An Expedient Synthesis of Dialkylphosphane–Borane Complexes from Sodium Phosphide, and Their Alkylation under Phase-Transfer Conditions

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Received 2 May 2007; revised 25 June 2007

Abstract: A group of seven achiral, α- and β-chiral dialkylphosphanes were synthesized in one step from sodium phosphide and alkyl sulfonates or sulfates. The corresponding borane complexes were further alkylated with alkyl, allyl, and benzyl bromides and mesylates to give tertiary mono- and diphosphanes, either via lithium phosphide–borane complexes at low temperature (45–78%) or under phase-transfer conditions (79–91%).

Key words: red phosphorus, phosphorus complexes, phosphanes, boron complexes, phase-transfer catalysis

Successful synthetic approaches to primary, secondary, and tertiary phosphanes are many and have been reviewed comprehensively.[2] General strategies to form C–P bonds involve nucleophilic or electrophilic displacement reactions, polar or radical addition to olefinic double bonds, and transition-metal-catalyzed coupling reactions. In view of the broad range of available (chiral) alcohols and their simple transformation into sulfonates, S_N2 reactions with phosphide should represent one of the most straightforward procedures to nonchiral and (α-)chiral mono-, di-, and trialkylphosphanes. But despite this obvious formal advantage of phosphorus nucleophiles, their practical usefulness is reduced because of the air-sensitivity, high cost, and toxicity of the parent-, monoalkyl-, and dialkylphosphane precursors (PH_3, RPH_2, and R_2PH, respectively). As demonstrated by Brandsma and co-workers, these problems can be overcome in part by preparing the required metal phosphide (M_3P) directly from phosphorus and a suitable metal,[3] an approach which avoids the handling of gaseous phosphane.[4]

Of particular interest is the synthesis of secondary aliphatic or aromatic phosphanes, key intermediates in the synthesis of tertiary phosphanes with two identical substituents. Their importance for the development of chiral ligands used in asymmetric catalysis is obvious. A modular approach enables the economic access to families of ligands that are usually required for screening experiments. The convenient isolation of secondary phosphanes as borane complexes,[5] which are easily deprotonated, makes them ideal precursors, which can be grafted subsequently on chiral or nonchiral backbones. Known syntheses of secondary phosphanes typically require coupling of a Grignard reagent with phosphorus trichloride,[6] coupling of a benzyl halide with ammonium phosphinate ($NH_4H_2PO_2$),[7] or the use of gaseous phosphane.[8] The coupling protocols need an additional step to convert R_2PCl or hydrolyzed products $R_2P(O)H$ and $R_2P(O)OH$ into R_2PH,[9] and, moreover, the procedure is not applicable to the production of α-chiral phosphanes from chiral precursors, because of the configurative lability of Grignard compounds.[10] The latter protocol involves handling of dangerous phosphane gas and is frequently less selective.[4] Another possibility is the formation of dialkyl(phenyl)phosphane (R_2PPh) from phenylphosphane (PH_2Ph) followed by selective cleavage of the P–Ph bond with lithium, and aqueous work-up.[11–13]

To overcome the above-mentioned difficulties, we developed a one-step procedure for the preparation of dialkylphosphanes from mesylates, tosylates, and cyclic sulfates and sodium phosphide, conveniently prepared from red phosphorus and sodium metal. This and further conversions into tertiary mono- and diphosphanes[14] are presented here.

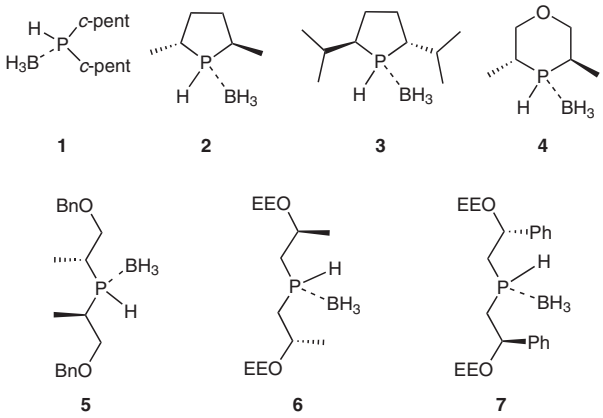


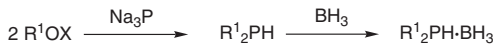
Figure 1 Secondary phosphane–borane complexes

In our early alkylation experiments, we investigated the reactivity of M_nP_m with various alkyl mesylates and it turned out that the cheap and commercially available calcium phosphide was inert under various conditions. This was attributed to its insolubility in organic solvents, while potassium and lithium phosphide gave complex mixtures or displayed low reactivity. Finally, sodium phosphide showed a reasonable reactivity and was used in all further conversions. Its preparation from red phosphorus and sodium in tetrahydrofuran proceeded smoothly at 50 °C in

SYNTHESIS 2007, No. 19, pp 2987–2994
Advanced online publication: 11.09.2007
DOI: 10.1055/s-2007-990777; Art ID: T07807SS

the presence of naphthalene (10%) to give a precipitate, which was separated and washed once with tetrahydrofuran.[15] Drying in vacuo left the reagent in 80–90% yield as a fine black powder, which displayed good reactivity and was sufficiently pure for the next step. The simple procedure could be performed easily on a gram scale by conventional Schlenk techniques, and the material could be stored under argon for prolonged periods of time without noticeable decomposition. Alternatively, this compound has been prepared from white phosphorus and sodium in inert organic solvents,[3,15] or at high temperature from the constituent elements,[16] and reacted with aldehydes or acyl chlorides to yield α-hydroxyalkyl phosphides or triacyl phosphides, respectively.[17]

