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General and Efficient One-Pot Synthesis of Tertiary Phosphane–Borane Complexes Containing Different Alkyl Groups and In Situ Facile Recycling of the Phosphorus Donor Reagent

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Tertiary symmetric and asymmetric phosphane–borane complexes containing different alkyl groups, including bulky groups, can be obtained by the addition of different Grignard reagents to benzothiadiphosphole **1** followed by direct complexation with BH_3·THF. Treatment of the resulting mixture with PCl_3 led to the reformation of the starting reagent **1**, which was recovered from the reaction mixture by simple crystallization. The phosphane complexes were purified by chromatography of the mother liquor. This procedure is highly atom-economic and environmentally friendly. All the reaction intermediates were identified.

Introduction

Phosphane–borane complexes are an important class of compounds that have attracted increasing interest since the first reported synthesis over 50 years ago.[1] In the phosphane–boranes, BH_3 is not only a valuable and protective group that can be easily removed, it also imparts useful reactivity features not found in typical tetracoordinated phosphorus derivatives.[2] Phosphane–borane complexes are now used in a variety of applications, including alkylations,[3] conjugate addition processes,[4] and the preparation of phosphorus-stabilized carbanions as precursors of various organophosphorus compounds.[5,6] Moreover, numerous recent studies have demonstrated the importance of tertiary phosphane–borane complexes in the synthesis of chiral phosphorus ligands[7] and have expanded the range of synthetic procedures by using air-stable phosphane–boranes instead of the analogous phosphanes. Tertiary phosphane–boranes are generally obtained by the reaction of the parent free phosphane with BH_3·THF and BH_3·SMe_2 complexes, $NaBH_4$/acetic acid[8] or directly from parent phosphane oxides by in situ reduction with $LiAlH_4$ in the presence of $NaBH_4$ and $CeCl_3$.[9] However, currently available methods for the synthesis of acyclic and cyclic tertiary phosphanes containing different alkyl groups usually require long and tedious procedures involving multiple steps[10–21] and, in some cases, are difficult and dangerous because they use pyrophoric and air-sensitive reagents such as primary and secondary phosphanes and halophosphanes. Moreover, in the case of acyclic alkyl tertiary asymmetrical phosphanes bearing unhindered alkyl substituents, available synthetic procedures result in poor yields.[10,11]

Recently, we reported[22] a new synthesis (Scheme 1) of symmetrical and asymmetrical secondary phosphanes **2** using benzothiadiphosphole **1**, a reagent developed by our group which is an air-stable solid that can be stored for several years without particular precautions.[23] Compound **1** is easily obtained by first treating *p*-methylthioanisole with PCl_3 and $AlCl_3$ (Scheme 1) followed by the separation of **1** from the final reaction mixture by simple crystallization. The subsequent addition of 2 equiv. of Grignard reagents to 1 equiv. of **1** gave, after quenching with acidic water, the secondary phosphanes **2** in high yields and the end product **3** (which is a residue of **1**). The separation of **2** from **3** was achieved by acid/base extraction followed by distillation. The simple treatment of **3** with PCl_3 quantitatively and immediately regenerated the starting reagent **1**, which can be reused without further purification (Scheme 1).[24] The intermediate involved in the synthesis of the phosphanes **2** from **1** might be a hypervalent phosphorus species such as **A**, as reported elsewhere.[25] We also reported a new efficient method for the synthesis of borane complexes **4** (70–85% yield) of the secondary phosphanes **2** by simple treatment of the reaction mixture with acetic acid followed by the in situ addition of the BH_3·THF complex.[22] Surprisingly, we found that the secondary phosphane **3** was not complexed by BH_3; this finding is of fundamental importance because it enables the recycling of **3**. In fact, after separating **3** from the reaction mixture by acid/base extraction followed by distillation, the starting reagent **1** was obtained by treating **3** with PCl_3 (Scheme 1).

