



Non-metal-templated approaches to bis(borane) derivatives of macrocyclic dibridgehead diphosphines via alkene metathesis

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Abstract

Two routes to the title compounds are evaluated. First, a ca. 0.01 M CH₂Cl₂ solution of H₃B·P((CH₂)₆CH=CH₂)₃ (1·BH₃) is treated with 5 mol % of Grubbs' first generation catalyst (0 °C to reflux), followed by H₂ (5 bar) and Wilkinson's catalyst (55 °C). Column chromatography affords H₃B·P(*n*-C₈H₁₇)₃ (1%), H₃B·P((CH₂)₁₃CH₂)(*n*-C₈H₁₇) (8%; see text for tie bars that indicate additional phosphorus–carbon linkages, which are coded in the abstract with italics), H₃B·P((CH₂)₁₃CH₂)((CH₂)₁₄P((CH₂)₁₃CH₂))·BH₃ (6·2BH₃, 10%), *in,out*-H₃B·P((CH₂)₁₄)₃·BH₃ (*in,out*-2·2BH₃, 4%) and the stereoisomer (*in,in/out,out*)-2·2BH₃ (2%). Four of these structures are verified by independent syntheses. Second, 1,14-tetradecanedioic acid is converted (reduction, bromination, Arbuzov reaction, LiAlH₄) to H₂P((CH₂)₁₄)PH₂ (**10**; 76% overall yield). The reaction with H₃B·SMe₂ gives **10**·2BH₃, which is treated with *n*-BuLi (4.4 equiv) and Br(CH₂)₆CH=CH₂ (4.0 equiv) to afford the tetraalkenyl precursor (H₂C=CH(CH₂)₆)₂(H₃B)P((CH₂)₁₄)P(BH₃)((CH₂)₆CH=CH₂)₂ (**11**·2BH₃; 18%). Alternative approaches to **11**·2BH₃ (e.g., via **11**) were unsuccessful. An analogous metathesis/hydrogenation/chromatography sequence with **11**·2BH₃ (0.0010 M in CH₂Cl₂) gives 6·2BH₃ (5%), *in,out*-2·2BH₃ (6%), and (*in,in/out,out*)-2·2BH₃ (7%). Despite the doubled yield of 2·2BH₃, the longer synthesis of **11**·2BH₃ vs 1·BH₃ renders the two routes a toss-up; neither compares favorably with precious metal templated syntheses.

Introduction

We have found that a variety of metal complexes with *trans*-phosphine ligands of the formula P((CH₂)_{*m*}CH=CH₂)₃ (**1**; *m* = 4–14) undergo threefold interligand ring closing alkene

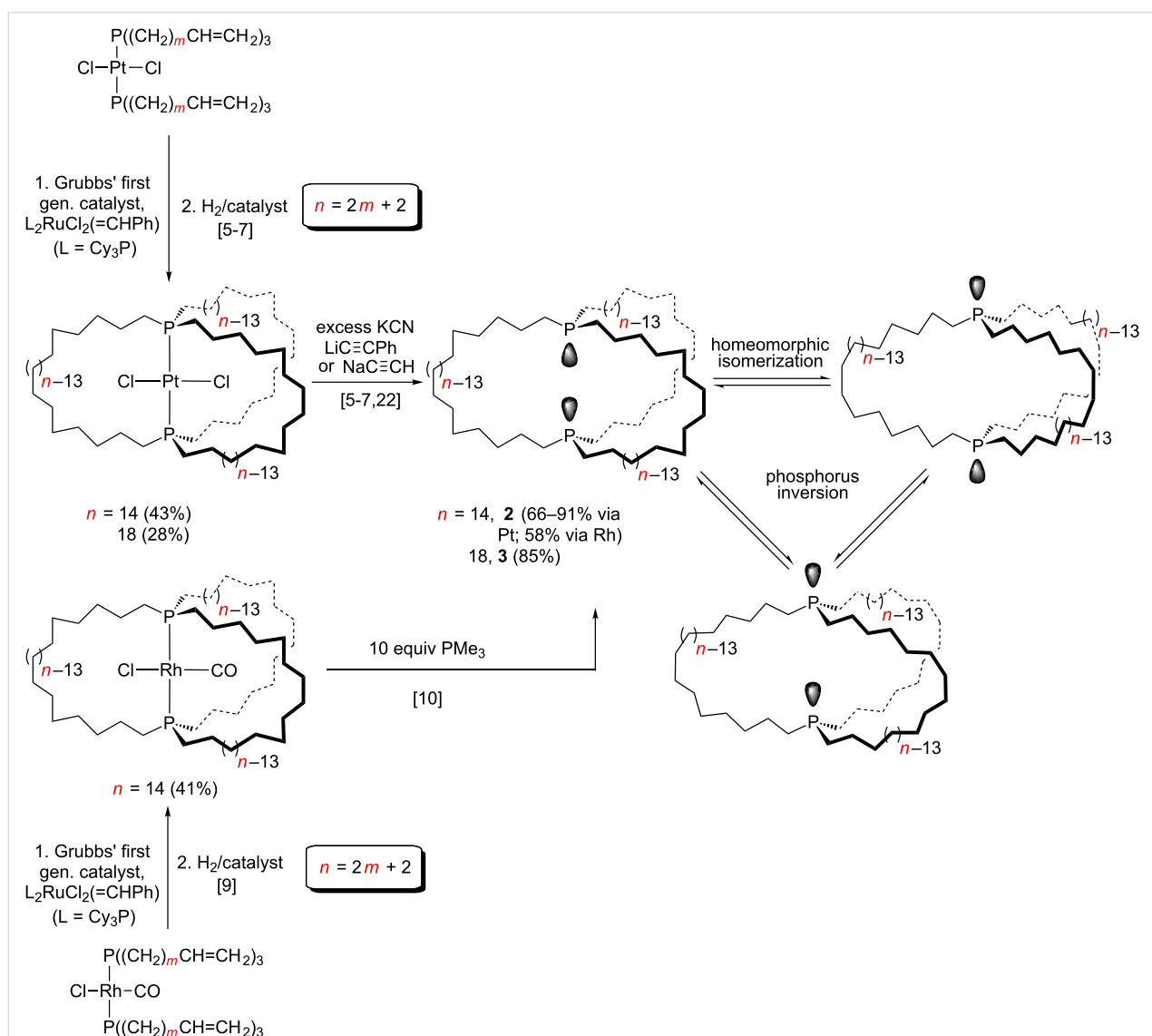
metatheses to give, after hydrogenations, metal complexes of *in,in* isomers of macrocyclic dibridgehead diphosphines [1–13]. Representative examples with square planar complexes are

shown in Scheme 1. Analogous sequences with trigonal bipyramidal substrates proceed in somewhat higher overall yields, as analyzed elsewhere [1–4]. Setaka has developed a similar chemistry in which the phosphorus atoms are replaced by silicon and the metal fragment by *p*-phenylene (*p*-C₆H₄) or related aromatic moieties [14–19]. These types of compounds are viewed as promising candidates for molecular gyroscopes [14–21].

We subsequently developed an interest in the free dibridgehead diphosphine ligands P((CH₂)_{*n*})₃P (*n* = 14, **2**; 18, **3**), prompted in part by the unexpected discovery of the facile demetalations shown in Scheme 1 [5,6,10,22]. Such compounds were previously known only for much smaller ring sizes (*n* ≤ 4) [23]. These reactions require excesses of certain nucleophiles, and the mechanisms remain under study. The yields are quite good,

but the routes are stoichiometric in precious metals. Although the metals can be recovered as species such as K₂Pt(CN)₄ or RhCl(PMe₃)₃, we have nonetheless sought to develop more economical protocols.

The analogous Fe(CO)₃ adducts are easily prepared [1–4], but in efforts to date it has not been possible to efficiently remove the dibridgehead diphosphine ligands from the low cost iron fragment. Oxidations that lead to the corresponding dibridgehead diphosphine dioxides (O=P((CH₂)_{*n*})₃P=O) have exhibited promise, but purification has been problematic [24]. Indeed, phosphine oxides are everyday precursors to phosphines, so we have considered various non-metal-templated routes to **2**·2(=O), **3**·2(=O), and related species. However, as described in the discussion section, the yields have not been competitive [25].