Table 1 Synthesis of Secondary Phosphanes from Sodium Phosphide



Entry	R^1	OX	Product	Yield[a] (%)
1	cyclopentyl	OTs	**1**[3b]	40–48[b]
2	(*S*,*S*)-CHMe$(CH_2)_2$CHMe[c]	OMs	**2**[4]	30–38[b]
3	(*S*,*S*)-CHMe$(CH_2)_2$CHMe[c]	$OS(O)_2O$[d]	**2**[4]	58
4	(*S*,*S*)-CH(*i*-Pr)$(CH_2)_2$CH(*i*-Pr)[c]	$OS(O)_2O$[d]	**3**[13]	20
5	(*S*,*S*)-CHMeCH_2OCH_2CHMe[c]	OMs	**4**[12]	56
6	(*S*)-CHMeCH_2OBn	OMs	**5**	54[14]
7	(*S*)-CH_2CH(Me)OEE[e]	OMs	**6**	65[14]
8	(*S*)-CH_2CH(Ph)OEE[e]	OMs	**7**	35

[a] Isolated yield after conversion into borane complexes.
[b] Yield depended on preparation scale.
[c] This group represents $R^1{}_2$.
[d] This group represents $(OX)_2$.
[e] EE = ethoxyethyl.

When a suspension of sodium phosphide[18] was stirred with one of various alkyl sulfonates or cyclic sulfates in tetrahydrofuran or *N*,*N*-dimethylformamide at elevated temperature, the corresponding secondary phosphane ($R^1{}_2PH$) formed in moderate to fair yield (Table 1). The products were isolated from the crude mixture by distillation or, more conveniently, after conversion into air-stable borane complexes (Table 1, Figure 1) and column chromatography. As expected, this protocol also worked well with α-chiral alkyl groups which reacted in an S_N2-type fashion with inversion of configuration. For temperatures not exceeding 50 °C, there was no evidence (by NMR spectroscopy) of partial racemization, which would give rise to the formation of *meso*-isomers.[19] In addition, β-chiral dialkylphosphanes **6** and **7** (Figure 1) were also synthesized under similar conditions. It is worth pointing out that the precursors for **4**–**7** are conveniently accessible from the chiral pool [**4**–**6** from ethyl (*S*)-lactate, **7** from ethyl (*S*)-mandelate]. In all cases the secondary phosphanes were predominantly formed. This is particularly notable for **5**–**7**, where even an excess of the mesylates did not yield tertiary phosphanes. We speculate that the inactivity of the last sodium atom at phosphorus is caused by its efficient trapping in a 'pseudo crown ether cage' formed by benzyloxy groups.

With a method permitting a single-step preparation of dialkylphosphanes (and their borane complexes), the latter could serve as phosphorus modules to build up libraries of tertiary phosphanes (e.g., **8**–**20**, Figure 2), provided an economic protocol for the introduction of a third substitu-

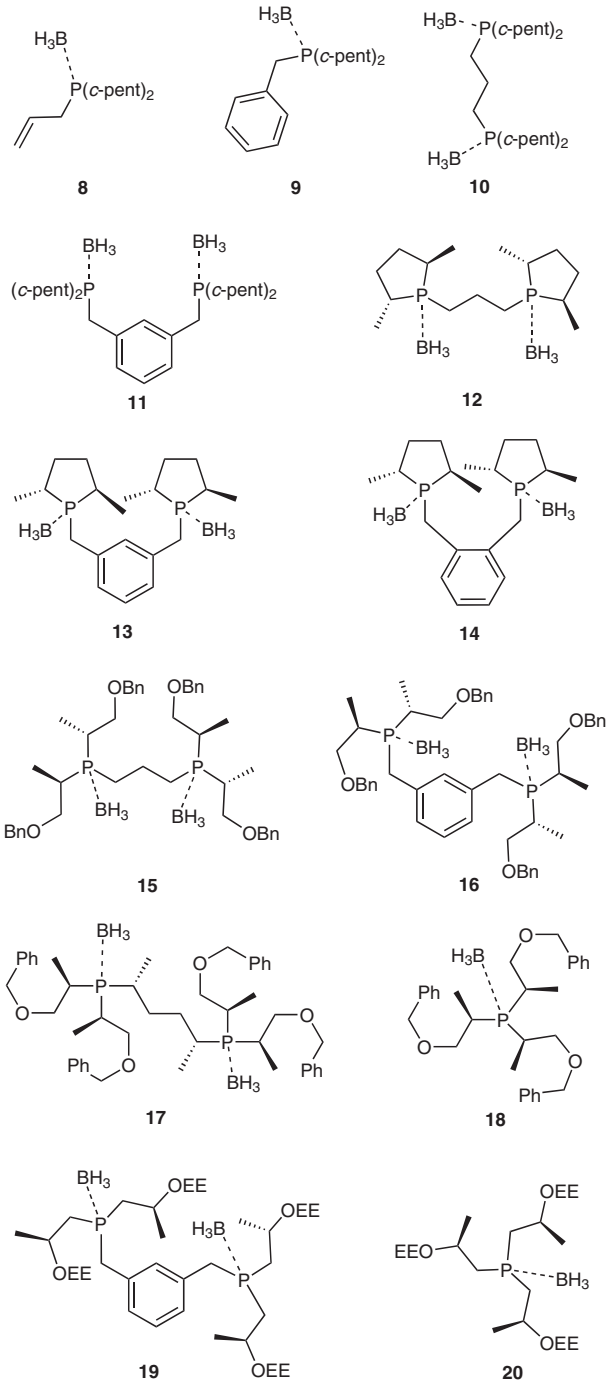


Figure 2 Tertiary mono- and diphosphanes

ent could be found. As expected, the dialkylphosphane–borane complexes ($R^1{}_2PH{\cdot}BH_3$) could be cleanly deprotonated with *n*-butyllithium as demonstrated for **5**.[20] Subsequent reaction with 1,3-bis(bromomethyl)benzene, (2*S*,5*S*)-hexane-2,5-diyl dimesylate, (*S*)-2-(benzyloxy)-1-methylethyl mesylate, or (*S*)-2-(1-ethoxyethoxy)-2-methylethyl mesylate afforded diphosphanes **16** and **17** and the C_3-symmetrical monophosphanes **18** and **20** in 64, 45, 78, and 74% yield, respectively (Figure 2, Table 2).