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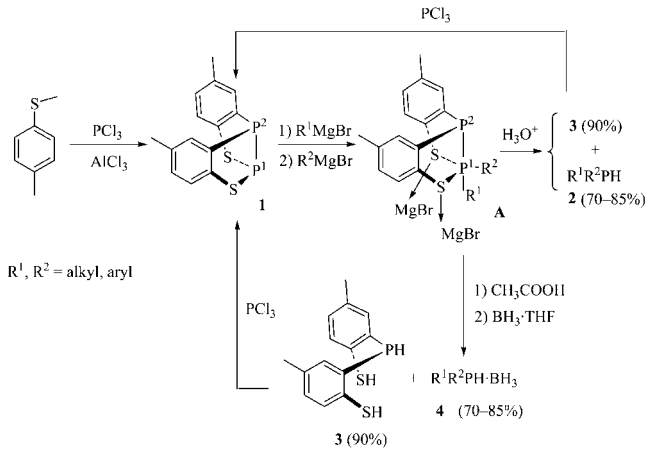
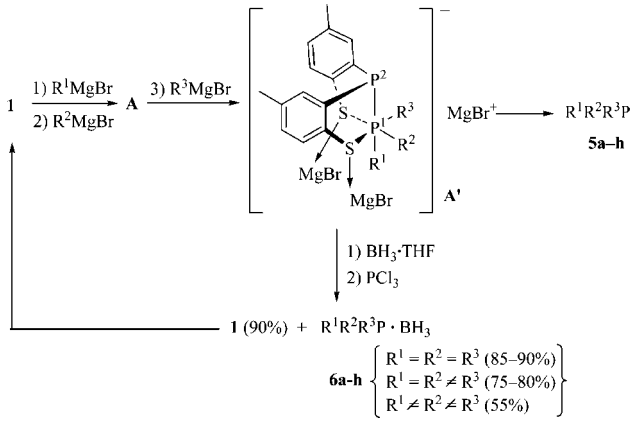


Scheme 1.

These previous findings, and the growing interest in the synthesis of tertiary phosphane–borane complexes, encouraged us to investigate the possibility of obtaining these complexes using the phosphorus donor reagent **1** in a one-pot procedure without the need to isolate the free phosphane precursor. Herein we report the results obtained: a direct and general one-pot synthesis of tertiary phosphane–borane complexes was achieved with a remarkable improvement in the outcome of the reaction represented by the possibility of quantitatively reforming in situ the starting phosphorus donor reagent **1**.

Results and Discussion

The synthesis of tertiary phosphane–boranes was first tested in the preparation of the symmetric phosphane–boranes **6a**,**b** containing three equal groups. For this purpose, we carried out the reaction between compound **1** and 3 equiv. of the Grignard reagent (as previously reported[25] to obtain acyclic tertiary phosphanes) and then we directly treated the reaction mixture containing the phosphanes **5a**,**b** with BH_3·THF. In this manner, tertiary phosphane–borane complexes **6a**,**b** were obtained in high yields (85–90%) without isolation of the free phosphanes (Scheme 2). After this, we tried to synthesize phosphane–boranes containing different alkyl groups which are both more difficult to obtain and more important from a synthetic viewpoint. The synthesis of the symmetrical ($R^1 = R^2 \neq R^3$) tertiary phosphanes **5c** and **5d** was achieved by adding, in the first step, 2 equiv. of a Grignard reagent to a solution of compound **1** and subsequently, after 4–5 min, by adding a second Grignard reagent (R^3MgBr). In the case of the synthesis of (cyclohexyl)dimethylphosphane (**5e**) and (isopropyl)-dimethylphosphane (**5f**) and their complexes with BH_3 (**6e**,**f**), the Grignard reagent bearing the bulkiest moiety (namely cyclohexyl- and isopropylmagnesium bromide, respectively) must be used in the first attack on reagent **1**. After the addition of this group to the P^1 phosphorus atom of reagent **1** in this first step, the high steric hindrance caused by the presence of the bulky alkyl group required us to carry out the following attack using a Grignard reagent with very small steric hindrance, such as methylmagnesium bromide. In this manner, phosphanes **5c–f** and their complexes with BH_3 (**6c–f**) were obtained in yields of 75–80%. It is worth noting that among compounds **5c–f** and **6c–f**, only **5e**[26] and **5f**[5a,27] (and the corresponding borane derivatives **6e**[28] and **6f**,[5a,5b,29]) are known. In particular, compounds **6e** and **6f**, bearing a bulky group, were obtained from phosphorus trichloride through a one-pot procedure in good yields (66 and 49%, respectively, owing to the steric hindrance of the first group). In addition, to the best of our knowledge, no other examples of a one-pot procedure for the synthesis of trialkylphosphane–boranes with at least two different *n*-alkyl groups have been reported so far. With our methodology it is possible to obtain also these latter phosphane–boranes and, at the same time, to recycle the starting phosphorus donor reagent **1** making the process atom-economic. The procedure works well also for the synthesis of phosphane derivatives containing three different *n*-alkyl groups ($R^1 \neq R^2 \neq R^3$). (butyl)(ethyl)hexylphosphane–borane (**6g**) was obtained in good yield by using a procedure in which three different Grignard reagents were added in three successive steps with very short reaction times between the steps. We found that the best yield (55%) can be achieved with a 1 min reaction time between the addition of the first and second Grignard reagents followed by a 2 min reaction time between the addition of the second and third Grignard reagents. It is important to note that in the literature there are very few examples of tertiary phosphanes containing three different *n*-alkyl groups; in all cases they were obtained by multi-step procedures and in poor yields.[11] The generality of this procedure for synthesizing tertiary phosphane–borane complexes was verified by the synthesis of the borane complex of a cyclic tertiary phosphane, namely the 1-ethylphosphinane–borane complex (**6h**) which was obtained in 70% yield.



