Angewandte
Communications

Phosphorus–Boron Oligomers

DOI: 10.1002/anie.201209703

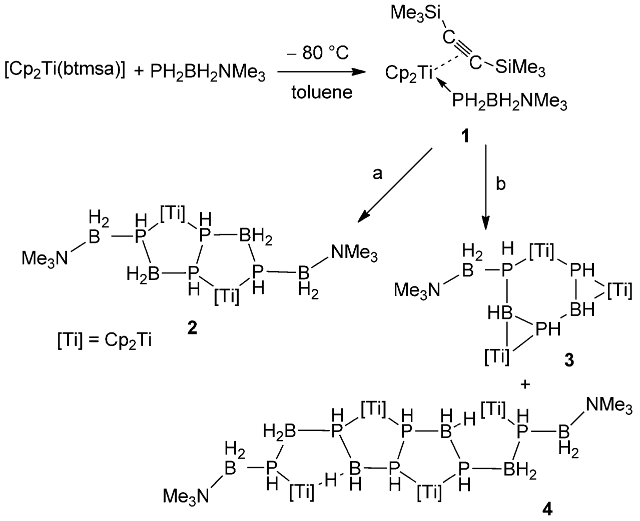
The Oligomerization of Phosphinoborane by Titanium Complexes**

*Christine Thoms, Christian Marquardt, Alexey Y. Timoshkin, Michael Bodensteiner, and Manfred Scheer**

Dedicated to Prof. H. Nöth on the occasion of his 85th birthday

Among inorganic monomers that are interesting for polymerization reactions to obtain inorganic polymers,[1] ammonia–borane is currently in the focus of interest owing to its high hydrogen content.[2] The metal-induced polymerization is widely studied,[3] and recently some progress was achieved for the recycling of the oligomerized material.[4] Compared to organic analogues, the 14-valence electron (VE) monomer H_3NBH_3 can be regarded as an ethane analogue. Following this comparison, the corresponding BN congener of ethylene would be the 12 VE species aminoborane (NH_2BH_2), which was only proposed to be a transient on the way to further oligomerization.[5] In contrast, the parent pair of heavier homologue H_3PBH_3 is very labile even at low temperatures, and it dissociates.[6] However, Denis et al. described dehydrocondensation of both components at higher temperatures (90 °C) catalyzed by $B(C_6F_5)_3$ to give a polymer of the presumed composition $[H_2P{-}BH_2]_n$.[7] It is ambiguous whether monomeric phosphinoborane is an intermediate of such a reaction. Thus some time ago we have been focused and finally succeeded on the synthesis of the Lewis base-stabilized parent phosphinoborane $PH_2BH_2NMe_3$.[8] It is a potential precursor compound for the unknown phosphinoborane PH_2BH_2, for which a defined synthetic approach does not exist, even by matrix-isolation techniques.[9] Initial investigations for its use in polymerization reactions show spontaneous polymerization by elimination of the base, resulting in a material with a high ceramic yield.[10] In contrast, Manners et al. could show alkane-analogous phosphine–boranes of the type RPH_2BH_3 to polymerize by using Rh^I catalysts or $\{Cp_2Ti\}$ in stoichiometric reactions.[11] The question thus arises as to whether the ethylene-analogous phosphinoborane $PH_2BH_2NMe_3$ can be used to monitor its oligomerization process, and if so, can a stepwise aggregation be achieved. Herein, we report first snapshots of the early transition-metal-supported oligomerization of this parent phosphinoborane.

For the oligomerization, a defined $\{Cp_2Ti\}$ source was needed, and we chose $[Cp_2Ti(btmsa)]$ (btmsa = bis(trimethylsilyl)acetylene) for which a clean elimination of the acetylene is known.[12] The reaction of the parent phosphinoborane $PH_2BH_2NMe_3$ with $[Cp_2Ti(btmsa)]$ depends on the reaction conditions, such as stoichiometry and temperature (Scheme 1). The resulting dinuclear (**2**), trinuclear (**3**), and tetranuclear (**4**) titanium compounds are unprecedented examples of transition-metal-mediated Group 13/15 oligomers formed by dehydro-oligomerization reactions. Formally, the phosphinoborane chains of the products can be regarded as head-to-tail dehydro-oligomers of two (in **2**) or three (in **3** and **4**) phosphinoboranes under partially loss of amines initiated by oxidative additions at $\{Cp_2Ti\}$ centers under hydrogen elimination and P–P coupling reactions to double the chains, as found in **2** and **4**.



Scheme 1. Generation of the complexes **1**–**4**. Reagents and conditions: a) + $PH_2BH_2NMe_3$, –80 °C→RT, –btmsa; b) –80 °C→RT, –btmsa.