Table 2 Synthesis of Tertiary Mono- and Diphosphanes by Deprotonation of **5** and **6** with *n*-Butyllithium

$R^1{}_2PH{\cdot}BH_3$ —(1. *n*-BuLi, 0 °C; 2. R^2X, 0–50 °C)→ $R^1{}_2R^2P{\cdot}BH_3$

Entry	$R^1{}_2PH{\cdot}BH_3$	R^2X	Product	Yield (%)
1	**5**	$BrCH_2(1,3\text{-}C_6H_4)CH_2Br$[a]	**16**	65
2	**5**	(*S*,*S*)-MsOCH(Me)-$(CH_2)_2$CH(Me)OMs[a]	**17**	45
3	**5**	(*S*)-$BnOCH_2$CH(Me)OMs	**18**	78[14]
4	**6**	(*S*)-EEOCH(Me)CH_2OMs[b]	**20**	74[14]

[a] This group represents 2 R^2X.
[b] EE = ethoxyethyl.

An attractive alternative was the coupling of secondary phosphane–borane complexes **1**, **2**, **5**, and **6** with allyl-, benzyl-, and alkyl bromides under phase-transfer conditions (Table 3). With a catalytic amount of tetrabutylammonium bromide in aqueous potassium hydroxide–toluene[21,22] the reactions proceeded smoothly at room temperature to give borane complexes of mono- and diphosphanes **8**–**16** and **19** (Figure 2). After chromatography or crystallization the borane complexes could be isolated in 79–91% yield (Table 3). In contrast, mesylates in general and α-branched alkyl bromides were found to be inert.

In summary, we have developed a single-step method for accessing various dialkylphosphanes including α-chiral compounds from alkyl sulfonates and sodium phosphide as an inexpensive and conveniently prepared precursor. This protocol is further characterized by its omission of the use of *tert*-butyl alcohol as a co-reagent, and the subsequent one-pot conversion of crude products into air-stable borane complexes. We further demonstrated their feasibility as phosphorus modules attachable to alkyl, allyl, or benzyl bromides under phase-transfer conditions or, after conversion into lithium dialkylphosphide–borane complexes, to mesylates at low temperature. This two-step sequence provides a short access to ligand families of the general formula $R^1{}_2PR^2$ and $R_2P{-}X{-}PR_2$. The application of new phosphanes as ligands in asymmetric catalysis is presently under investigation.

Table 3 Synthesis of Tertiary Mono- and Diphosphanes under Phase-Transfer Conditions

$R^1{}_2PH{\cdot}BH_3$ + R^2Br —(30% aq KOH; PhMe, TBAB, r.t.)→ $R^1{}_2R^2P{\cdot}BH_3$

Entry	$R^1{}_2PH{\cdot}BH_3$	R^2	Product	Yield (%)
1	**1**	All	**8**	79
2	**1**	Bn	**9**[21]	88
3	**1**	$(CH_2)_3$[a]	**10**	83
4	**1**	$CH_2(1,3\text{-}C_6H_4)CH_2$[a]	**11**	90
5	**2**	$(CH_2)_3$[a]	**12**	86
6	**2**	$CH_2(1,3\text{-}C_6H_4)CH_2$[a]	**13**	90
7	**2**	$CH_2(1,2\text{-}C_6H_4)CH_2$[a]	**14**	80
8	**5**	$(CH_2)_3$[a]	**15**	91
9	**5**	$CH_2(1,3\text{-}C_6H_4)CH_2$[a]	**16**	90
10	**6**	$CH_2(1,3\text{-}C_6H_4)CH_2$[a]	**19**	88

[a] This group represents $R^2{}_2$ of $(R^2X)_2$.

Melting points were determined on a Kofler melting point apparatus, and are uncorrected. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AM 400 spectrometer at 400.13 MHz (^1H), 100.61 MHz (^{13}C), and 161.98 MHz (^{31}P); the samples were dissolved in $CDCl_3$ and the chemical shifts δ are reported in ppm relative to the residual solvent peaks at δ = 7.24 (^1H) and δ = 77.00 (^{13}C). $^{13}C\{^1H\}$ NMR spectra were recorded in a *J*-modulated mode; signals are assigned as C, CH_2, or CH_3; undesignated signals refer to CH resonances. MS (EI, 50 eV or 70 eV) or ESI-MS determinations were carried out on a Finnigan MAT 8230 spectrometer. HRMS determinations were carried out on a Finnigan MAT 8230 spectrometer. Optical rotations were measured with a Perkin Elmer polarimeter 243 equipped with a 1-dm thermostatted cell. PE, CH_2Cl_2, and EtOAc were distilled, absolute DMF from CaH_2, THF from sodium benzophenone ketyl, Et_2O and *n*-hexane from LAH; 1.6 or 2.5 M solns of *n*-BuLi in *n*-hexane, and 1 M $BH_3{\cdot}$THF in THF were used. All the other chemicals were analytical grade and used without further purification.