	a	b	c	d	e	f	g	h
R^1	*n*Bu	*n*Hex	*n*Hex	Et	*c*Hexyl	*i*Pr	*n*Hex	R^1, R^2 = $(CH_2)_5$
R^2	*n*Bu	*n*Hex	*n*Hex	Et	Me	Me	*n*Bu	
R^3	*n*Bu	*n*Hex	*n*Bu	*n*Pent	Me	Me	Et	Et

Scheme 2.

It is noteworthy that in all cases, simultaneously with the formation of the tertiary phosphanes, the reaction leads to the formation of the magnesium salt of compound **3**, which is the residue of the starting reagent **1**. As it is known that tertiary phosphane–borane complexes are characterized by good chemical stability, we wanted to see whether the magnesium salt of compound **3** can be transformed in situ into reagent **1** by direct addition of PCl_3 to the crude reaction mixture. Thus, after accomplishment of the complexation of the tertiary phosphanes to give the corresponding borane complexes and removal of excess BH_3, the precursor magnesium salt of **3** was transformed in situ into reagent **1** by the addition of a small excess of PCl_3 to the reaction mixture. The reformed reagent **1** was almost quantitatively separated from the reaction mixture by simple crystallization,[30] whereas the phosphane–borane complex, present in the mother liquor, was purified by chromatography. Compared with the previous procedure[24] for the recycling of compound **1**, which involved treatment of the reaction mixture containing the magnesium salt of **3** with acidic water followed by the isolation of **3**, this new in situ recycling process is very easy and fast. The procedure reported here is made possible by the chemical stability of tertiary phosphane–borane complexes in the presence of PCl_3, which can be added directly to the reaction mixture.

It is interesting to make a comparison between the complexation procedure used in the present case for the synthesis of tertiary borane–phosphanes and that previously used for the synthesis of complexes of secondary phosphanes. The complexation of secondary phosphanes[22] requires the addition of acetic acid before BH_3·THF in order to break the pentacoordinate intermediate **A** produced in the reaction (Scheme 1), which is more stable than the hexacoordinate intermediate **A′** (formed after addition of a third Grignard reagent to give tertiary phosphanes, Scheme 2) which spontaneously collapses. In addition, acetic acid is also necessary as a proton source to form the P–H bond in secondary phosphanes. Clearly, in our complexation of tertiary phosphanes, the addition of acetic acid is not necessary because in this case the hexacoordinate intermediate **A′** is the direct precursor of the tertiary phosphanes. Furthermore, we chose BH_3·THF as the complexation agent because, after complete transformation of the tertiary phosphanes at –8 to –5 °C into the corresponding borane complexes, the excess BH_3 can be easily removed simply by allowing the reaction mixture to stand at room temperature. In fact, the decomposition at room temperature of the BH_3·THF complex produces gaseous BH_3 and THF (the reaction solvent). The use of other complexation agents such as BH_3·Me_2S or $NaBH_4$/acetic acid must be avoided because the PCl_3 added in situ in the recycling of the magnesium salt of compound **3** to the starting reagent **1** could react with these borane sources which are not easy to remove at room temperature.