Scheme 1: Syntheses of gyroscope like platinum and rhodium complexes and dibridgehead diphosphines derived therefrom.

Another preliminary point concerns the ability of macrocyclic dibridgehead diphosphorus compounds to exhibit *in/out* isomerism [26]. As shown in Scheme 1, there are three limiting configurations for **2** and **3**: *in,in*, *out,out*, and *in,out* (identical to *out,in*). The first two, as well as the degenerate *in,out* pair, can rapidly interconvert by a process termed homeomorphic isomerization [26,27], which is akin to turning the molecules inside out. Readers are referred to earlier publications in this series for additional details [22,25,28–30]. Interconversions between the *in,in/out,out* and *in,out/out,in* manifolds require phosphorus inversion and temperatures considerably in excess of 100 °C.

In this paper, we describe two non-metal-templated approaches to **2** that are based upon metatheses of phosphine boranes of alkene containing phosphines. The first involves the monophosphorus precursor $\text{H}_3\text{B}\cdot\text{P}((\text{CH}_2)_6\text{CH}=\text{CH}_2)_3$ (**1**·BH₃) [31], and the second a diphosphorus precursor in which one of the methylene chains linking the two phosphorus atoms has already been installed. The advantages and limitations of each are analyzed in detail. Some of the results (Scheme 2) have appeared in the supporting information of a preliminary communication [28], and others in a dissertation [32].

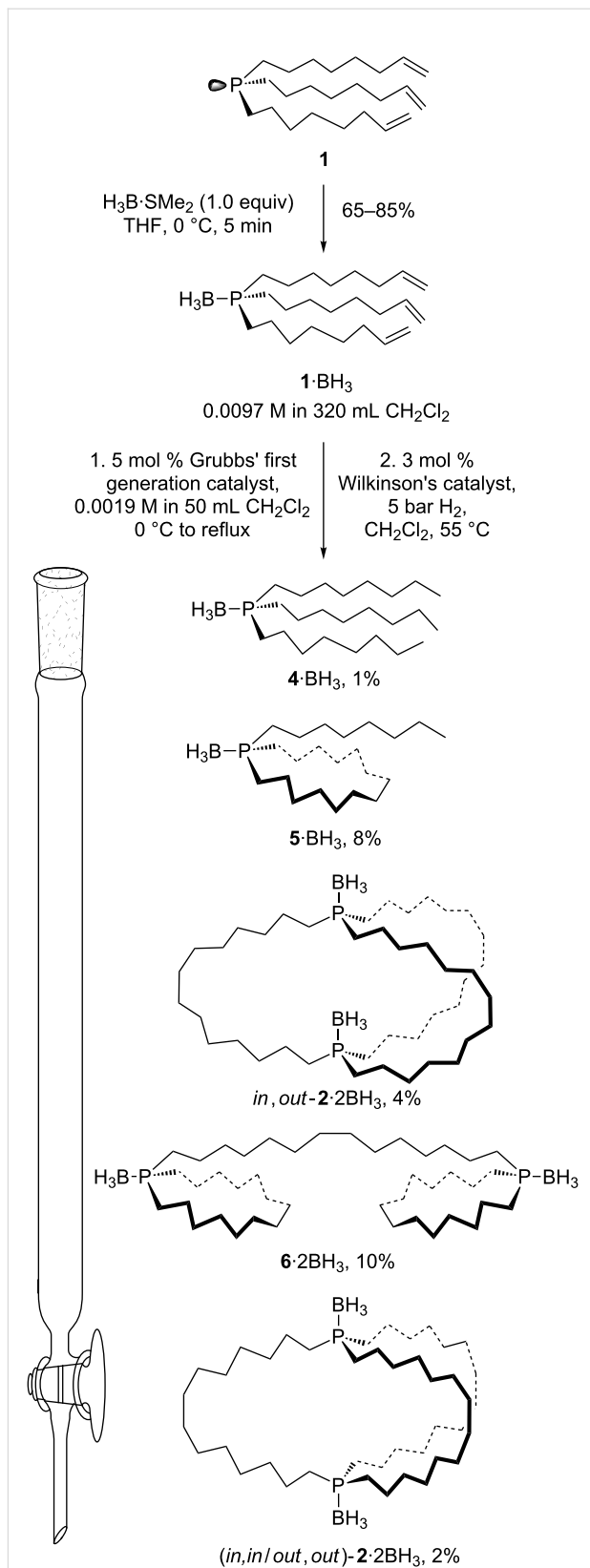
Results

1. Monophosphorus precursors

As reported earlier [31], the alkene containing phosphine $\text{P}((\text{CH}_2)_6\text{CH}=\text{CH}_2)_3$ (**1**) can be prepared in 87% yield from the reaction of PCl_3 and $\text{MgBr}(\text{CH}_2)_6\text{CH}=\text{CH}_2$. Following the addition of $\text{H}_3\text{B}\cdot\text{SMe}_2$, the phosphine borane **1**·BH₃ can be isolated in 65–85% yields [31], as shown in Scheme 2. It is critical to avoid an excess of $\text{H}_3\text{B}\cdot\text{SMe}_2$, as this brings the C=C units into play. In fact, when substoichiometric amounts of $\text{H}_3\text{B}\cdot\text{SMe}_2$ are added to THF solutions of purified **1**·BH₃, gels immediately form.

A ca. 0.01 M CH_2Cl_2 solution of **1**·BH₃ and a ca. 0.002 M CH_2Cl_2 solution of Grubbs' first generation catalyst (3 mol %) were combined at 0 °C. The mixture was warmed to room temperature, and a second charge of Grubbs' catalyst added (2 mol %). The sample was refluxed, and then filtered through silica gel. The filtrate was concentrated and treated with H₂ (5 bar) and Wilkinson's catalyst (55 °C). The mixture was taken to dryness and the residue tediously chromatographed on a silica gel column. Numerous fractions were collected and analyzed by TLC. The mass recovery from the column was 33% of theory (for complete metathesis).

More than ten mobile products could be discerned, but only five could be isolated in pure form and ultimately identified. These are described in order of elution. Each was analyzed by NMR (¹H, ³¹P{¹H}, ¹³C{¹H}; always CDCl₃) and IR spectroscopy,



Scheme 2: Synthesis and alkene metathesis of the monophosphorus precursor **1**·BH₃.

mass spectrometry, and microanalysis, as summarized in the experimental section. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra proved to be most diagnostic of structure, and were analyzed in detail. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were all very similar (broad apparent doublets due to phosphorus boron coupling).

First, traces of a colorless oil were obtained. The ^1H NMR spectrum showed a characteristic triplet at 0.83 ppm consistent with a terminal methyl group. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum exhibited eight signals, two of which were phosphorus coupled doublets. One of the singlets (14.0 ppm) was typical of a terminal methyl group. Based upon these data, and the integration of the ^1H NMR spectrum, the oil was assigned as the hydrogenated phosphine borane $\text{H}_3\text{B}\cdot\text{P}(n\text{-C}_8\text{H}_{17})_3$ (**4**· BH_3), a known compound [33]. The yield was only 1%.

Next, another colorless oil eluted. The ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra again exhibited signals characteristic of a methyl group (0.86 ppm, t; 14.0 ppm, s). Integration of the ^1H NMR spectrum established a 14:1 area ratio for the methylene (1.62–1.19 ppm) and methyl signals. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum featured one set of seven signals and another set of eight with an intensity ratio of approximately 2:1. The less intense set resembled the signals arising from the *n*-octyl groups in **4**· BH_3 . The more intense set was very similar to the signals arising from the cyclic $\text{H}_3\text{B}\cdot\text{P}(\text{CH}_2)_{13}\text{CH}_2$ substructures of **6**· 2BH_3 (described below) and a phosphine borane $\text{H}_3\text{B}\cdot\text{PPh}((\text{CH}_2)_{13}\text{CH}_2)$ reported earlier [34]. The mass spectrum exhibited an intense ion at m/z 340 (5^+ , 93%), and no ions of higher mass. Hence, the oil was assigned

as the monocyclic intramolecular metathesis product $\text{H}_3\text{B}\cdot\text{P}((\text{CH}_2)_{13}\text{CH}_2)(n\text{-C}_8\text{H}_{17})$ (**5**· BH_3 ; see Scheme 2). The yield was 8%.