Sodium Phosphide[3]

To a soln of naphthalene (128 mg, 1 mmol) in THF (10 mL) in a Schlenk tube under argon was added Na metal (230 mg, 10 mmol) in the form of small chunks, and the mixture was stirred for 30 min; the addition of red phosphorus (102 mg, 3.3 mmol), previously dried by sequential washings with EtOH, benzene, and THF, followed. During stirring of the mixture for 12 h at 50 °C, a finely divided black precipitate of Na_3P formed. The disappearance of Na metal indicated completion of the conversion. The supernatant soln was removed by suction, and the precipitate was washed with THF and dried under vacuum.

Yield: 80–90%.

Dicyclopentylphosphane–Borane Complex (1)

Powdered black Na_3P (1.50 g, 15 mmol) was placed in a Schlenk tube and suspended in degassed anhyd THF (80 mL). The mixture was cooled to 0 °C and a soln of cyclopentyl tosylate (7.69 g, 32 mmol) in THF (20 mL) was added slowly. The mixture was stirred for 10 h at 55 °C and subsequently cooled to r.t.; then MeOH (5 mL) was added and the solids were collected by filtration. After evaporation of the solvents under vacuum, fractional distillation of the crude residue afforded dicyclopentylphosphane. This can optional-

ly be converted into the borane complex by stirring with an excess of BH_3·THF in THF at 0 °C for 1 h to give **1**.

Yield: 1.03–1.22 g (40–48%); white deliquescent solid; mp 25–30 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.43 (dm, J_{PH} = 350 Hz, 1 H), 2.17–2.10 (m, 2 H), 2.00–1.84 (m, 4 H), 1.70–1.55 (m, 12 H), 0.81–0.00 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.10 (d, J = 36.2 Hz), 30.10 (CH_2), 28.30 (d, J = 2.2 Hz, CH_2), 26.24 (d, J = 8.3 Hz, CH_2), 26.12 (d, J = 7.7 Hz, CH_2).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 15.86 (m).

MS (EI, 70 eV, 30 °C): *m*/*z* (%) = 170 (100) [$M^+ - BH_3$].

(2*R*,5*R*)-2,5-Dimethylphospholane–Borane Complex (2)

Powdered Na_3P (180 mg, 1.8 mmol) and anhyd DMF (5 mL) were placed in a Schlenk tube and cooled to 0 °C. To this suspension was added (2*S*,5*S*)-hexane-2,5-diol dimesylate (493 mg, 1.8 mmol) in DMF (5 mL) and the mixture was stirred for 24 h at 40 °C. After the mixture had cooled to r.t., H_2O (0.5 mL) was added and stirring was continued for 30 min. The addition of degassed pentane (30 mL) followed, and vigorous stirring was continued for another 30 min. The pentane layer was transferred by a Teflon cannula to a cooled 1 M soln of BH_3·THF in THF (3 mL, 3 mmol, 2 equiv), and after the mixture had stirred at r.t. for 2 h, chilled 2% HCl (3 mL) was added. The aqueous layer was extracted with Et_2O (2 × 25 mL), and the combined organic phases were washed with H_2O (1 × 40 mL) and brine (1 × 40 mL) and dried ($MgSO_4$). Filtration and evaporation of solvents left a colorless oil which was purified by column chromatography (silica gel, CH_2Cl_2–PE, 20:80); this yielded borane complex **2**. (Similar treatment of the corresponding cyclic sulfate yielded up to 58% of product.)

Yield: 78–99 mg (30–38%); $[\alpha]_D^{20}$ +3.2 ± 0.5 (*c* 0.3, $CHCl_3$) {Lit.[13] $[\alpha]_D^{20}$ +3.3 (*c* 0.3, $CHCl_3$}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.31 (dm, J_{PH} = 349 Hz, 1 H), 2.58–2.43 (m, 1 H), 2.26–1.99 (m, 3 H), 1.50–1.27 (m, 2 H), 1.28 (dd, J = 6.8, 15.6 Hz, 3 H), 1.21 (dd, J = 7.3, 16.9 Hz, 3 H), 0.90–0.00 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.68 (d, J = 2.4 Hz, CH_2), 35.58 (CH_2), 32.27 (d, J = 37.1 Hz), 26.99 (d, J = 34.6 Hz), 16.80 (d, J = 3.0 Hz, CH_3), 15.06 (d, J = 5.0 Hz, CH_3).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 24.88 (m).

MS (EI, 70 eV, 30 °C): *m*/*z* (%) = 129 (14) [M^+]; 116 (100) [$M^+ - BH_3$].

(2*R*,5*R*)-2,5-Diisopropylphospholane–Borane Complex (3)

The cyclic sulfate corresponding to **3**, prepared according to a published procedure,[23] reacted with Na_3P as described for **2** to yield **3**.

Yield: 20%; white solid; $[\alpha]_D^{20}$ –80.2 ± 2.0 (*c* 0.15, $CHCl_3$) {Lit.[13] $[\alpha]_D^{20}$ –81.2 (*c* 0.1, $CHCl_3$}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.63 (dm, J = 349 Hz, 1 H), 2.25–1.85 (m, 4 H), 1.75 (m, 1 H), 1.49–1.18 (m, 3 H), 1.06 (d, J = 6.8 Hz, 3 H), 1.04 (d, J = 6.4 Hz, 3 H), 0.97 (d, J = 6.6 Hz, 3 H), 0.96 (d, J = 6.0 Hz, 3 H), 0.91–0.20 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.85 (d, J = 37.0 Hz), 42.46 (d, J = 33.7 Hz), 32.22 (d, J = 3.0 Hz), 31.95 (CH_2), 31.09 (d, J = 6.0 Hz, CH_2), 28.30 (d, J = 4.6 Hz), 23.74 (d, J = 3.3 Hz, CH_3), 22.72 (d, J = 4.3 Hz, CH_3), 21.55 (d, J = 3.0 Hz, CH_3), 21.46 (CH_3).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 6.65 (m).