The reaction between $[Cp_2Ti(btmsa)]$ and one equivalent of $PH_2BH_2NMe_3$ proceeds already at –80 °C with exclusive

---

[*] Dr. C. Thoms, M. Sc. C. Marquardt, Dr. M. Bodensteiner, Prof. Dr. M. Scheer
Institut für Anorganische Chemie, Universität Regensburg
93040 Regensburg (Germany)
E-mail: manfred.scheer@ur.de
Homepage: http://www.ur.de/chemistry-pharmacy/inorganic-chemistry-scheer/
Prof. Dr. A. Y. Timoshkin
St. Petersburg State University
University pr. 26, 198504 Old Peterhoff, St. Petersburg (Russia)

[**] This work was comprehensively supported by the Deutsche Forschungsgemeinschaft and the Alexander von Humboldt Foundation (A.Y.T. for a reinvitation fellowship). The COST action CM0802 PhoSciNet is gratefully acknowledged. The authors thank E. Wuttke (Universität Konstanz) for the EPR measurements.

Supporting information for this article (full synthetic and spectroscopic details for **1**–**4**, crystallographic details, EPR details, and full details and references of the DFT calculations) is available on the WWW under http://dx.doi.org/10.1002/anie.201209703.

formation of the adduct **1** in almost quantitative yield according to ^{31}P NMR spectroscopic investigations. A downfield shift is observed at $\delta = -106.9$ ppm compared to the free monomer ($\delta = -215.5$ ppm). The red crystalline compound **1** is only stable in the solid state up to −60 °C. Above this temperature it decomposes, whereas in solution the signal of **1** disappears in the ^{31}P NMR spectra with increasing temperature, and free btmsa is found in the ^{1}H NMR spectrum at room temperature. The green paramagnetic compound **3** is formed from this solution by hydrogen elimination, which was monitored by ^{1}H NMR spectroscopy ($\delta = 4.50$ ppm in [D$_8$]toluene; lit. $\delta = 4.55$ ppm).[13] If a second equivalent of $PH_2BH_2NMe_3$ is added to the solution of **1** at low temperatures and the mixture is then warmed to ambient temperature, the blue paramagnetic chain product **2** was generated under formation of hydrogen. Moreover, another blue paramagnetic product **4** revealing the longest chain of $PHBH_2$ units to date was isolated as a minor product from the reaction solution of **3**.

The composition and the sequence of products obtained according to the reaction conditions applied show the elimination of the btmsa ligand from the complex **1** as the initial step of the reaction series. The subsequent formation of **3** indicates that a head-to-tail dehydro-oligomerization of phosphinoboranes occurs. The incomplete dehydrogenation of one of the phosphinoborane units in **3** suggest the intermediacy of the phosphido complex [$Cp_2TiH(PHBH_2NMe_3)$] (**A**) formed by oxidative addition of the P–H function of the remaining phosphinoborane ligand of the former **1**. A subsequent β-H elimination could proceed to give dihydrogen and transient [$Cp_2Ti(PHBHNMe_3)$] (**B**), which could be an intermediate of the formation of **3** besides **A**. By addition of a second equivalent of $PH_2BH_2NMe_3$ to **A**, hydrogen elimination and subsequent P–P bond formation occur to form the chain complexes **2** and **4**. P–H activation and consequent P–P bond formation were shown by Stephan to be the key pathways in the reaction between a Ti^{II} precursor and primary phosphines.[14]

Owing to the paramagnetic nature of **2**, **3**, and **4** (see below), only **1** could be characterized by NMR spectroscopy.[15] Moreover, the products **2** and **3**, which are stable at room temperature, reveal a molecular ion peak in the mass spectra and show in the IR spectra the expected B–H and P–H stretching frequencies. Compounds **2**–**4** are soluble in polar organic solvents such as THF or toluene, but should not be dissolved in halogenated solvents, owing to decomposition caused by the formation of [Cp_2TiX_2] (X = halogen). The remarkable structural features of all of the compounds have been unambiguously confirmed by X-ray diffraction studies.[15]

In the red crystalline compound **1** (Figure 1), owing to the steric demand of the additional $PH_2BH_2NMe_3$ ligand the dihedral angle between the two Cp ligands is 49.5(1)°, which is larger compared to the starting compound [Cp_2Ti(btmsa)] (46.6°).[16] The C20–C21 bond length of the coordinating acetylene is 1.287(4) Å, which is almost the average of a normal C–C triple bond (1.181 Å) and a usual C–C double bond (1.331 Å). In the starting material [Cp_2Ti(btmsa)], an almost equal C–C bond length of 1.283(6) Å is found.[16] The P1–B1 bond length of 1.981(4) Å in **1** corresponds to a single bond and is in good agreement with that of free $PH_2BH_2NMe_3$ (1.976(2) Å).[8] The Ti1–P1 distance is 2.592(1) Å and therefore only slightly longer than the reported Ti–P distance of 2.527(2) Å in [$Cp_2Ti(PMe_3)_2$].[17]