The third product was also a colorless oil. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum exhibited seven signals, three of which were phosphorus coupled doublets (second spectrum from top, Figure 1). Analogous coupling patterns are found with the free dibridgehead diphosphines **2** and **3** in Scheme 1. No NMR signals diagnostic of methyl groups were present, and further analysis is presented along with that for an isomer below.

A white powder was obtained next. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum exhibited fourteen signals, half of which were approximately twice as intense as the others. Two signals of each set exhibited phosphorus coupling. The overall pattern was quite similar to those shown by metal complexes with *cis* or *trans* coordinating diphosphine ligands of the formula $\text{P}(\text{CH}_2)_{13}\text{CH}_2((\text{CH}_2)_{14})\text{P}(\text{CH}_2)_{13}\text{CH}_2$ (**6**) [6,7,12,13,35]. This suggested the diphosphine diborane structure **6**· 2BH_3 (see Scheme 2), which is derived from one metathesis involving alkenyl moieties on different phosphorus atoms, and two metatheses of alkenyl moieties on identical phosphorus atoms. The yield was 10%. The structure has been confirmed by an independent synthesis (detachment of the diphosphine from a platinum complex followed by borane addition) and a crystal structure [6].

Finally, another white powder was obtained. As with the previous oil isolated above, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum exhib-

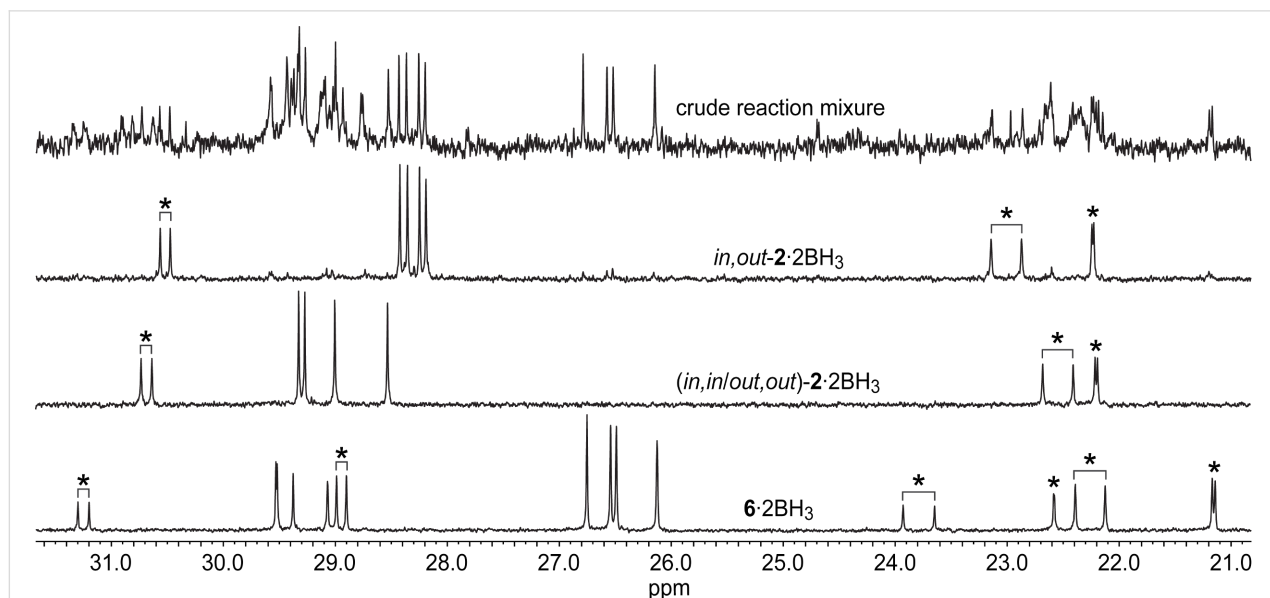


Figure 1: The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (CDCl_3 , 100 MHz) of *in,out*-**2**· 2BH_3 , (*in,in/out,out*)-**2**· 2BH_3 , **6**· 2BH_3 , and the crude reaction mixture after hydrogenation from Scheme 5 (top); doublets are marked with an asterisk.

ited seven signals, three of which were phosphorus coupled doublets (third spectrum from top, Figure 1). Both spectra were consistent with dibridgehead diphosphine diboranes $\text{H}_3\text{B}\cdot\text{P}((\text{CH}_2)_{14})_3\text{P}\cdot\text{BH}_3$ ($2\cdot 2\text{BH}_3$) derived from threefold intermolecular metatheses of $1\cdot\text{BH}_3$. Based upon independent syntheses from the dibridgehead diphosphines **2** obtained in Scheme 1 [6], they were assigned as *in,out*- $2\cdot 2\text{BH}_3$ (4%) and the stereoisomer (*in,in/out,out*)- $2\cdot 2\text{BH}_3$ (2%), as shown in Scheme 2. The depiction of the latter as an *out,out* (vs *in,in*) isomer in Scheme 2 is arbitrary, but represents the form found in a confirming crystal structure [6].

Parallel reactions were conducted with Grubbs' second generation catalyst and the nitro-Grela catalyst [36]. However, the combined yields of **2** diminished.

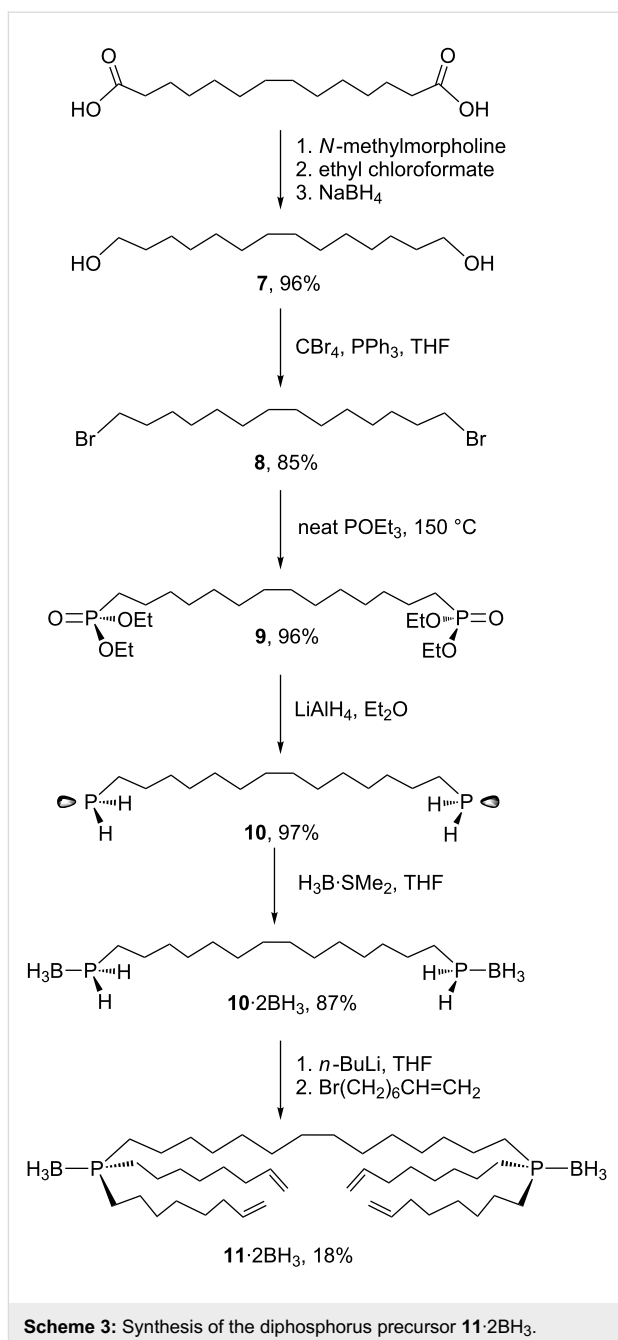
2. Diphosphorus precursors

Since the yields of the cage like diphosphine diboranes $2\cdot 2\text{BH}_3$ in Scheme 2 were – as expected – very low, alternative strategies were considered. The poor mass balance was attributed, at least in part, to the formation of oligomeric products that were retained on the column. Improvements might be expected from precursors in which one of the methylene chains tethering the two phosphorus atoms was pre-formed. Thus, we set out to prepare a tetraalkenyl metathesis precursor as shown in Scheme 3.