MS (EI, 70 eV, 30 °C): *m*/*z* (%) = 172 (69) [$M^+ - BH_3$].

(3*R*,5*R*)-3,5-Dimethyl-1,4-oxaphosphinane–Borane Complex (4)

Powdered Na_3P (162 mg, 1.62 mmol) was suspended in anhyd DMF (5 mL) and the (*S*,*S*)-dimesylate of 1-(2-hydroxypropoxy)propan-2-ol (470 mg, 1.62 mmol) dissolved in DMF (2.5 mL) was added dropwise. The reaction mixture was stirred for 16 h at 45 °C. After the mixture had cooled to r.t., H_2O (0.5 mL) was added and the mixture was stirred for 30 min; the addition of pentane (30 mL) followed and stirring was continued for another 30 min. The organic layer was added dropwise to a 1 M soln of BH_3·THF in THF (3 mL, 3 mmol) in an ice bath, and the mixture was stirred for 2 h at r.t. before the excess reagent was destroyed with chilled 2% HCl (3 mL). The organic phase was separated and the aqueous layer was extracted with pentane (2 × 25 mL). The organic layers were washed with H_2O (1 × 40 mL) and brine (1 × 40 mL) and dried ($MgSO_4$). After removal of the solvents, the crude product was purified by chromatography (silica gel, CH_2Cl_2–PE, 40:60); this gave **4** as a highly volatile oil.

Yield: 132 mg (56%); $[\alpha]_D^{20}$ –41.1 (*c* 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.49 (dm, J_{PH} = 349 Hz, 1 H), 4.11 (ddd, J = 4.7, 12.3, 16.0 Hz, 1 H), 3.93 (ddd, J = 3.8, 12.4, 16.0 Hz, 1 H), 3.74 (ddd, J = 2.7, 8.1, 12.2 Hz, 1 H), 3.32 (ddd, J = 10.0, 10.7, 12.2 Hz, 1 H), 2.11–1.97 (m, 2 H), 1.29 (dd, J = 7.7, 16.5 Hz, 3 H), 1.15 (dd, J = 7.3, 16.1 Hz, 3 H), 0.97–0.00 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 73.61 (d, J = 7.8 Hz, CH_2), 73.13 (d, J = 7.6 Hz, CH_2), 22.72 (d, J = 32.7 Hz), 22.52 (d, J = 32.2 Hz), 13.12 (d, J = 2.3 Hz, CH_3), 12.03 (d, J = 3.0 Hz, CH_3).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 6.04 (m).

MS (EI, 70 eV, 30 °C): *m*/*z* (%) = 146 (3) [M^+], 132 (100) [$M^+ - BH_3$].

(*R*,*R*)-Bis[2-(benzyloxy)-1-methylethyl]phosphane–Borane Complex (5)

Anhyd DMF (5 mL) was added to Na_3P (264 mg, 2.64 mmol) and the suspension was cooled to 0 °C. A soln of (*S*)-2-(benzyloxy)-1-methylethyl methanesulfonate (1.62 g, 7.26 mmol) in THF (5 mL) was added at 0 °C to moderate the exothermic reaction, and the mixture was stirred for 10 h at 45 °C. All solvents were evaporated under vacuum, and THF (10 mL) was added to the residue; this gave a gray suspension. An excess of 1 M BH_3·THF complex in THF (10 mL, 3.3 equiv) was dropped in at 0 °C, and after the mixture had stirred at r.t. for 2 h it was carefully quenched with ice-cooled 2% HCl (20 mL) followed by Et_2O (40 mL). The aqueous layer was extracted with Et_2O (2 × 25 mL) and the combined organic phases were washed with H_2O (1 × 40 mL) and brine (1 × 40 mL) and dried ($MgSO_4$). Filtration and evaporation of solvents gave a yellowish oil, which was purified by column chromatography (silica gel, Et_2O–PE, 5:95); this gave **5**.

Yield: 614 mg (54%); colorless oil; $[\alpha]_D^{20}$ –4.2 ± 0.09 (*c* 4.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.25 (m, 10 H), 4.62 (dm, J_{PH} = 371 Hz, 1 H), 4.51 (dd, J = 5.9, 11.8 Hz, 2 H), 4.40 (dd, J = 6.0, 11.9 Hz, 2 H), 3.70–3.52 (m, 4 H), 2.47–2.28 (m, 2 H), 1.23 (dd, J = 7.3, 14.9 Hz, 3 H), 1.19 (dd, J = 7.3, 16.6 Hz, 3 H), 0.91–0.00 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.86 (C), 137.80 (C), 128.36, 128.30, 127.71, 127.67, 127.61, 73.25 (CH_2), 73.14 (CH_2), 71.37 (d, J = 2.3 Hz, CH_2), 71.00 (d, J = 2.3 Hz, CH_2), 26.52 (d, J = 33.6 Hz) 26.09 (d, J = 33.6 Hz), 14.16 (d, J = 2.3 Hz, CH_3), 12.54 (d, J = 1.5 Hz, CH_3).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 9.86 (m).

MS (EI, 50 eV, 90 °C): *m*/*z* (%) = 343 (8) [M^+].

HRMS (EI): *m*/*z* (%) calcd for $C_{20}H_{29}BO_2P$: 343.2002; found: 343.1991.