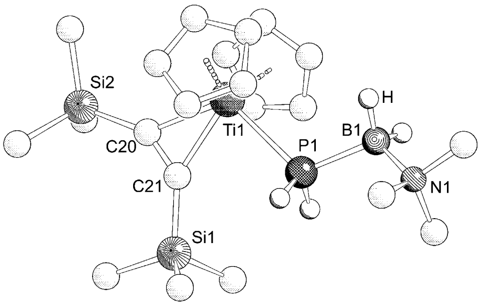


Figure 1. Molecular structure of **1** in the crystal. Carbon-bound hydrogen atoms are omitted for clarity.

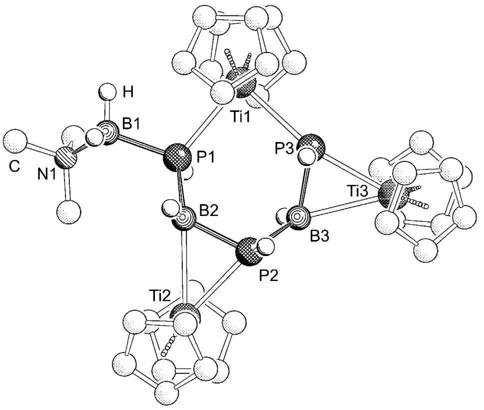


Figure 2. Molecular structure of **3** in the crystal. Carbon-bound hydrogen atoms are omitted for clarity.

The X-ray structure of the green trimerization product **3** (Figure 2) shows a six-membered metallacycle in a boat conformation, consisting of alternating phosphorus and boron atoms and one titanium atom (Ti1) of a titanocene fragment. Although each Group 13/15 atom has lost one hydrogen substituent compared to the starting compound $PH_2BH_2NMe_3$, the boranyl group BH_2NMe_3 at P1 remains intact. Furthermore, two titanocene fragments are coordinated side-on at the P2–B2 and P3–B3 bonds, which is the most striking feature of **3** and to the best of our knowledge the first reported of this kind.[18] Whereas the exocyclic P–B bond (1.990(3) Å) is in the same range as in the starting material,[8] the side-on coordinated bonds (1.936(3)–1.968(3) Å) are slightly shorter. The terminal Ti–P distances between Ti1 and P1 (2.6209(8) Å) or P3 (2.5960(7) Å) are almost equal and in a common range.[17] In the paramagnetic compound [$Cp_2Ti(PPh_2)(PMe_3)$] they are slightly longer (2.636(3) Å and 2.681(3) Å) than in **3**.[19] The side-on coordinated Ti–P distances (Ti2–P2 2.5224(8) Å, Ti3–P3 2.5462(7) Å) are slightly shorter than the discussed terminal bonds. In the complex [$Ti(ebthi)(P_2Ph_2)$] (ebthi = ethylene-1,2-bis(η^5-

4,5,6,7-tetrahydro-1-indenyl), containing a side-on coordinating P_2 unit, the Ti−P distances are in a similar range (2.525(2) Å).[20] Indeed, the Ti−B distances (Ti2−B2 2.702(3) Å, Ti3−B3 2.605(3) Å) are significantly longer than for known Ti−B bonds (for example, 2.335(5) Å in $[Cp_2Ti(HBO_2C_6H_4)_2]$[21] or 2.51(2) Å in the titanium carborane compound $[Cp^*(\eta^5\text{-}C_2B_9H_{11})Ti(N{=}CMe_2)(MeCN)]$).[22] However, the values are considerably smaller than the sum of the van der Waals radii (3.92 Å), indicating that Ti−B interaction is present.