The first step, a previously reported reduction of commercial 1,14-tetradecanedioic acid to 1,14-tetradecanediol (**7**) [37], was followed by an Appel reaction to give 1,14-dibromotetradecane (**8**) [38–43]. An Arbuzov reaction then afforded the diphosphonate $(\text{EtO})_2\text{P}((\text{CH}_2)_{14})\text{P}(=\text{O})(\text{OEt})_2$ (**9**) [44]. Subsequent reduction with LiAlH_4 gave the diprimary diphosphine $\text{H}_2\text{P}((\text{CH}_2)_{14})\text{PH}_2$ (**10**) in 76% yield from **7** as a foul smelling white powder.

It has been shown that borane adducts of primary phosphines can be doubly deprotonated, and that the resulting phosphorus dianions can be bis(alkylated) [45–47]. Thus, the diphosphine **10** and $\text{H}_3\text{B}\cdot\text{SMe}_2$ were reacted to give the diphosphine diborane $\text{H}_2(\text{H}_3\text{B})\text{P}((\text{CH}_2)_{14})\text{P}(\text{BH}_3)\text{H}_2$ ($10\cdot 2\text{BH}_3$) as a white solid in 87% yield. A subsequent reaction with *n*-BuLi (4.4 equiv) and $\text{Br}(\text{CH}_2)_6\text{CH}=\text{CH}_2$ (4.0 equiv) gave the tetraalkenyl target $(\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_6)_2(\text{H}_3\text{B})\text{P}((\text{CH}_2)_{14})\text{P}(\text{BH}_3)((\text{CH}_2)_6\text{CH}=\text{CH}_2)_2$ ($11\cdot 2\text{BH}_3$), but in only 18% yield.

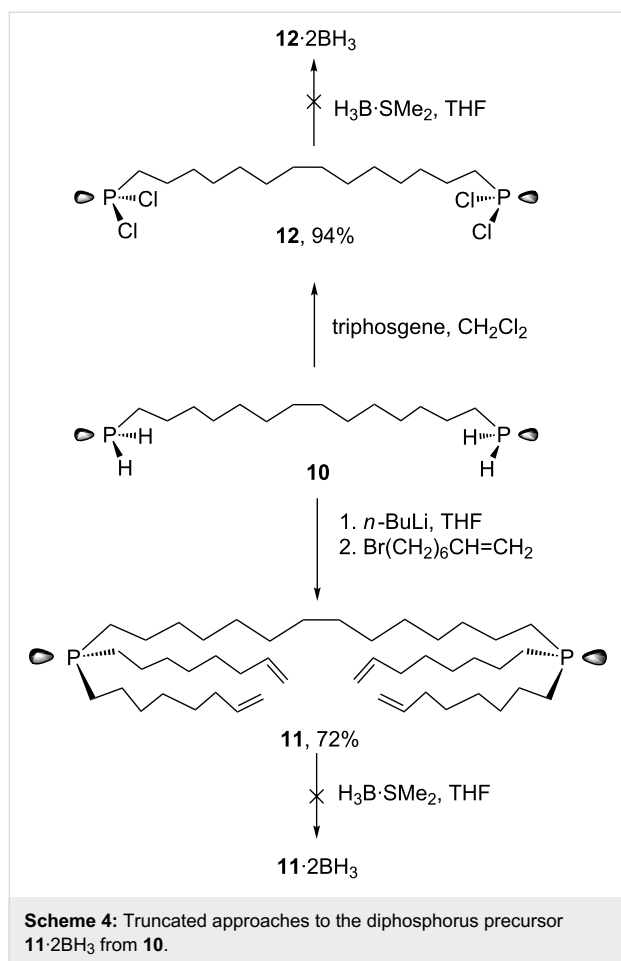
Accordingly, two alternative routes to $11\cdot 2\text{BH}_3$ were considered. The initial step for the first is depicted in Scheme 4. Primary phosphines can be doubly deprotonated, analogously to borane adducts, and the phosphorus dianions subsequently bis(alkylated) [34,48]. Thus, **10** was treated with *n*-BuLi



Scheme 3: Synthesis of the diphosphorus precursor $11\cdot 2\text{BH}_3$.

(4.1 equiv) and then $\text{Br}(\text{CH}_2)_6\text{CH}=\text{CH}_2$ (4.0 equiv). Work-up gave the target compound $(\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_6)_2\text{P}((\text{CH}_2)_{14})\text{P}((\text{CH}_2)_6\text{CH}=\text{CH}_2)_2$ (**11**) in 72% yield. However, all attempts to convert **11** to $11\cdot 2\text{BH}_3$ gave only traces of the latter. Mainly insoluble material formed, which was presumed to be oligomeric and possibly derived from B–H additions to the alkenyl groups.

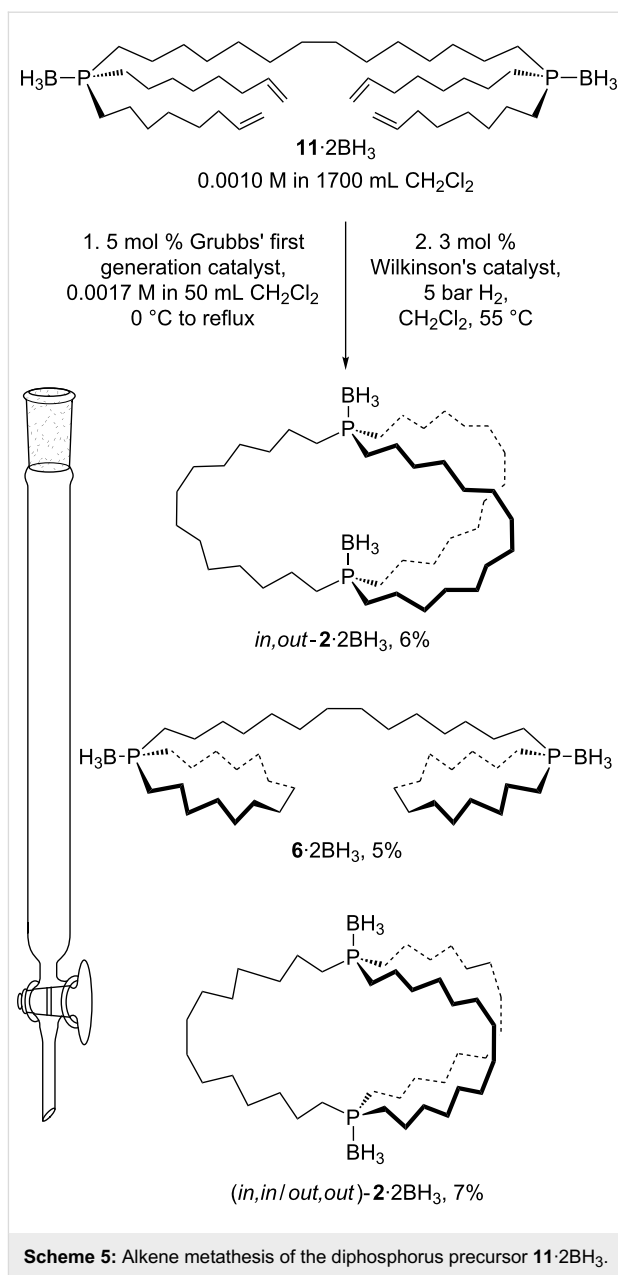
In the second approach, **10** was first converted to the tetrachloride $\text{Cl}_2\text{P}((\text{CH}_2)_{14})\text{PCl}_2$ (**12**) in 94% yield using triphosgene, a standard reagent for the chlorination of phos-



phorus–hydrogen bonds [49]. Since a direct reaction with an excess of the Grignard reagent BrMg(CH₂)₆CH=CH₂ would give **11**, a dead end, initial conversion to the bis(borane) adduct **12**·2BH₃ was envisioned. However, reactions of **12** and H₃B·SMe₂ (2.1 equiv) afforded only insoluble material.