The easy obtainment of tertiary phosphanes through our procedure can be explained by the formation of hypervalent phosphorus intermediates (penta- and hexacoordinate) such as **A** and **A′** (see Schemes 1 and 2). The formation of such intermediates is favoured by the "dibenzo-butterfly" structure of **1**, as we reported for the synthesis of cyclic tertiary phosphanes.[31]

It is noteworthy that previously[25,31] we thought that the hexacoordinate intermediate **A′** required a nucleophilic attack, for example, by water or an acid in order to decompose it. During this study, however, we observed by ^{31}P NMR spectroscopy that **A′** is unstable and spontaneously collapses to give the corresponding tertiary phosphanes, presumably due to its high steric hindrance. Consequently, about 30–40 min after the addition of the last Grignard reagent, BH_3·THF can be added to the reaction mixture to form complexes of the tertiary phosphanes formed by the spontaneous decomposition of **A′**. It is important to wait until the reaction between intermediate **A** and the final Grignard reagent producing the tertiary phosphane has gone to completion (at least 30 min) before adding BH_3·THF. If this reaction has not gone to completion, BH_3 may complex with the hypercoordinated intermediates, thereby hindering the evolution of the process leading to the desired products.

To gain more information about the mechanism of this reaction, we performed the reaction between compound **1** and *n*-butylmagnesium bromide in an NMR tube and monitored the progress of the reaction using ^{31}P NMR spectroscopy. After the addition of 2 equiv. of *n*-butylmagnesium bromide to a THF solution containing 1 equiv. of **1**, we observed the formation of the pentacoordinate intermediate **A** [δ = –31.6 (d, $^1J_{P–P}$ = 169 Hz), –43.3 (d, $^1J_{P–P}$ = 169 Hz) ppm]. This intermediate was stable and could remain in solution in the NMR tube for about 1 h. Then, after addition of a small excess of *n*-butylmagnesium bromide, we observed the slow disappearance of the pentacoordinate intermediate signals and appearance of two signals corresponding to the tributylphosphane **5a** (δ = –31.6 ppm) and the magnesium salt of **3** (δ = –57.7 ppm), respectively. Concomitant signals at δ = 60.1 (d, $^1J_{P–P}$ = 225 Hz) and –48.7 (d, $^1J_{P–P}$ = 225 Hz) ppm were ascribed to the P^2 and P^1 atoms, respectively, of the intermediate **A′**[32] and were observed only during the initial stage of the reaction because this intermediate readily decomposes to form the tertiary phosphane **5a** and the magnesium salt of **3**.

Conclusions

A one-pot method for synthesizing tertiary phosphane–borane complexes containing different alkyl groups without prior isolation of the free phosphanes is reported. The method is general because it can be used to obtain acyclic, cyclic, symmetrical and asymmetrical phosphane–borane complexes and, for known compounds, the yields are higher than those previously reported. The most important aspect of this procedure is the direct reformation of the starting reagent **1** in the reaction mixture and its recovery by simple crystallization, making the full process both highly atom-economic and environmentally friendly. It should be noted that this improved synthetic procedure avoids the long and tedious workup associated with the use of air- and moisture-sensitive compounds.

Experimental Section

General: ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded at 400, 100.56 and 161.89 MHz, respectively, with a Varian Mercury 400 instrument. Chemical shifts are referenced to TMS for ^{1}H NMR in $CDCl_3$ or to the solvent (δ =1.8 ppm for ^{1}H NMR in [D_8]THF), to the solvent for ^{13}C NMR (δ =77.0 ppm for $CDCl_3$ and 26.7 ppm for [D_8]THF) and to external standard 85% H_3PO_4 for ^{31}P NMR. *J* values are given in Hz. Mass spectra were recorded at an ionisation voltage of 70 eV. Flash chromatography (FC) was performed on silica gel (0.040–0.063 mm). Melting points were determined with a Büchi apparatus and are uncorrected. The IR spectra of compounds **6a**–**h** showed characteristic bands near 2370 and 2350 (BH_3 asymm. and symm. str.), 1190–1120 and 1080–1040 (BH_3 asymm. and symm. def.), and 790–720 cm^{-1} (P–C). THF was distilled from sodium/benzophenone ketyl, and all solvents were purified appropriately and degassed immediately prior to use. All Grignard reagents used were commercially available or prepared from bromoalkane and magnesium turnings and were titrated immediately prior to use by standard methods.[33] Air- and moisture-sensitive solutions and reagents were handled in dried apparatus under dry argon using standard Schlenk-type techniques. Physicochemical data for the new compounds **6b**, **6d**, **6e**, **6h** and **6i** and also for known compounds for which only partial data have been reported are given below.