The molecular structures of **2** (Figure 3) and **4** (Figure 4) are related and consist of chains of phosphinoborane units coordinated to titanocene fragments so that five-membered metallacycles, fused by a P−P bond, are formed. This bicyclic structure is reminiscent of the related organic compound bicyclo[3.3.0]octane. Every Group 13/15 atom has four substituents. However, in comparison to the starting compound, each boron atom retains its two hydrogen substituents, while each phosphorus atom has just one. The new generated P−P bonds (2.235(1) Å in **2** and 2.216(13) Å in **4**) are on the order of P−P single bond. In the structure of **4**, along with the anellated five-membered rings, two $\{Cp_2Ti\}$ units are coordinated to the neighboring B_2P_2 units, forming an overall tetracyclic structure with two central fused five-membered rings and two terminal anellated six-membered rings. The experimentally observed distances between the phosphorus and the boron atoms in **2** are all in a narrow range from 1.970(8) Å to 1.977(9) Å, which are typical for P−B single bonds; the corresponding distances in **4** reveal a wider distance variety (1.90(2) Å–1.981(15) Å) but are still in a common single bond length range.[8] The Ti−P bonds distances are in the typical range (**2**: 2.615(10) Å–2.679(11) Å and **4**: 2.498(10) Å–2.678(10) Å).[17] However, the P−B and P−Ti distances of **4** that deviate most compared to **2** are located in the Ti···H-containing six-membered rings.

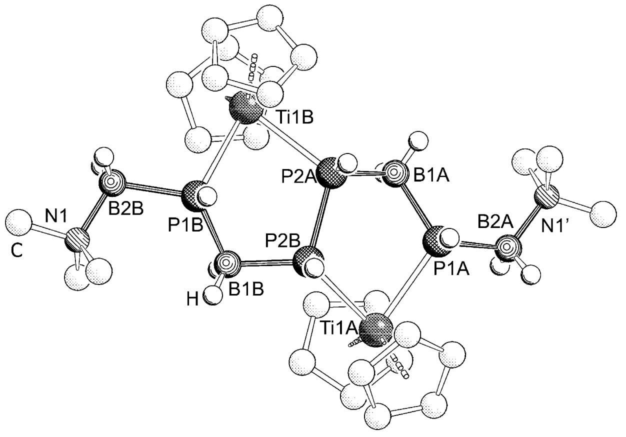


Figure 3. Molecular structure of **2**. Carbon-bound hydrogen atoms are omitted for clarity.

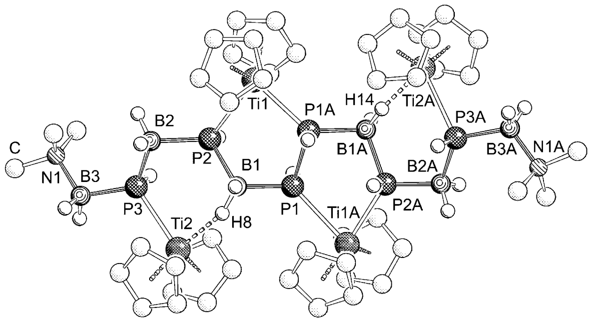


Figure 4. Molecular structure of **4**. Carbon-bound hydrogen atoms are omitted for clarity.

The magnetic properties of **2** and **3** were determined by the Evans method. The effective magnetic moment of **3** was found to be $\mu_{\text{eff}} = 2.48$, whereas for **2** a value of 1.81 was determined. As **4** was the minor product, it was not possible to isolate a pure sample of **4** to carry out magnetic measurements. Moreover, EPR investigations[15] were carried out for **2** and **3** as solids and in solutions, showing complex spectra with unresolved hyperfine splittings. They are reminiscent of $\{Cp_2Ti^{III}\}$ compounds containing phosphanido[19] and amidinate substituents[23] and are consistent with the density functional (DFT) calculations.[24]

To clarify the electronic structures, DFT calculations at the B3LYP/pVDZ level of theory have been executed.[15] It is interesting that **2** and **4** have a different orientation of P−H hydrogen atoms. In **2**, all of the hydrogen atoms are oriented on the one side of the heterocycle (Figure 3), while in **4** three are down and three up (Figure 4). Theoretical computations show that these orientations are the energetically most favorable form for each of the compounds. Alternative isomers are predicted to be by 9 and 6 $kJ\,mol^{-1}$ higher in energy for **2** and **4**, respectively.[15] For **2**, a triplet ground state with a spin density of 1.07 at each titanium atom has been calculated. Therefore, the formal oxidation state of both titanium atoms is +III. The next excited electronic state, a singlet state, is 101 $kJ\,mol^{-1}$ higher in energy. Complex **2** has a μ_{eff} value of 1.81 at 300 K. This value is not consistent with the expected value of 2.38 for two $S = 1/2$ centers. This discrepancy could be accounted for by antiferromagnetic exchange between the two Ti centers or by spin–orbit coupling. Computational results reveal a quartet ground state for **3**, which is very close in energy to the following excited doublet and sextet states ($\Delta E = 7$ and 14 $kJ\,mol^{-1}$). According to Mulliken atomic spin densities, in the doublet state the single unpaired electron is located at Ti1. The quartet ground state has one unpaired electron at Ti1 and one at Ti2, and the spin density of the third unpaired electron is split between Ti2 and B2. The sextet state features a single unpaired electron on each titanium atom, two additional unpaired electrons are equally shared by Ti2 and B2, and Ti3 and B3. The most striking feature of **3** is its structural flexibility: small energy changes (below 15 $kJ\,mol^{-1}$) between electronic states are accompanied by significant structural changes: for example, the Ti3−B3 distance varies from 3.101 Å in doublet state to 2.309 Å in the quartet and 2.748 Å in the sextet state. DFT calculations predict that the difference in energy between the triplet and the quintet state of **4** is very small (0.2 $kJ\,mol^{-1}$); they are essentially degenerate. Both in the triplet and quintet state, all four Ti atoms possess one unpaired electron each. For the quintet state