Thus, despite the low yield of the final step in Scheme 3, reasonable quantities of the diphosphine diborane **11**·2BH₃ could be stockpiled. As shown in Scheme 5, **11**·2BH₃ was subjected to a metathesis/hydrogenation/column chromatography sequence similar to that for **1**·BH₃ in Scheme 2. However, a tenfold higher dilution was used in the metathesis step (0.0010 M as compared to 0.010 M).

Figure 1 shows a ¹³C{¹H} NMR spectrum of the crude product after hydrogenation stacked above spectra of the three products that could be isolated after the rather tedious column chromatography: the dibridgehead diphosphine diborane *in,out*-2·2BH₃, its constitutional isomer **6**·2BH₃, and its stereoisomer (*in,in/out,out*)-2·2BH₃. It can be inferred from the top spectrum that the three products were the major components and moreover present in approximately equal amounts. However, the isolated



yields were affected by the challenging separation. In particular, *in,out*-2·2BH₃ and **6**·2BH₃ eluted very closely, rendering some mixed fractions unavoidable and lowering the amounts of pure products.

Compared to the metathesis/hydrogenation sequence for **1**·BH₃ (Scheme 2) the yields of *in,out*-2·2BH₃ and (*in,in/out,out*)-2·2BH₃ (Scheme 5) are higher but still poor. Taking into account the overall yields (three steps from PCl₃ and BrMg(CH₂)₆CH=CH₂ in the first synthesis vs seven steps from 1,14-tetradecanedioic acid in the second), the latter route does not offer any advantage, even if one were to improve the conversion of **10**·2BH₃ to **11**·2BH₃.

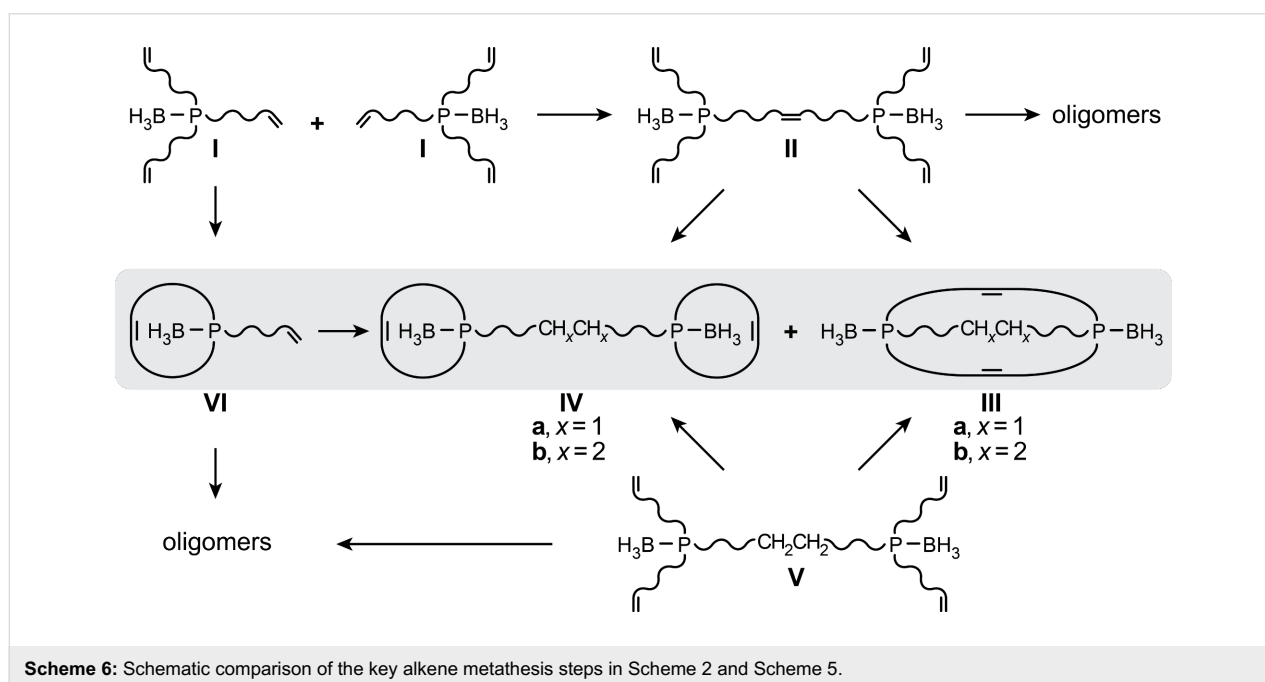
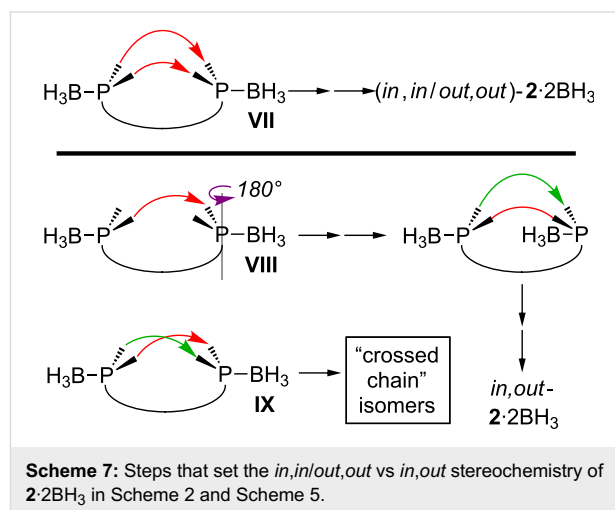
Discussion

As contrasted in Scheme 6, Scheme 2 and Scheme 5 present two conceptually related routes to the isomeric title compound $2 \cdot 2\text{BH}_3$. In the first, two trialkenylphosphine boranes ($1 \cdot \text{BH}_3 = \text{I}$) must undergo metathesis. The first productive step is intermolecular, giving a diphosphorus compound with a $\text{P}(\text{CH}_2)_6\text{CH}=\text{CH}(\text{CH}_2)_6\text{P}$ tether **II** that is positioned for subsequent intramolecular ring closing steps. Those involving alkenyl groups from different phosphorus atoms are productive (leading to $2 \cdot 2\text{BH}_3$ via hydrogenation of **IIIa**), and those involving groups from the same phosphorus atoms are non-productive (leading to $6 \cdot 2\text{BH}_3$ via hydrogenation of **IVa**). In the second, the starting material has a preformed $\text{P}(\text{CH}_2)_{14}\text{P}$ tether ($11 \cdot 2\text{BH}_3 = \text{V}$), and the four alkenyl groups have reactivity options ($\rightarrow$ **IIIb** or **IVb**) analogous to those of intermediate **II** with the $\text{P}(\text{CH}_2)_6\text{CH}=\text{CH}(\text{CH}_2)_6\text{P}$ tether. Importantly, all of these steps are presumed to be largely under kinetic control, consistent with experience with the types of metatheses in Scheme 1 [1-13,34].