Preparation of Acyclic Tertiary Phosphane–Boranes 6a–g. Typical Two-Step Procedure: The first Grignard reagent (R^1MgBr, 2.4 mmol) was added to a solution of benzothiadiphosphole **1** (0.306 g, 1.0 mmol) in anhydrous THF (10 mL) under dry argon. After 4–5 min, the second Grignard reagent (R^2MgBr, 1.2 mmol) was added. After about 30–40 min, the flask was immersed in a salt/ice bath (–5 to –8 °C) and the BH_3·THF complex (1.5–2.0 mmol) was added portionwise (first 1 mmol, then after about 1 h, 0.5 mmol was added every 30 min). The salt/ice bath was removed, and the reaction mixture was allowed to stand at room temperature. The resulting solution was stirred under a gentle pressure of argon (in order to remove the excess BH_3), and then PCl_3 was added (1.5 mmol). After 5–10 min, the reaction mixture was treated with an acidic (HCl) aqueous solution (0.5 mL), and the solvent was partially removed under vacuum. Extraction with CH_2Cl_2, treatment with anhydrous Na_2SO_4 and concentration under vacuum gave a mixture of the phosphane–borane complex and reagent **1**. Compound **1** was recovered by crystallization from CH_2Cl_2/diethyl ether in 70–80% yield. Flash chromatography (FC) of the concentrated mother liquor gave phosphane–borane complexes **6c** and **6d** in 75–80% yield and a further amount of **1** in 10–20% yield. The tertiary phosphane–borane complex **6g** was obtained in 45% yield (it was easily separated from the other possible phosphane–borane complexes by FC) according to the method described above for preparing **6c**,**d**, except that in this case two different Grignard reagents, R^1MgBr (1.2 mmol) and R^2MgBr (1.2 mmol), were added to **1** in the first step (instead of 2.4 mmol of the same organometallic compound) and the third Grignard reagent R^3MgBr (1.2 mmol) was added in the second step. When $R^1 = R^2 = R^3$, the three Grignard reagents (3.2 mmol) were simultaneously added to a solution of benzothiadiphosphole **1**, and the phosphane–borane complexes **6a**,**b** were obtained in 85–90% yields. For the synthesis of tertiary phosphanes containing bulky moieties, such as (cyclohexyl)dimethylphosphane–borane (**6e**) and (isopropyl)dimethylphosphane–borane (**6f**), the Grignard reagent with the bulkiest group was added first.

Formation of the Intermediate A (with $R^1 = R^2 = n$Bu): Benzothiadiphosphole **1** (0.010 g, 0.033 mmol) was introduced into an NMR tube and dissolved under argon in [D_8]THF (1.0 mL). When the solid had dissolved, *n*BuMgBr (2 equiv.) was added. The ^{31}P NMR spectrum showed the immediate disappearance of the starting reagent **1** and the appearance of signals ascribed to the pentacoordinate intermediate **A** with the following spectroscopic data. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.40–7.30 (m, 2 H), 7.29 (dd, *J* = 7.7, *J* = 6.0 Hz, 2 H), 6.72 (d, *J* = 7.9 Hz, 2 H), 2.17 (s, 6 H), 2.14–1.90 (m, 4 H), 1.70–1.50 (m, 4 H), 1.48–1.30 (m, 4 H), 1.30–0.80 (m, 6 H) ppm. ^{13}C NMR (100.56 MHz, $CDCl_3$, 25 °C, CH, CH_2 and CH_3): δ = 134.5 (d, J_{P-P} = 14 Hz), 134.1 (d, J_{C-P} = 3 Hz), 129.9, 30.7 (dd, J_{C-P} = 17 Hz, *J* = 6 Hz), 29.2 (d, J_{C-P} = 14 Hz), 26.2 (d, J_{C-P} = 15 Hz), 20.7, 14.1 ppm. ^{31}P NMR (161.89 MHz, $CDCl_3$, 25 °C): δ = –31.6 (d, $^1J_{P-P}$ = 169 Hz), –43.3 (d, $^1J_{P-P}$ = 169 Hz) ppm.