Table 1: Thermodynamic characteristics of gas-phase processes, calculated at the B3LYP/pVDZ level of theory.[a]

No.	Process	ΔE°_0[b]	ΔH°_{298}[c]	ΔS°_{298}[d]	ΔG°_{298}[e]
1	$[\mathrm{Cp_2Ti(btmsa)}] + \mathrm{PH_2BH_2NMe_3} \rightarrow \mathbf{1}$	−10.8	−2.1	−196.5	56.5
2	$\mathbf{1} \rightarrow [\mathrm{Cp_2Ti(PH_2BH_2NMe_3)}] + \mathrm{btmsa}$	21.0	13.6	212.9	−49.8
3	$[\mathrm{Cp_2Ti(btmsa)}] + \mathrm{PH_2BH_2NMe_3} \rightarrow [\mathrm{Cp_2Ti(PH_2BH_2NMe_3)}] + \mathrm{btmsa}$	10.2	11.6	16.3	6.7
4	$2\,\mathbf{1} + 2\,\mathrm{PH_2BH_2NMe_3} \rightarrow \mathbf{2} + 2\,\mathrm{H_2} + 2\,\mathrm{NMe_3} + 2\,\mathrm{btmsa}$	−115.5	−152.7	363.8	−261.1
5	$3\,\mathbf{1} \rightarrow \mathbf{3} + 2.5\,\mathrm{H_2} + 2\,\mathrm{NMe_3} + 3\,\mathrm{btmsa}$	203.0	139.9	814.0	−102.8
6	$4\,\mathbf{1} + 2\,\mathrm{PH_2BH_2NMe} \rightarrow \mathbf{4} + 3\,\mathrm{H_2} + 2\,\mathrm{NMe_3} + 4\,\mathrm{btmsa}$	−143.6	−216.0	804.3	−455.8
7	$\mathbf{2} + 2\,\mathbf{1} \rightarrow \mathbf{4} + 2\,\mathrm{NMe_3} + 2\,\mathrm{btmsa} + \mathrm{H_2}$	−28.1	−63.3	440.5	−194.7
8	$\mathbf{3} + \mathbf{1} + 2\,\mathrm{PH_2BH_2NMe} \rightarrow \mathbf{4} + 0.5\,\mathrm{H_2} + \mathrm{btmsa}$	−346.6	−355.9	−9.7	−353.0

[a] Data are given for compounds in their respective ground states (see the Supporting Information). [b] Reaction energies ΔE°_0 [kJ mol^{-1}]. [c] Standard enthalpies ΔH°_{298} [kJ mol^{-1}]. [d] Reaction entropies ΔS°_{298} [J mol^{-1} K^{-1}]. [e] Gibbs energies ΔG°_{298} [kJ mol^{-1}].

Mulliken atomic spin densities are +1.06 for central and +1.08 for terminal titanium atoms, while in the triplet state one of the terminal titanium atoms has Mulliken atomic spin density −1.08. Owing to low energy differences between electronic states for the gaseous compounds, it is expected that packing may alter the ground electronic state of the molecule in the solid compounds **3** and **4**.

Thermodynamic characteristics for the major reactions for the formation of compounds **1**–**4** are summarized in Table 1. Formation of **1** from [Cp$_2$Ti(btmsa)] and $\mathrm{PH_2BH_2NMe_3}$ is exothermic by only 2 kJ mol^{-1} and entropically unfavorable, suggesting that **1** should be stable only at low temperatures in excess of $\mathrm{PH_2BH_2NMe_3}$, as was found experimentally. Note that dissociation of **1** with elimination of $\mathrm{PH_2BH_2NMe_3}$ is slightly more preferable than elimination of btmsa (process 2), although the Gibbs energy difference between two dissociation channels (process 3) is small (6.7 kJ mol^{-1}), suggesting that both reactions may occur simultaneously. Formation of **2** from **1** upon addition of $\mathrm{PH_2BH_2NMe_3}$ (process 4) is exothermic by 153 kJ mol^{-1}. In contrast, formation of **3** from **1** (process 5) is endothermic by 140 kJ mol^{-1}, but the process is very favorable by entropy, which results in substantial negative Gibbs energy of −103 kJ mol^{-1}. Thus, formation of **3** is entropically favorable. In contrast, formation of **4** from **1** and $\mathrm{PH_2BH_2NMe}$ (process 6) is exothermic by 216 kJ mol^{-1}.