Although the second route intuitively seems more favorable, after the initial intermolecular metathesis of $1 \cdot \text{BH}_3$ (**I**), both require an equivalent series of steps to reach (after hydrogenation) $2 \cdot 2\text{BH}_3$. One reason $1 \cdot \text{BH}_3$ is an inferior substrate is that following the initial generation of a $\text{P}(\text{CH}_2)_6\text{CH}=\text{Ru}$ species, two $\text{P}(\text{CH}_2)_6\text{CH}=\text{CH}_2$ moieties remain available for non-productive intramolecular ring closing metathesis (giving **VI**). In contrast, with the analogous intermediate derived from $11 \cdot 2\text{BH}_3$ (**V**), there is only one $\text{P}(\text{CH}_2)_6\text{CH}=\text{CH}_2$ moiety that can give non-productive chemistry. It is also worth noting that

high dilution provides less of an advantage in Scheme 2, as one wants to favor intermolecular over intramolecular metatheses in the first step. In Scheme 5, one wants to avoid intermolecular metatheses at all stages.

At present, we have no rationale for the *in,out* vs (*in,in/out,out*) isomer ratios for $2 \cdot 2\text{BH}_3$. However, it is easy to map the sequence leading to each, as shown in Scheme 7. When there is only one tether between the two phosphorus atoms, the phosphorus–boron bonds can be arrayed in an *anti* fashion, as depicted in **VII**. When subsequent metatheses join alkenyl groups in the *syn* positions on each phosphorus atom (front to front and rear to rear), (*in,in/out,out*)- $2 \cdot 2\text{BH}_3$ must result (as drawn in Scheme 7, the *out,out* isomer would be the kinetic



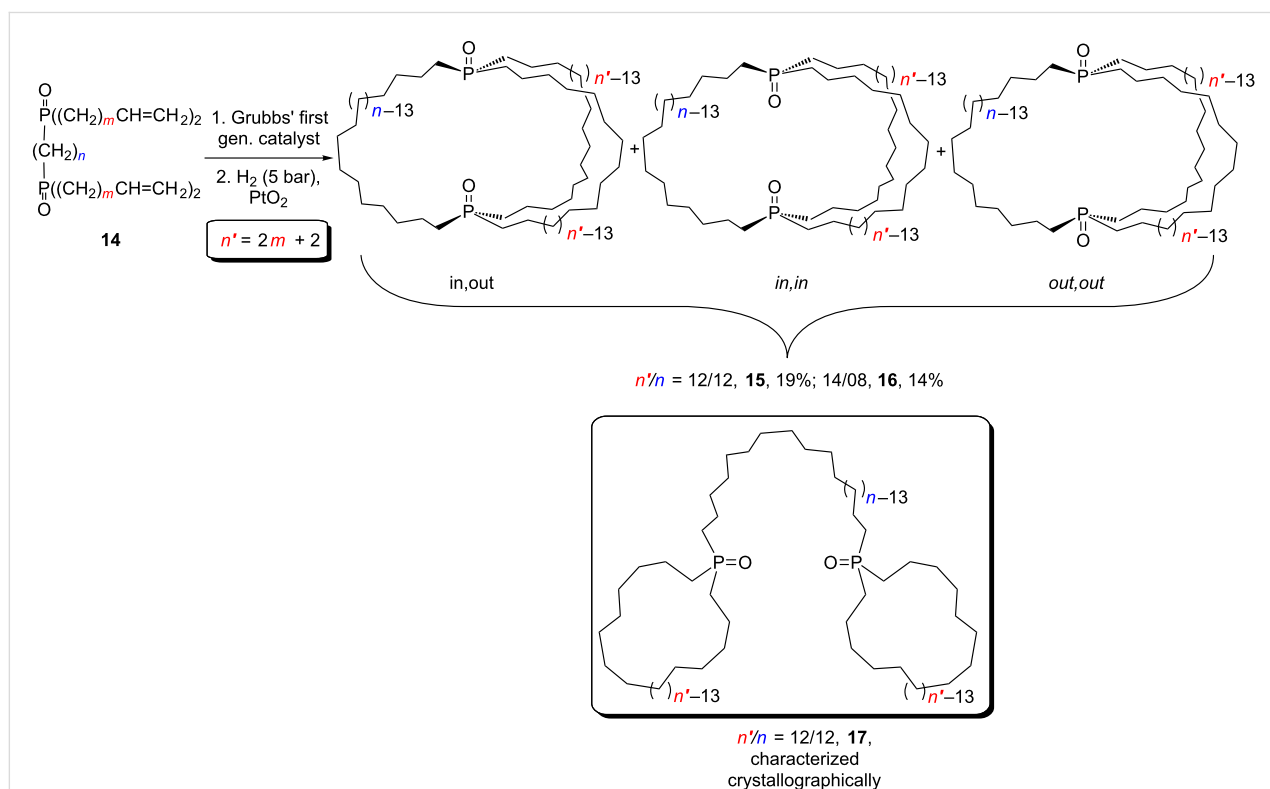
product). When the first metathesis does not join the *syn* positions, as in **VIII** (front to rear), one phosphorus–boron bond must subsequently be rotated by 180° to create a *syn* orientation for the second metathesis.

Of course, if the first metathesis step does not require a *syn* relationship (per **VIII**), the same possibility can be entertained for the second (see **IX**). This would lead to an isomeric bicyclic compound with "crossed chains". We have sought to access such species by conducting metatheses of substrates of the types in Scheme 1 that give thirty-three membered macrocycles ($n = 30$) [7]. However, none have so far been detected. Other types of crossed chain *in/out* isomer systems have in fact been realized [25,30].

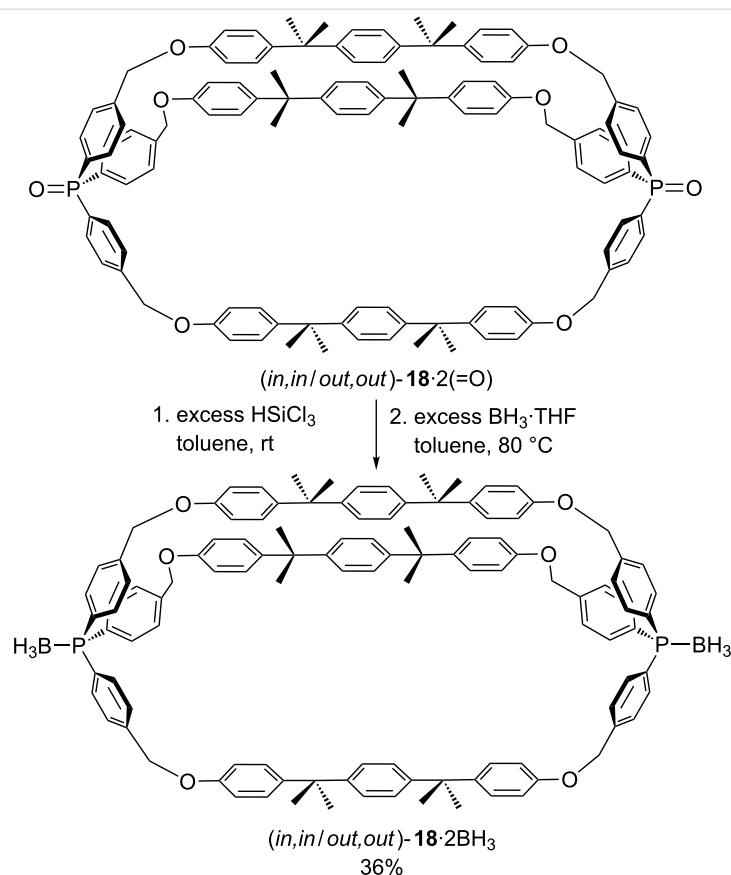
As communicated earlier [28] and will be described more fully in a later paper, both isomers of **2**·2BH₃ are easily deprotected to give the respective isomers of the dibridgehead diphosphine **2** in high yields. Since phosphine oxides are also easily converted to phosphines, one could consider parallel approaches to **2** via metatheses of the phosphine oxide (O=P((CH₂)₆CH=CH₂)₃ (**1**(=O)) or diphosphine dioxide (H₂C=CH(CH₂)₆)₂(O=P((CH₂)₁₄)P(=O)((CH₂)₆CH=CH₂)₂ (**11**·2(=O)). Given the poor results with **1**·BH₃ in Scheme 2, no attempt has been made to explore similar reactions with **1**(=O).