(*S*,*S*)-Bis[2-(1-ethoxyethoxy)propyl]phosphane–Borane Complex (6)

Anhyd THF (20 mL) was added to powdered Na_3P (1.10 g, 11 mmol) and the suspension was cooled to 0 °C. A soln of (*S*)-2-(1-ethoxyethoxy)propyl methanesulfonate (7.91 g, 35 mmol) in THF (15 mL) was added dropwise, and the mixture was stirred for 30 min at 0 °C and then for 10 h at 30 °C. The mixture was cooled to 0 °C and BH_3·THF (25 mL, 25 mmol) was added slowly. After 30 min, H_2O (0.2 mL) was added and the mixture was stirred for 1 h. The mixture was diluted with Et_2O (150 mL) and H_2O (40 mL) and the aqueous layer was extracted with Et_2O (50 mL). The combined organic layers were washed with sat. $NaHCO_3$ (1 × 100 mL) and brine (1 × 50 mL) and dried ($MgSO_4$). Evaporation of solvents left a colorless oil, which was purified by column chromatography (silica gel, Et_2O–PE, 20:80); this gave **6** as a mixture of diastereomers, which was directly used in subsequent reactions.

Yield: 2.21 g (65%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = ~4.8 (dm, *J* = 371 Hz, 1 H, PH), 4.73–4.70 (m, 2 H), 4.09–3.99 (m, 2 H), 3.57–3.54 (m, 2 H), 3.47–3.44 (m, 2 H), 2.07–1.74 (m, 4 H), 1.30–1.14 (m, 18 H), 0.91–0.20 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 100.52–97.72 (8 signals), 70.13–60.07 (19 signals), 30.83–15.26.(37 signals).

^{31}P NMR (162 MHz, $CDCl_3$): δ = –22.52 to –24.74 (br m).

ESI-MS: *m*/*z* (%) = 307.2 (100) [M^+ – 1].

(*S*,*S*)-Bis[2-(1-ethoxyethoxy)-2-phenylethyl]phosphane–Borane Complex (7) and (*S*,*S*)-Bis(2-hydroxy-2-phenylethyl)phosphane–Borane Complex

To a suspension of Na_3P (320 mg, 3.2 mmol) in anhyd THF (5 mL) was added (*S*)-2-(1-ethoxyethoxy)-2-phenylethyl methanesulfonate (2.48 g, 8.6 mmol) in THF at 0 °C, and the mixture was stirred for 10 h at 50 °C. An excess of 1 M BH_3·THF in THF (7 mL) was added at 0 °C, followed by H_2O (100 μL) after 30 min, and stirring was continued for 2 h at r.t. The mixture was diluted with H_2O (25 mL) and Et_2O (75 mL) and the aqueous phase was extracted with Et_2O (30 mL). The organic phases were washed with sat. $NaHCO_3$ (20 mL) and brine (20 mL) and dried ($MgSO_4$). Chromatographic purification (Et_2O–PE, 40:60) afforded **7** as a crude mixture of diastereomers, which was used without further purification in the next step; yield: 485 mg (35%). For characterization, a sample of **7** was deprotected by stirring with a catalytic amount of a soln of *p*-TsOH in EtOH for 30 h at r.t. Neutralization with $NaHCO_3$ and extractive workup with Et_2O was followed by chromatography (EtOAc–PE, 30:70); this yielded the diol; yield: 78%.

$[\alpha]_D^{20}$ +60.4 (*c* 1.0, EtOH).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10–7.35 (m, 10 H), 5.06 (m, 2 H), 4.88 (dm, J_{PH} = 379 Hz, 1 H), 2.68 (br s, 2 H), 2.43 (m, 1 H), 2.30 (m, 1 H), 2.12 (m, 2 H), 0.00–1.30 (br m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.68 (d, *J* = 9.3 Hz, C), 143.32 (d, *J* = 9.1 Hz), 128.81, 128.79, 128.27, 128.20, 125.48, 125.39, 70.57 (d, *J* = 3.4 Hz), 70.04 (d, *J* = 1.8 Hz), 31.44 (d, *J* = 33.2 Hz, CH_2), 30.79 (d, *J* = 34.0 Hz, CH_2).

^{31}P NMR (162 MHz, $CDCl_3$): δ = –20.39 (m).

MS (EI, 70 eV, 130 °C): *m*/*z* (%) = 274 (5) [$M^+ – BH_3$].

HRMS (EI): *m*/*z* (%) calcd for $C_{16}H_{19}O_2P$: 274.1123; found: 274.1118.

Phosphane–Borane Complexes 8–16 and 19 under Phase-Transfer Conditions (Method A); General Procedure

To an ice-cooled mixture of the appropriate secondary phosphane–borane complex $R^1{}_2PH{\cdot}BH_3$ (1.50 mmol) and TBAB (16.2 mg) in 30% aq KOH (10.4 mL) and toluene (3.2 mL) was added the appropriate mono- or dibromide R^2X or $(R^2X)_2$ (1.0 or 0.5 mmol, respectively), and the mixture was vigorously stirred for 16 h at r.t. Et_2O (25 mL) was added and the organic phase was washed with H_2O (3 × 10 mL) and brine (1 × 10 mL) and dried ($MgSO_4$). After evaporation, the crude product was purified either by column chromatography or by crystallization from PE.

Allyldicyclopentylphosphane–Borane Complex (8)

Yield: 79%; colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.86–5.74 (m, 1 H), 5.17–5.10 (m, 2 H), 2.47 (br dd, *J* = 7.6, 10.8 Hz, 2 H), 2.03 (m, 2 H), 1.88–1.49 (m, 16 H), 0.50 to –0.03 (br m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 129.65 (d, *J* = 7.6 Hz), 118.93 (d, *J* = 8.7 Hz, CH_2), 32.30 (d, *J* = 34.4 Hz), 28.76 (d, *J* = 31.8 Hz, CH_2), 27.90 (d, *J* = 2.1 Hz, CH_2), 27.75 (CH_2), 26.51 (d, *J* = 9.1 Hz, CH_2), 25.99 (d, *J* = 8.6 Hz, CH_2).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 29.22 (m).