Preparation of the Unsymmetrical Tertiary Phosphane–Borane 6g. Three-Step Procedure: The first and the second Grignard reagents (R^1MgBr, 1.0 mmol + R^2MgBr, 1.0 mmol) were sequentially added (1 min between the two steps) to a solution of benzothiadiphosphole **1** (0.306 g, 1.0 mmol) in anhydrous THF (10 mL) under dry argon. After 2 min, the third Grignard reagent (R^3MgBr, 1.2 mmol) was added. After about 30–40 min, the flask was immersed in a salt/ice bath (–5 to –8 °C) and the BH_3·THF complex (1.5–2.0 mmol) was added portionwise (firstly 1 mmol, then after about 1 h, 0.5 mmol every 30 min). The salt/ice bath was removed, and the reaction mixture was allowed to stand at room temperature. The resulting solution was stirred under a gentle pressure of argon (in order to remove excess BH_3), then PCl_3 was added (1.5 mmol). After 5–10 min, the reaction mixture was treated with an acidic (HCl) aqueous solution (0.5 mL), and the solvent was partially removed under vacuum. Extraction with CH_2Cl_2, treatment with anhydrous Na_2SO_4 and concentration under vacuum gave a mixture of the phosphane–borane complex and reagent **1**. Compound **1** was recovered by crystallization from CH_2Cl_2/diethyl ether in 70–80% yield. FC of the mother liquor gave unsymmetrical phosphane–borane complex **6g** in 55% yield and a further amount of compound **1** in 10–20% yield.

Preparation of 1-Ethylphosphinane–Borane (6h): The bis(Grignard) reagent $BrMg(CH_2)_5MgBr$ (1 mmol) was added to a solution of **1** (0.306 g, 1 mmol) in THF (10 mL) at room temperature. The mixture was stirred for 15 min, and then ethylmagnesium bromide (1 mmol) was added. The reaction mixture was stirred for 1 h, after which the flask was immersed in a salt/ice bath (–5 to –8 °C), and the BH_3·THF complex (1.5–2.0 mmol) was added portionwise (firstly 1 mmol, then after about 1 h, 0.5 mmol every 30 min). The salt/ice bath was removed, and the reaction mixture was allowed to stand at room temperature. The obtained solution was stirred under a gentle pressure of argon (in order to remove the excess of BH_3), and then PCl_3 was added (1.5 mmol). After 5–10 min, the reaction mixture was treated with an acidic (HCl) aqueous solution (0.5 mL), and the solvent was partially removed under vacuum. Extraction with CH_2Cl_2, treatment with anhydrous Na_2SO_4 and concentration under vacuum gave a mixture of the phosphane–borane complex and reagent **1**. Compound **1** was recovered by crystallization from CH_2Cl_2/diethyl ether in 70–80% yield. FC of the mother liquor gave 1-ethylphosphinane–borane (**6h**) in 70% yield and a further amount of compound **1** in 10–20% yield.

Tributylphosphane–Borane (6a): Colourless oil, 0.185 g (85%), R_f = 0.10 (*n*-hexane/ethyl acetate, 85:15). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.62–1.52 (m, 6 H), 1.53–1.35 (m, 12 H), 0.93 (t, *J* = 7.0 Hz, 9 H), 0.38 (br. q, $J_{B-H} \approx$ 82 Hz, 3 H) ppm. ^{13}C NMR (100.56 MHz, $CDCl_3$, 25 °C): δ = 24.9 (d, *J* = 2.2 Hz), 24.6 (d, *J* = 12.3 Hz), 24.0 (d, *J* = 34.9 Hz), 13.8 ppm. ^{31}P NMR (161.89 MHz,

$CDCl_3$, 25 °C): δ = 15.0 (br. q, J_{B-P} = 54 Hz) ppm. MS (70 eV, EI): *m/z* (%) = 202 (66) $[M - BH_3]^+$, 183 (100), 152 (20), 108 (81), 77 (29), 51 (77). HRMS: calcd. for $C_{12}H_{30}BP$ 216.2178; found 216.2175.

Trihexylphosphane–Borane (6b): Colourless oil, 0.27 g (90%), R_f = 0.25 (*n*-hexane/ethyl acetate, 85:15). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.60–1.43 (m, 10 H), 1.42–1.24 (m, 20 H), 0.89 (t, *J* = 6.9 Hz, 9 H), 0.50 (br. q, $J_{B-H} \approx 100$ Hz, 3 H) ppm. ^{13}C NMR (100.56 MHz, $CDCl_3$, 25 °C): δ = 31.6, 31.2 (d, *J* = 12.2 Hz), 23.4 (d, *J* = 35.0 Hz), 22.9 (d, *J* = 2.1 Hz), 22.8, 14.3 ppm. ^{31}P NMR (161.89 MHz, $CDCl_3$, 25 °C): δ = 15.0 (m) ppm. MS (70 eV, EI): *m/z* (%) = 286 (30) $[M - BH_3]^+$, 271 (19), 257 (60), 229 (100), 202 (41), 187 (25), 159 (39), 146 (40), 132 (56), 117 (23), 90 (28), 76 (72), 62 (44). HRMS: calcd. for $C_{18}H_{42}BP$ 300.3117; found 300.3118.