However, as shown in Scheme 8, it has proved possible to synthesize the diphosphine dioxides **14**, in which the two phosphorus atoms are tethered by a methylene chain, in two steps in 66–68% overall yields from diethyl phosphonate ((O=)PH(OEt)₂), Grignard reagents BrMg(CH₂)_{*m*}CH=CH₂, base (NaH), and appropriate α,ω -dibromides Br(CH₂)_{*n*}Br [25]. Following metathesis and hydrogenation, these afford dibridgehead diphosphine oxides **15** and **16** in 14–19% yields. This is slightly better than the combined yield of *in,out*- and (*in,in/out,out*)-**2**·2BH₃ in Scheme 5, although the data are not strictly comparable as the ring sizes differ. It has not yet proved possible to efficiently separate the *in/out* isomers of **15** and **16**. However, byproducts derived from metatheses of alkenyl groups on the same phosphorus atom – such as **17** (comparable to **6**·2BH₃) – appear to form in much smaller amounts.

To our knowledge, only one macrocyclic dibridgehead diphosphine diborane has been previously reported, (*in,in/out,out*)-**18**·2BH₃ in Scheme 9 [50,51]. This features triarylphosphorus bridgeheads and *p*-phenylene containing tethers that are long enough to allow rapid homeomorphic isomerization. The precursor **18**·2(=O) was prepared by a threefold Williamson ether synthesis in surprisingly high yields (61% *in,in/out,out* and *in,out* combined) [50,51], likely aided by the geminal dialkyl effect associated with the quaternary centers [52].

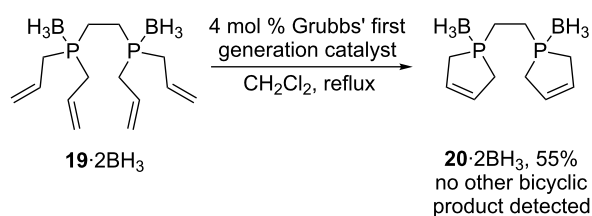


Scheme 8: Another non-metal-templated approach to dibridgehead diphosphorus compounds.



Scheme 9: Previously synthesized dibridgehead diphosphine diboranes.

Finally, it should be noted that a number of alkene containing phosphine boranes have been employed in metathesis reactions [53,54]. In particular, the tetraalkenyl diphosphine diborane **19**·2BH₃ in Scheme 10 represents a downsized version of **11**·2BH₃. A species analogous to **6**·2BH₃, **20**·2BH₃, is obtained in much higher yield than any of the products in Scheme 5 [53]. Hence, selectivities can strongly depend upon the lengths of the methylene segments in the precursor.



Scheme 10: Alkene metathesis of the tetraalkenyldiphosphine diborane **19**·2BH₃.

Conclusion

In conclusion, this work constitutes a further installment in the evolution of synthetic strategies for dibridgehead diphosphorus

compounds that employ alkene metathesis. The new approaches (Scheme 2; Scheme 3 and Scheme 5) lack metal templates, which differentiates them from the routes presented in Scheme 1. However, neither is competitive with Scheme 1, despite eliminating the requirement for stoichiometric amounts of precious metals. Furthermore, preassembling a diphosphine diborane substrate per Scheme 3 and Scheme 5 is not competitive with the "shotgun" approach in Scheme 2, and both routes require comparably demanding preparative column chromatography. Hence, the most promising direction for future research would seem to be templated syntheses via non-precious metals [55]. This remains an area of ongoing investigation in our laboratory and further results will be reported in due course.

Experimental

General. Reactions (except hydrogenations) were conducted under inert atmospheres using standard Schlenk techniques. All chromatography was carried out under aerobic conditions. Additional data are supplied in Supporting Information File 1.

Metathesis/hydrogenation of $\text{H}_3\text{B}\cdot\text{P}((\text{CH}_2)_6\text{CH}=\text{CH}_2)_3$ (1**·BH₃; Scheme 2 [32]).** A Schlenk flask was charged with **1**·BH₃ (1.177 g, 3.110 mmol) [31] and CH_2Cl_2 (320 mL; the re-

sulting solution was 0.0097 M in 1-BH_3) and cooled to 0 °C. A solution of Grubbs' first generation catalyst (0.077 g, 0.094 mmol, 3 mol %) in CH_2Cl_2 (50 mL) was added dropwise via syringe with stirring over 1 h. The cooling bath was removed. After 2 h, additional Grubbs' first generation catalyst was added as a solid (0.051 g, 0.062 mmol, 2 mol %). The flask was fitted with a condenser and the mixture was refluxed overnight, cooled to room temperature, and passed through a SiO_2 pad (3 cm), which was rinsed with CH_2Cl_2 . The eluate was concentrated to ca. 20 mL by rotary evaporation, and transferred to a Fischer–Porter bottle. Wilkinson's catalyst (0.086 g, 0.093 mmol, 3 mol %) was added, and the bottle was partially evacuated and charged with hydrogen (5 bar). The sample was kept at 55 °C for 60 h. The solvent was removed and the residue was placed at the top of a chromatography column (SiO_2 , 3.5×36 cm), which was eluted with hexanes/ CH_2Cl_2 (3:1 to 1:3 v/v) and then CH_2Cl_2 . Fractions were assayed by TLC, combined where appropriate, and slowly evaporated to dryness in a fume hood. Some fractions (0.091 g total out of the recovered mass of 0.344 g) consisted of unidentified and/or impure products, or oligomers and polymers. Products that could be characterized are as follows (in order of elution).

$\text{H}_3\text{B}\cdot\text{P}(n\text{-C}_8\text{H}_{17})_3$ ($4\cdot\text{BH}_3$ [33]; 0.007 g, 0.018 mmol, 1%), colorless oil. Anal. calcd for $\text{C}_{24}\text{H}_{54}\text{BP}$ (384.47): C, 74.98; H, 14.16; found: C, 74.93; H, 14.02; ^1H NMR (400 MHz, CDCl_3) δ 1.53–1.37 (m, 12H, CH_2), 1.33–1.30 (m, 6H, CH_2), 1.26–1.23 (m, 24H, CH_2), 0.83 (t, $^3J_{\text{HH}} = 6.9$ Hz, 9H, CH_3), 0.47 and 0.19 (br apparent d, 3H, BH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 31.7 (s, CH_2), 31.1 (d, $J_{\text{CP}} = 12.0$ Hz, CH_2), 29.0 (s, CH_2), 28.9 (s, CH_2), 22.9 (d, $J_{\text{CP}} = 34.3$ Hz, CH_2), 22.50 (s, CH_2), 22.48 (s, CH_2), 14.0 (s, CH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ 15.9 and 15.5 (br apparent d); IR (oil film): 2926 (s), 2856 (m), 2366 (m), 1463 (m), 1413 (w), 1378 (w), 1135 (w), 1061 (m), 1034 (w), 807 (w), 764 (w), 722 (m) cm^{-1} ; MS (EI) [56]: 384 (M^+ , <1%), 370 ($[\text{M} - \text{BH}_3]^+$, 79%).

$\text{H}_3\text{B}\cdot\text{P}((\text{CH}_2)_{13}\text{CH}_2)(n\text{-C}_8\text{H}_{17})$ ($5\cdot\text{BH}_3$; 0.090 g, 0.25 mmol, 8%), colorless oil. Anal. calcd for $\text{C}_{22}\text{H}_{48}\text{BP}$ (354.40): C, 74.56; H, 13.65; found: C, 74.27; H, 13.52; ^1H NMR (500 MHz, CDCl_3) δ 1.62–1.19 (m, 42H, CH_2), 0.86 (t, 3H, $^3J_{\text{HH}} = 7.0$ Hz, CH_3), 0.48 and 0.26 (br apparent d, 3H, BH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 31.7 (s, CH_2), 31.2 (d, $J_{\text{CP}} = 12.6$ Hz, CH_2), 29.03 (s, CH_2), 29.01 (s, CH_2), 28.9 (d, $J_{\text{CP}} = 11.1$ Hz, 2CH_2), 26.7 (s, 2CH_2), 26.53 (s, 2CH_2), 26.48 (s, 2CH_2), 26.1 (s, 2CH_2), 23.8 (d, $J_{\text{CP}} = 35.4$ Hz, CH_2), 22.57 (d, $J_{\text{CP}} = 1.2$ Hz, 2CH_2), 22.55 (s, CH_2), 22.3 (d, $J_{\text{CP}} = 33.6$ Hz, CH_2), 21.2 (d, $J_{\text{CP}} = 3.3$ Hz, 2CH_2), 14.0 (s, CH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3) δ 15.6 and 15.2 (br apparent d); IR (oil film): 2926 (s), 2856 (m), 2366 (m), 1459 (m), 1417 (w), 1135 (w), 1061 (m), 811 (m), 760 (m), 722 (m) cm^{-1} ; MS

(EI) [56]: 340 ($[\text{M} - \text{BH}_3]^+$, 93%), 228 ($[\text{M} - \text{BH}_3 - \text{C}_8\text{H}_{17} + 1]^+$, 100%).