Based on these theoretical predictions, from the thermodynamic point of view, low-temperature conditions should favor formation of **4** rather than **3**. Easy dissociation of **1** with $\mathrm{PH_2BH_2NMe_3}$ evolution may provide the excess of $\mathrm{PH_2BH_2NMe_3}$ for process 6 (formation of **4**). Alternative formation of **4** by addition of two molecules of **1** to **2** (process 7) is exothermic by 63 kJ mol^{-1}, and favorable by entropy. However, mechanistic considerations show that this reaction is not expected to be plausible. To form **4**, **1** should be added to different sides of **2** (spatially separated centers), but the process requires elimination of only one mole of dihydrogen (two spatially separated hydrogen atoms). A dimer-involved mechanism, similar to one proposed recently for the hydrogen splitting,[12] may be operational in this case but it is highly unlikely. Thus, formation of **4** by direct reaction of **2** with excess of **1** is doubtful. Formation of **4** from **3**, **1**, and excess of $\mathrm{PH_2BH_2NMe_3}$ (process 8) is very exothermic. Such transformation can be facilitated by aforementioned structural flexibility of **3** in a low-lying excited state. This is consistent with the experimental observation of **4** in the mother liquor of **3**.

It is of interest to compare the coordination of phosphinoboranes on early and late transition metals. An alkene-type side-on coordination of substituted phosphinoboranes on Pt has been recently reported by Bourissou et al.[18] The different nature of the interaction between B–P and early (Ti) or rather late (Pt) transition metals can be seen from the experimental bond distances. For example, experimental Pt–B distances are shorter than Pt–P bonds,[18] while for **3** both Ti–B distances are longer than Ti–P, despite much smaller radii of boron atom compared to phosphorus. Moreover, experimental Pt–B distance (2.23 Å)[18] is much shorter than experimental Ti–B distances in **3** (2.61 Å and 2.70 Å). This trend is in contrast to the almost equal radii of Ti and Pt atoms. Both observations indicate different bonding patterns in Ti and Pt compounds. MO analysis of **3** at experimental geometry further corroborates these conclusions.[15] In contrast to the late transition metal Pt, there is no interaction between the B–P fragment as a whole unit and the Ti atom. Major contribution comes from the orbital overlap from P2 and P3 atoms to d orbitals of Ti2 and Ti3. There is also a similar overlap of d orbitals of Ti2 and Ti3 with B2 and B3 atoms, which results in a three-center P–Ti–B interaction. Highest SOMOs are predominantly d orbitals of Ti2 and Ti3.

The results have shown that the phosphinoborane $\mathrm{PH_2BH_2NMe_3}$ is an excellent ethylene-like monomer to study its stepwise aggregation on titanium complex centers to form long unprecedented phosphinoborane catenae, which are reminiscent of organic chain molecules. In contrast to ethylene polymerization, the inorganic analogues oligomerize by an additional dehydrocoupling, leading to P–P coupled oligomers in polynuclear complexes. The chosen titanocene shows to be an ideal starting material for this study, as on one hand it monitors the initial step of the aggregation by forming the simple adduct **1**. On the other hand, the obtained chains are stabilized by formed five- or six-membered titanaheterocycles, a principle that seems to be the key to isolate the novel products. Moreover, the formed products are open-shell species revealing the titanium-complex-induced electronic redistribution processes during the dehydrogenation couplings. Further study of the oligomerization of these phosphinoborane monomers by different transition metals and under various conditions will lead to novel insight into the ongoing processes.

Received: December 4, 2012
Revised: January 22, 2013
Published online: April 10, 2013

Keywords: boron · inorganic oligomers · oligomerization · phosphorus · titanium

---

[1] a) J. E. Mark, H. R. Allcock, R. West, *Inorganic Polymers, 2nd ed.*, Oxford University Press, Oxford, **2005**; b) V. Chandrasekhar, *Inorganic and Organometallic Polymers*, Springer, Berlin, **2005**; c) Z. Liu, L. Song, S. Zhao, J. Huang, L. Ma, J. Zhang, J. Lou, P. M. Ajayan, *Nano Lett.* **2011**, *11*, 2032; d) I. Manners, *Angew. Chem.* **1996**, *108*, 1712–1731; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1602–1621.

