{NMe}_3$ (**2d**: $\text{R} = n\text{Pr}$; **2e**: $\text{R} = n\text{Hex}$) led to the formation of oligomeric and polymeric species in the presence of **1** according to NMR studies. (Figures S1–S2) However, despite the presence of **1**, these reactions require increasingly long reaction times and exhibit preparative challenges during purification upon upscaling beyond NMR scale. Moreover, it appears that due to longer reaction times, there is a competition with the thermally-induced polymerization. Detailed further studies will be the focus of future work.

Lastly, due to the recently reported thermal oligomerization of $t\text{BuHAsBH}_2\text{NMe}_3$ (**2i**),^[13d] the reactivity of arsinoboranes towards **1** was also investigated. However, neither **2i** nor the parent arsinoborane $\text{H}_2\text{AsBH}_2\text{NMe}_3$ **2h** led to any detected polymerization at 20 °C in the presence of **1**.

Therefore, we assume that the substrate must be sterically hindered at the phosphorus atom, as the observed lack of reactivity of $\text{H}_2\text{PBH}_2\text{NMe}_3$ (**2b**) or $\text{MePHBH}_2\text{NMe}_3$ (**2c**) towards **1** indicates that the formation of a P–Ti bond is prevented. Two substituents on the phosphorus, as studied for **2f** and **2g**, also impede the reaction, indicating an optimum in steric hindrance is provided by only one alkyl substituent. The electron

density on the group 15 atom is of importance as well, as no reaction with substrates **2g–2i** were observed, all revealing rather low electron density on the pnictogen atom due to electron-withdrawing groups in the case of **2g** or the less nucleophilic nature of the arsenic derivatives **2i–2h**, even if a group with a positive inductive effect as in the case of $t\text{BuAsHBH}_2\text{NMe}_3$ (**2i**) is present.

These findings were used for the consideration of the reaction pathway. In the past, we discovered that the oligomerization of $\text{H}_2\text{PBH}_2\text{NMe}_3$ (**2b**) on $[\text{Cp}_2\text{Ti}]$ fragments include the formation of B–Ti and B–H...Ti bonds,^[14] similar observations were noted in the oligomerization of aminoboranes.^[20] Since it was observed that steric hindrance is beneficial and prevents P–Ti bond formation, we propose that the first step of the polymerization involves a B–H...Ti interaction and thereby the fixation of the first monomer on the metal center occurs (Scheme 2). The exo carbon moiety can subsequently assist in the elimination of the stabilizing Lewis base NMe_3 , lowering the reaction barrier for the chain propagation (Scheme 2). Computational studies show that the hydrogen atoms on the terminal BH_2 group next to the NMe_3 are more electronegative than hydrogens on the BH_2 moiety between two $t\text{BuHP}$ groups (see: Supporting Information, section 5), so a chain migration is likely to happen. This step can be followed by NMe_3 elimination for further chain growth or by a termination step and release of the free polymer later in the cycle. While we cannot exclude the possibility that a P–Ti bond formation occurs during the polymerization process, this is not indicated by the obtained data about the reaction and the resulting polymer up to this point. Additional experiments as well as more detailed computational studies are necessary to verify the proposed mechanism, as several attempts to isolate an intermediate or a



Scheme 2. Proposed catalytic cycle for the chain-growth coordination polymerization of **2a** (scheme showing one insertion event). Release of polymer $[t\text{BuPH-BH}_2]_n$ (**3a**) after n cycles.

product from a stoichiometric reaction of a phosphinoborane not undergoing polymerization were not successful up to this point. However, the current model fits the present data, presenting a first-order chain growth mechanism. This mechanism might also explain the decrease in chain length with increasing catalyst load, since for example a terminal BH_2 unit on the growing chain can be coordinated by a second catalyst moiety, and thus terminating the process.

Conclusions

In summary, we reported the first example of a transition-metal mediated polymerization of a Lewis base-stabilized group 13/15 compound. Furthermore, it shows for the first time that transition metal complexes can also catalyze the polymerization of less polar H-P-B moieties. The reaction appears to be homogenous in nature, presumably via a chain-growth coordination-polymerization mechanism. While the metal-free polymerization of $t\text{BuHPBH}_2\text{NMe}_3$ provides a higher molecular mass of the resulting polymer, the addition of bis(η^5 : η^1 -adamantylidene)pentamethyltitanium offers a much faster generation of the polymer (30 min at 20°C) and allows the use of milder reaction conditions, by generating a similar high molar mass polymer and thereby possibly increasing the substrate scope towards thermolabile monomers in the future. Furthermore, future work will focus on expanding the potential of transition metal catalysis for the synthesis of related inorganic polymers.

Experimental Section

Experimental procedures for the synthesis of all compounds, analytical data and quantum chemical calculations are described in the Supporting Information.^[7,12a,b,13a,d,17,18,21–26]

Supporting Information

The authors have cited additional references within the Supporting Information.^[21–26]

Acknowledgements

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: inorganic polymers · phosphorus · boron · polymerization reaction · titanium

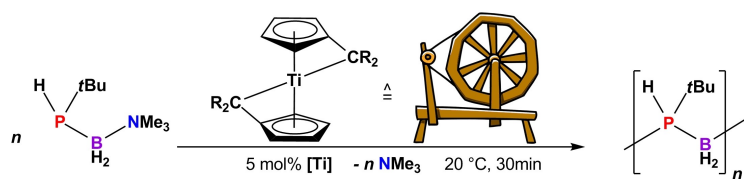
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Catalytic amounts of bis(η^5 : η^1 -pentafulvene)titanium in the reaction with Lewis base-stabilized phosphino-borane monomers provide a convenient new route to polyphosphino-boranes. This method offers access to high molecular mass materials under

very mild conditions and short reaction times. The findings represent an unprecedented example of a transition-metal mediated polymerization of Lewis base-stabilized alkylphosphino-borane.

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Titanium-Catalyzed Polymerization of a Lewis Base-Stabilized Phosphino-borane