***in,out-H* $\text{H}_3\text{B}\cdot\text{P}((\text{CH}_2)_{14})_3\text{P}\cdot\text{BH}_3$** (*in,out-2* $\cdot 2\text{BH}_3$; 0.039 g, 0.057 mmol, 4%), colorless oil. Anal. calcd for $\text{C}_{42}\text{H}_{90}\text{B}_2\text{P}_2$ (678.73): C, 74.32; H, 13.37; found: C, 73.86; H, 13.49; ^1H NMR (500 MHz, CDCl_3) δ 1.56–1.51 (m, 12H, PCH_2), 1.49–1.42 (m, 12H, CH_2), 1.39–1.33 (m, 12H, CH_2), 1.31–1.21 (m, 48H, CH_2), 0.45 and 0.27 (br apparent d, 6H, BH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 30.5 (d, $J_{\text{CP}} = 11.3$ Hz, CH_2), 28.35 (s, CH_2), 28.28 (s, CH_2), 28.2 (s, CH_2), 28.1 (s, CH_2), 23.0 (d, $J_{\text{CP}} = 34.3$ Hz, CH_2), 22.2 (d, $J_{\text{CP}} = 1.9$ Hz, CH_2); $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3) δ 15.6 and 15.4 (br apparent d); IR (oil film): 2926 (s), 2853 (m), 2366 (w), 1459 (w), 1413 (w), 1135 (w), 1061 (m), 803 (w), 722 (w) cm^{-1} ; MS (MALDI $^+$, THAP) [56]: 651.6 ($[\text{M} - 2\text{BH}_3 + 1]^+$, 100%).

$\text{H}_3\text{B}\cdot\text{P}((\text{CH}_2)_{13}\text{CH}_2)(\text{CH}_2)_{14}\text{P}((\text{CH}_2)_{13}\text{CH}_2)\cdot\text{BH}_3$ ($6\cdot 2\text{BH}_3$; 0.101 g, 0.149 mmol, 10%), white solid, mp 96 °C (capillary). Anal. calcd for $\text{C}_{42}\text{H}_{90}\text{B}_2\text{P}_2$ (678.73): C, 74.32; H, 13.37; found: C, 73.92; H, 13.47. The identity of this compound, which has been independently synthesized, has been confirmed crystallographically [6]. ^1H NMR (500 MHz, CDCl_3) δ 1.65–1.14 (br m, 84H, CH_2), 0.49 and 0.26 (br apparent d, 6H, BH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 31.3 (d, $J_{\text{CP}} = 12.6$ Hz, CH_2), 29.54 (s, CH_2), 29.53 (s, CH_2), 29.4 (s, CH_2), 29.1 (s, CH_2), 29.0 (d, $J_{\text{CP}} = 11.1$ Hz, 2CH_2), 26.8 (s, 2CH_2), 26.6 (s, 2CH_2), 26.5 (s, 2CH_2), 26.1 (s, 2CH_2), 23.8 (d, $J_{\text{CP}} = 35.3$ Hz, CH_2), 22.6 (d, $J_{\text{CP}} = 1.0$ Hz, CH_2), 22.3 (d, $J_{\text{CP}} = 33.5$ Hz, 2CH_2), 21.2 (d, $J_{\text{CP}} = 3.3$ Hz, 2CH_2); $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3) δ 15.6 and 15.2 (br apparent d); IR (powder film): 2922 (s), 2853 (m), 2366 (m), 1459 (m), 1417 (w), 1135 (w), 1061 (m), 791 (w), 722 (m) cm^{-1} ; MS (EI) [56]: 678 (M^+ , 9%), 665 ($[\text{M} - \text{BH}_3]^+$, 100%), 652 ($[\text{M} - 2\text{BH}_3 + 1]^+$, 72%).

***(in,in/out,out)-H* $\text{H}_3\text{B}\cdot\text{P}((\text{CH}_2)_{14})_3\text{P}\cdot\text{BH}_3$** (*(in,in/out,out-2* $\cdot 2\text{BH}_3$; 0.016 g, 0.024 mmol, 2%), colorless oil that solidified to give a white powder, mp 112 °C. Anal. calcd for $\text{C}_{42}\text{H}_{90}\text{B}_2\text{P}_2$ (678.73): C, 74.32; H, 13.37; found: C, 74.71; H, 13.34; ^1H NMR (500 MHz, CDCl_3) δ 1.55–1.50 (m, 12H, CH_2), 1.47–1.39 (m, 12H, CH_2), 1.37–1.32 (m, 12H, CH_2), 1.29–1.21 (m, 48H, CH_2), 0.38 and 0.26 (br apparent d, 6H, BH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 30.6 (d, $J_{\text{CP}} = 12.1$ Hz, CH_2), 29.23 (s, CH_2), 29.17 (s, CH_2), 28.9 (s, CH_2), 28.4 (s, CH_2), 22.5 (d, $J_{\text{CP}} = 34.1$ Hz, CH_2), 22.1 (d, $J_{\text{CP}} = 2.7$ Hz, CH_2); $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3) δ 14.9 and 14.7 (br apparent d); IR (powder film): 2922 (s), 2853 (s), 2366 (m), 1467 (m), 1413 (w), 1131 (w), 1061 (m), 807 (w), 760 (w), 718 (m) cm^{-1} ; MS (MALDI $^+$, THAP) [56]: 702.0 ($[\text{M} + \text{Na}]^+$, 98%), 666.0 ($[\text{M} - \text{BH}_3 + 1]^+$, 100%).

Metathesis/hydrogenation of $(\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_6)_2(\text{H}_3\text{B})\text{P}((\text{CH}_2)_{14})\text{P}(\text{BH}_3)((\text{CH}_2)_6\text{CH}=\text{CH}_2)_2$ (11**·2BH₃; Scheme 5 [32]).** Diphosphine diborane **11**·2BH₃ (1.222 g, 1.672 mmol), CH₂Cl₂ (1700 mL; the resulting solution was 0.0010 M in **11**·2BH₃), Grubbs' first generation catalyst (0.069 g, 0.083 mmol, 5 mol %), Wilkinson's catalyst (0.046 g, 0.050 mmol, ca. 3 mol %), and H₂ were combined in a procedure analogous to that used for **1**·BH₃. An identical work-up gave *in,out*-**2**·2BH₃ (0.072 g, 0.106 mmol, 6%, minor impurities evident by ¹³C{¹H} NMR), **6**·2BH₃ (0.056 g, 0.083 mmol, 5%, minor impurities evident by ¹³C{¹H} NMR), and (*in,in/out,out*)-**2**·2BH₃ (0.075 g, 0.111 mmol, 7%), along with several fractions consisting of unidentified and/or impure products, or oligomers and polymers. Spectroscopic data for *in,out*-**2**·2BH₃, (*in,in/out,out*)-**2**·2BH₃, and **6**·2BH₃ matched those reported above.

Supporting Information

Supporting Information File 1

Additional experimental data.

[<https://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-14-211-S1.pdf>]

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56. The most intense peak of the isotope envelope is given; *m/z* (relative intensity, %). THAP = 2,4,6-trihydroxyacetophenone matrix.

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