[2] a) Z. Liu, T. B. Marder, *Angew. Chem.* **2008**, *120*, 248–250; b) V. Pons, R. T. Baker, *Angew. Chem.* **2008**, *120*, 9742–9744; *Angew. Chem. Int. Ed.* **2008**, *47*, 9600–9602; c) F. H. Stephens, V. Pons, R. T. Baker, *Dalton Trans.* **2007**, 2613–2626; d) G. Alcaraz, S. Sabo-Etienne, *Angew. Chem.* **2010**, *122*, 7326–7335; *Angew. Chem. Int. Ed.* **2010**, *49*, 7170–7179; e) M. E. Sloan, A. Staubitz, T. J. Clark, C. A. Russell, G. C. Lloyd-Jones, I. Manners, *J. Am. Chem. Soc.* **2010**, *132*, 3831–3841; f) A. Staubitz, A. P. M. Robertson, I. Manners, *Chem. Rev.* **2010**, *110*, 4023–4078.

[3] a) A. Staubitz, A. Presa Soto, I. Manners, *Angew. Chem.* **2008**, *120*, 6308–6311; *Angew. Chem. Int. Ed.* **2008**, *47*, 6212–6215; b) J. R. Vance, A. P. M. Robertson, K. Lee, I. Manners, *Chem. Eur. J.* **2011**, *17*, 4099–4103; c) R. Dallanegra, A. P. M. Robertson, A. B. Chaplin, I. Manners, A. S. Weller, *Chem. Commun.* **2011**, *47*, 3763–3765; d) A. Staubitz, M. E. Sloan, A. P. M. Robertson, A. Friedrich, S. Schneider, P. J. Gates, J. Schmedt auf der Günne, I. Manners, *J. Am. Chem. Soc.* **2010**, *132*, 13332–13345; e) B. L. Dietrich, K. I. Goldberg, D. M. Heinekey, T. Autrey, J. C. Linehan, *Inorg. Chem.* **2008**, *47*, 8583–8585; f) H. C. Johnson, A. P. M. Robertson, A. B. Chaplin, L. J. Sewell, A. L. Thompson, M. F. Haddow, I. Manners, A. S. J. Weller, *J. Am. Chem. Soc.* **2011**, *133*, 11076–11079.

[4] A. D. Sutton, A. K. Burrell, D. A. Dixon, E. B. Garner III, J. C. Gordon, T. Nakagawa, K. C. Ott, J. P. Robinson, M. Vasiliu, *Science* **2011**, *331*, 1426–1429.

[5] a) V. Pons, R. T. Baker, N. K. Szymczak, D. H. Heldebrant, J. C. Linehan, M. H. Matus, D. J. Grant, D. A. Dixon, *Chem. Commun.* **2008**, 6597–6599; b) W. J. Shaw, J. C. Linehan, N. K. Szymczak, D. J. Heldebrant, C. Yonker, D. M. Camaioni, *Angew. Chem.* **2008**, *120*, 7603–7606; *Angew. Chem. Int. Ed.* **2008**, *47*, 7493–7496.

[6] H. Schmidbaur, T. Wimmer, J. Lachmann, G. Müller, *Chem. Ber.* **1991**, *124*, 275–278.

[7] J.-M. Denis, H. Forintos, H. Szelke, L. Toupet, T.-N. Pham, P.-J. Madec, A.-C. Gaumonz, *Chem. Commun.* **2003**, 54–55.

[8] K.-C. Schwan, A. Timoshkin, M. Zabel, M. Scheer, *Chem. Eur. J.* **2006**, *12*, 4900–4908; for the precursor compounds cf.: U. Vogel, P. Hoemensch, K.-Ch. Schwan, A. Y. Timoshkin, M. Scheer, *Chem. Eur. J.* **2003**, *9*, 515–519.

[9] Only theoretical calculations give insight into the bonding situation of such monomers: a) T. L. Allen, W. H. Fink, *Inorg. Chem.* **1992**, *31*, 1703–1705; b) T. L. Allen, A. C. Scheiner, H. F. Schaefer III, *Inorg. Chem.* **1990**, *29*, 1930–1936; c) M. B. Coolidge, W. T. Borden, *J. Am. Chem. Soc.* **1990**, *112*, 1704–1706; d) H.-J. Himmel, *Dalton Trans.* **2003**, 3639–3649; e) H.-J. Himmel, *Eur. J. Inorg. Chem.* **2003**, 2153–2163.