MS (EI, 70 eV, 30 °C): *m*/*z* (%) = 223 (17) [M^+ – 1].

HRMS (EI): calcd for $C_{13}H_{23}P$: 210.1537; found: 210.1527.

Benzyldicyclopentylphosphane–Borane Complex (9)

Yield: 88%; mp 80–83 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.16 (m, 5 H), 3.01 (d, *J* = 10.6 Hz, 2 H), 1.99–1.87 (m, 2H), 1.77–1.42 (m, 16 H), 0.91 to –0.1 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.53 (d, *J* = 6.8 Hz, C), 129.63 (d, *J* = 3.7 Hz), 128.47 (d, *J* = 1.6 Hz), 126.76 (d, *J* = 2.3 Hz), 32.26 (d, *J* = 33.8 Hz), 30.75 (d, *J* = 29.2 Hz, CH_2), 28.01 (d, *J* = 1.4 Hz, CH_2), 27.89 (CH_2), 26.55 (d, *J* = 9.2 Hz, CH_2), 26.01 (d, *J* = 8.5 Hz, CH_2).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 31.33 (m).

MS (EI, 70 eV, 40 °C): *m*/*z* (%) = 274 (4.3) [M^+].

HRMS (EI): *m*/*z* calcd for $C_{17}H_{25}P$: 260.1694; found: 260.1688.

1,3-Bis(dicyclopentylphosphanyl)propane–Bis(borane) Complex (10)

Yield: 83%; mp 66–68 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.09–1.95 (m, 4 H), 1.89–1.74 (m, 10 H), 1.74–1.53 (m, 28 H), 0.7 to –0.1 (br m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.45 (d, *J* = 35.2 Hz), 28.41 (d, *J* = 1.7 Hz, CH_2), 28.21 (CH_2), 26.73 (d, *J* = 9.1 Hz, CH_2), 26.53 (d, *J* = 8.7 Hz, CH_2), 24.75 (dd, *J* = 11.0, 31.3 Hz, CH_2), 18.28 (CH_2).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 28.27 (m).

MS (EI, 70 eV, 130 °C): *m*/*z* (%) = 407 (12) [M^+].

HRMS (EI): *m*/*z* calcd for $C_{23}H_{47}B_2P_2$: 407.3348; found: 407.3339.

1,3-Bis[(dicyclopentylphosphanyl)methyl]benzene–Bis(borane) Complex (11)

Yield: 90%; mp 136–138 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22–7.07 (m, 4 H), 3.00 (d, *J* = 11.0 Hz, 4 H), 2.08–1.95 (m, 4 H), 1.83–1.46 (m, 32 H), 0.91–0.00 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.05 (dd, *J* = 1.6, 6.0 Hz, C), 130.90 (pseudo t, *J* = 3.7 Hz), 128.54 (pseudo t, *J* = 2.1 Hz), 128.30 (dd, *J* = 2.2, 3.0 Hz), 32.49 (d, *J* = 33.7 Hz), 30.69 (d, *J* = 29.1 Hz,

CH_2), 28.03 (CH_2), 27.9 (CH_2), 26.50 (d, J = 9.1 Hz, CH_2), 26.03 (d, J = 7.7 Hz, CH_2).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 31.71 (m).

MS (EI, 70 eV, 200 °C): *m*/*z* (%) = 469 (6) [M^+].

HRMS (EI): *m*/*z* calcd for $C_{28}H_{47}BP_2$: 455.3282; found: 455.3296.

1,3-Bis[(2*R*,5*R*)-2,5-dimethylphospholan-1-yl]propane–Bis(borane) Complex (12)

Yield: 86%; mp 86–90 °C; $[\alpha]_D^{20}$ +12.2 (*c* 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.19–1.97 (m, 8 H), 1.85–1.71 (m, 2 H), 1.69–1.54 (m, 4 H), 1.32 (m, 4 H), 1.22 (dd, J = 7.4, 15.9 Hz, 6 H), 1.15 (dd, J = 7.1, 13.6 Hz, 6 H), 0.91–0.00 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.83 (d, J = 3.1 Hz, CH_2), 34.39 (CH_2), 33.64 (d, J = 37.0 Hz), 32.08 (d, J = 33.7 Hz), 23.20 (dd, J = 11.5, 26.7 Hz, CH_2), 16.66 (CH_2), 15.72 (d, J = 4.6 Hz, CH_3), 13.36 (d, J = 2.3 Hz, CH_3).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 38.68 (m).

MS (EI, 70 eV, 80 °C): *m*/*z* (%) = 299 (34) [M^+].

HRMS (EI): *m*/*z* calcd for $C_{15}H_{32}BP_2$: 285.2075; found: 285.2066.

1,3-Bis{[(2*R*,5*R*)-2,5-dimethylphospholan-1-yl]methyl}benzene–Bis(borane) Complex (13)

Yield: 90%; mp 116–120 °C; $[\alpha]_D^{20}$ +127 (*c* 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.13 (m, 4 H), 2.97 (dd, J = 8.5, 13.4 Hz, 2 H), 2.75 (dd, J = 13.7, 14.7 Hz, 2 H), 2.22–2.03 (m, 8 H), 1.47–1.26 (m, 4 H), 1.26 (dd, J = 7.2, 13.4 Hz, 6 H), 0.81 (dd, J = 7.2, 16.5 Hz, 6 H), 0.91–0.00 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.65 (dd, J = 2.3, 4.7 Hz, C), 131.96 (t, J = 4.0 Hz), 128.60 (t, J = 2.1 Hz), 128.44 (dd, J = 3.2, 4.2 Hz), 34.60 (d, J = 2.7 Hz, CH_2), 34.41 (d, J = 35.2 Hz), 34.35 (CH_2), 30.72 (d, J = 32.9 Hz), 28.73 (d, J = 23.3 Hz, CH_2), 15.48 (d, J = 4.0 Hz, CH_3), 13.28 (d, J = 2.7 Hz, CH_3).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 39.50 (m).