(Butyl)dihexylphosphane–Borane (6c): Colourless oil, 0.21 g (77%), R_f = 0.35 (*n*-hexane/ethyl acetate, 85:15). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.52–1.45 (m, 6 H), 1.43–1.27 (m, 12 H), 1.26–1.19 (m, 8 H), 0.86 (t, *J* = 7.5 Hz, 3 H), 0.82 (t, *J* = 6.8 Hz, 6 H), 0.31 (br. q, $J_{B-H} \approx 82$ Hz, 3 H) ppm. ^{13}C NMR (100.56 MHz, $CDCl_3$, 25 °C): δ = 31.6, 31.3 (d, *J* = 12.7 Hz), 25.0 (d, *J* = 1.6 Hz), 24.7 (d, *J* = 12.3 Hz), 23.4 (d, *J* = 34.6 Hz), 23.1 (d, *J* = 34.2 Hz), 22.9 (d, *J* = 1.5 Hz), 22.8, 14.3, 13.9 ppm. ^{31}P NMR (161.89 MHz, $CDCl_3$, 25 °C): δ = 15.2 (m) ppm. MS (70 eV, EI): *m/z* (%) = 258 (33) $[M - BH_3]^+$, 229 (16), 201 (20), 174 (37), 132 (25), 118 (23), 104 (436), 76 (100), 62 (81), 55 (81). HRMS: calcd. for $C_{16}H_{38}BP$ 272.2804; found 272.2807.

Diethyl(pentyl)phosphane–Borane (6d): Colourless oil, 0.13 g (75%), R_f = 0.37 (*n*-hexane/ethyl acetate, 90:10). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.66–1.54 (m, 4 H), 1.56–1.43 (m, 4 H), 1.40–1.30 (m, 4 H), 1.12 (dt, *J* = 15.3 Hz, *J* = 7.6 Hz, 6 H), 0.90 (t, *J* = 7.3 Hz, 3 H), 0.37 (br. q, $J_{B-H} \approx 94$ Hz, 3 H) ppm. ^{13}C NMR (100.56 MHz, $CDCl_3$, 25 °C): δ = 33.4 (d, *J* = 12.0 Hz), 22.1, 22.2, 22.3 (d, *J* = 2.2 Hz), 15.6 (d, *J* = 37.3 Hz), 13.8, 6.7 (d, *J* = 2.9 Hz) ppm. ^{31}P NMR (161.89 MHz, $CDCl_3$, 25 °C): δ = 19.2 (br. q, $J_{B-P} \approx 59$ Hz) ppm. MS (70 eV, EI): *m/z* (%) = 160 (34) $[M - BH_3]^+$, 143 (12), 117 (20), 104 (49), 90 (47), 76 (100), 59 (33). HRMS: calcd. for $C_9H_{24}BP$ 174.1709; found 174.1707.

(Cyclohexyl)dimethylphosphane–Borane (6e):[5a] Yellow greasy oil, 0.127 g (80%), R_f = 0.29 (*n*-hexane/ethyl acetate, 80:20). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.94–1.50 (m's, 7 H), 1.34–1.15 (m, 4 H), 1.23 (d, *J* = 10.3 Hz, 6 H), 0.42 (br. dq, $J_{B-H} \approx 95$ Hz, $J_{P-H} \approx 15$ Hz, 3 H) ppm. ^{13}C NMR (100.56 MHz, $CDCl_3$, 25 °C): δ = 34.8 (d, *J* = 37.2 Hz), 26.8 (d, *J* = 10.6 Hz), 26.42, 26.13, 8.93 (d, *J* = 37.5 Hz) ppm. ^{31}P NMR (161.89 MHz, $CDCl_3$, 25 °C): δ = 9.6 (br. q, $J_{B-P} \approx 62$ Hz) ppm. MS (70 eV, EI): *m/z* (%) = 144 (13) $[M - BH_3]^+$, 129 (2), 103 (7), 83 (18), 64 (65), 55 (100). HRMS: calcd. for $C_8H_{20}BP$ 158.1396; found 158.1398.