[10] C. Marquardt, A. Stauber, M. Scheer, unpublished results.

[11] a) H. Dorn, R. A. Singh, J. A. Massey, A. J. Lough, I. Manners, *Angew. Chem.* **1999**, *111*, 3540–3543; *Angew. Chem. Int. Ed.* **1999**, *38*, 3321–3323; b) C. A. Jaska, I. Manners, *J. Am. Chem. Soc.* **2004**, *126*, 1334–1335; c) C. A. Jaska, I. Manners, *J. Am. Chem. Soc.* **2004**, *126*, 9776–9785; d) H. Dorn, R. A. Singh, J. A. Massey, J. M. Nelson, C. A. Jaska, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **2000**, *122*, 6669–6678; e) T. J. Clark, J. M. Rodezno, S. B. Clendenning, S. Aouba, P. M. Brodersen, A. J. Lough, H. E. Ruda, I. Manners, *Chem. Eur. J.* **2005**, *11*, 4526–4534.

[12] a) V. V. Burlakov, U. Rosenthal, P. V. Petrovskii, V. B. Shur, M. E. Vol'pin, *Organomet. Chem. USSR* **1988**, *1*, 953–954; b) U. Rosenthal, A. Ohff, M. Michalik, H. Görls, V. V. Burlakov, V. B. Shur, *Angew. Chem.* **1993**, *105*, 1228–1230; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1193–1195; c) V. V. Burlakov, A. V. Polyakov, A. I. Yanovsky, Y. T. Struchkov, V. B. Shur, M. E. Vol'pin, U. Rosenthal, H. Görls, *J. Organomet. Chem.* **1994**, *476*, 197–206; d) J. Hiller, U. Thewalt, M. Polasek, L. Petrusova, V. Varga, P. Sedmera, K. Mach, *Organometallics* **1996**, *15*, 3752–3759; e) T. Beweries, S. Hansen, M. Kessler, M. Klahn, U. Rosenthal, *Dalton Trans.* **2011**, *40*, 7689–7692.

[13] J. Y. C. Chen, A. A. Martí, N. J. Turro, K. Komatsu, Y. Murata, R. G. Lawler, *J. Phys. Chem. B* **2010**, *114*, 14689–14695.

[14] a) J. D. Masuda, A. J. Hoskin, T. W. Graham, C. Beddie, M. C. Fermin, N. Etkin, D. W. Stephan, *Chem. Eur. J.* **2006**, *12*, 8696–8707; b) J. Ho, D. W. Stephan, *Inorg. Chem.* **1994**, *33*, 4595–4597.

[15] See the Supporting Information.

[16] U. Rosenthal, V. V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg, *Organometallics* **2003**, *22*, 884–900.

[17] L. B. Kool, M. D. Rausch, H. G. Alt, M. Herberhold, U. Thewalt, B. Wolf, *Angew. Chem.* **1985**, *97*, 425–426; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 394–401.

[18] For the coordination of a substituted phosphinoborane on a late transition metal, see: A. Amgoune, S. Ladeira, K. Miqueu, D. Bourissou, *J. Am. Chem. Soc.* **2012**, *134*, 6560–6563; at early transition metals cf.: H. Helten, B. Dutta, J. R. Vance, M. E. Sloan, M. F. Haddow, S. Sproules, D. Collison, G. R. Whittell, G. C. Lloyd-Jones, I. Manners, *Angew. Chem.* **2013**, *125*, 455–458; *Angew. Chem. Int. Ed.* **2013**, *52*, 437–440.

[19] D. G. Dick, D. W. Stephan, *Organometallics* **1991**, *10*, 2811–2816.

[20] S. Xin, H. G. Woo, J. F. Harrod, E. Samuel, A.-M. Lebuis, *J. Am. Chem. Soc.* **1997**, *119*, 5307–5313.

[21] C. N. Muhoro, X. He, J. F. Hartwig, *J. Am. Chem. Soc.* **1999**, *121*, 5033–5046.

[22] C. Kreuder, R. F. Jordan, H. Zhang, *Organometallics* **1995**, *14*, 2993–3001.

[23] O. Theilmann, M. Ruhmann, A. Villinger, A. Schulz, W. W. Seidel, K. Kaleta, T. Beweries, P. Arndt, U. Rosenthal, *Angew. Chem.* **2010**, *122*, 9469–9473; *Angew. Chem. Int. Ed.* **2010**, *49*, 9282–9285.

[24] For difficulties involving EPR spectroscopy on triplet systems, see: R. Krieger, J. Voitländer, *Z. Naturforsch. A* **1972**, *27*, 1082–1093.