(Isopropyl)dimethylphosphane–Borane (6f):[5a,5b] Greasy solid, 0.092 g (78%), R_f = 0.22 (*n*-hexane/ethyl acetate, 80:20). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.88–1.76 (m, 1 H), 1.24 (d, *J* = 10.0 Hz, 6 H), 1.16 (dd, *J* = 15.1 Hz, *J* = 7.2 Hz, 6 H), 0.43 (br. dq, $J_{B-H} \approx 95$ Hz, $J_{P-H} \approx 16$ Hz, 3 H) ppm. ^{13}C NMR (100.56 MHz, $CDCl_3$, 25 °C): δ = 24.9 (d, *J* = 36.4 Hz), 16.7 (d, *J* = 26.6 Hz), 8.8 (d, *J* = 36.5 Hz) ppm. ^{31}P NMR (161.89 MHz, $CDCl_3$, 25 °C): δ = 13.4 (br. q, $J_{B-P} \approx 61$ Hz) ppm. MS (70 eV, EI): *m/z* (%) = 104 (80) $[M - BH_3]^+$, 89 (15), 74 (32), 62 (100). HRMS: calcd. for $C_5H_{16}BP$ 118.1083; found 118.1079.

(Butyl)(ethyl)hexylphosphane–Borane (6g): Colourless oil, 0.12 g (55% by the three-step procedure), 0.097 g (45% by the two-step procedure), R_f = 0.31 (*n*-hexane/ethyl acetate, 90:10). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.68–1.25 (m, 18 H), 1.12 (dt, *J* = 8.0, *J* = 15.6 Hz, 3 H), 0.93 (t, *J* = 7.2 Hz, 3 H), 0.89 (t, *J* = 7.0 Hz, 3 H), 0.62 (br. q, $J_{B-H} \approx 97$ Hz, 3 H) ppm. ^{13}C NMR (100.56 MHz, $CDCl_3$, 25 °C): δ = 31.6, 31.3 (d, *J* = 13.0 Hz), 25.0 (d, *J* = 2.7 Hz), 24.7 (d, *J* = 12.8 Hz), 22.9 (d, *J* = 34.5 Hz), 22.8 (d, *J* = 2.3 Hz), 22.8, 22.7 (d, *J* = 34.1 Hz), 16.4 (d, *J* = 34.6 Hz), 14.3, 13.9, 7.1 (d, *J* = 2.6 Hz) ppm. ^{31}P NMR (161.89 MHz, $CDCl_3$, 25 °C): δ = 17.2 (br. q, $J_{B-P} \approx 56$ Hz) ppm. MS (70 eV, EI): *m/z* (%) = 202 (34) $[M - BH_3]^+$, 187 (12), 173 (57), 145 (55), 131 (13), 118 (29), 103 (18), 90 (100), 76 (84), 62 (59), 55 (16). HRMS: calcd. for $C_{12}H_{30}BP$ 216.2178; found 216.2180.

1-Ethylphosphinane–Borane (6h): Colourless oil, 0.116 g (80%), R_f = 0.27 (*n*-hexane/ethyl acetate, 80:20). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.97–1.42 (m, 12 H), 1.14 (dt, *J* = 7.8, *J* = 16.1 Hz, 3 H), 0.43 (br. q, $J_{B-H} \approx 93$ Hz, 3 H) ppm. ^{13}C NMR (100.56 MHz, $CDCl_3$, 25 °C): δ = 24.6 (d, *J* = 5.8 Hz), 21.3 (d, *J* = 11.0 Hz), 21.1 (d, *J* = 39.4 Hz), 16.3 (d, *J* = 35.7 Hz), 6.4 (d, *J* = 1.69 Hz) ppm. ^{31}P NMR (161.89 MHz, $CDCl_3$, 25 °C): δ = 5.6 (br. q, $J_{B-P} \approx$ 63 Hz) ppm. MS (70 eV, EI): *m/z* (%) = 141 (16) $[M - 3H]^+$, 130 (100) $[M - BH_3]^+$, 102 (73), 74 (50). HRMS: calcd. for $C_7H_{18}BP$ 144.1239; found 144.1236.

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