MS (EI, 70 eV, 100 °C): *m*/*z* (%) = 362 (15) [M^+].

HRMS (EI): *m*/*z* calcd for $C_{20}H_{38}B_2P_2$: 362.2642; found: 362.2648.

1,2-Bis{[(2*R*,5*R*)-2,5-dimethylphospholanyl]methyl}benzene–Bis(borane) Complex (14)

Yield: 80%; mp 163–167 °C; $[\alpha]_D^{20}$ +211 (*c* 0.33, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18–7.09 (m, 4 H), 3.62 (dd, J = 6.9, 14.7 Hz, 2 H), 2.77 (pseudo t, J = 15.2 Hz, 2 H), 2.26–2.06 (m, 8 H), 1.49–1.34 (m, 4 H), 1.32 (dd, J = 6.4, 13.0 Hz, 6 H), 0.86 (dd, J = 6.9, 15.7 Hz, 6 H), 0.8 to –0.1 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.82 (t, J = 4.4 Hz, C), 130.58 (dd, J = 2.4, 3.8 Hz), 127.06 (t, J = 2.5 Hz), 34.70 (d, J = 3.4 Hz, CH_2), 34.44 (CH_2), 34.34 (d, J = 35.5 Hz), 32.05 (d, J = 33.2 Hz), 27.17 (d, J = 22.3 Hz, CH_2), 15.11 (d, J = 3.9 Hz, CH_3), 13.69 (d, J = 2.5 Hz, CH_3).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 38.68 (m).

MS (EI, 70 eV, 110 °C): *m*/*z* (%) = 362 (33) [M^+].

HRMS (EI): *m*/*z* calcd for $C_{20}H_{38}B_2P_2$: 362.2642; found: 362.2635.

1,3-Bis{(*R*,*R*)-bis[2-(benzyloxy)-1-methylethyl]phosphanyl}propane–Bis(borane) Complex (15)

Chromatography (silica gel, Et_2O–PE, 30:70); yield: 91%; colorless oil; $[\alpha]_D^{20}$ +10.1 (*c* 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.22 (m, 20 H), 4.45 (d, J = 11.9 Hz, 2 H), 4.43 (br s, 4H), 4.41 (d, J = 11.9 Hz, 2 H), 3.72–3.50 (m, 8 H), 2.28–2.17 (m, 4 H), 1.80–1.62 (m, 6 H), 1.17 (dd, J = 4.6, 7.3 Hz, 6 H), 1.14 (dd, J = 3.3, 7.2 Hz, 6 H), 0.91–0.00 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.02 (C), 137.89 (C), 128.39, 128.35, 127.76, 127.70, 127.64, 73.18 (CH_2), 73.14 (CH_2), 71.31 (d, J = 3.6 Hz, CH_2), 71.21 (CH_2), 28.63 (d, J = 31.6 Hz), 28.12 (d, J = 31.6 Hz), 22.79 (dd, J = 12.3, 30.5 Hz, CH_2), 18.28 (CH_2), 12.49 (CH_3), 12.20 (d, J = 2.3 Hz, CH_3).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 29.57 (m).

MS (EI, 70 eV, 250 °C): *m*/*z* (%) = 729 (7) [M^+].

HRMS (EI): *m*/*z* calcd for $C_{43}H_{61}O_4BP_2$: 714.4138; found: 714.4152.

1,3-Bis({(*R*,*R*)-bis[2-(benzyloxy)-1-methylethyl]phosphanyl}methyl)benzene–Bis(borane) Complex (16) by Deprotonation Followed by Alkylation (Method B); Typical Procedure

Borane complex **5** (310 mg, 0.90 mmol) was dissolved in anhyd THF (4 mL) and the soln was cooled to 0 °C. To this 1.6 M *n*-BuLi in hexane (0.6 mL, 0.95 mmol) was added dropwise and the mixture was stirred for 20 min at 0 °C. The temperature was lowered to –78 °C and 1,3-bis(bromomethyl)benzene (119 mg, 0.45 mmol) in THF (2.5 mL) was added and the mixture was allowed to warm to r.t. After quenching with 1 M HCl (5 mL) and extractive workup with CH_2Cl_2 (2 × 25 mL), the crude diborane complex was purified by column chromatography (silica gel, Et_2O–PE, 10:90 to 30:70); this yielded **16**.

Yield: 226 mg (64%); colorless oil.

Compound **16** can also be prepared by Method A.

Chromatography (silica gel, Et_2O–PE, 30:70); yield: 90%; colorless oil; $[\alpha]_D^{20}$ +20.1 (*c* 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.22 (m, 20 H), 7.15–7.07 (m, 4 H), 4.40 (d, J = 12.5 Hz, 2 H), 4.40 (br s, 4 H), 4.37 (d, J = 12.5 Hz, 2 H), 3.65 (ddd, J = 5.1, 9.5, 11.8 Hz, 2 H), 3.61–3.44 (m, 8 H), 3.15 (dd, J = 13.1, 13.5 Hz, 2 H), 3.08 (dd, J = 13.1, 14.0 Hz, 2 H), 2.35–2.16 (m, 4 H), 1.19 (pseudo t, J = 7.3 Hz, 6 H), 1.16 (pseudo t, J = 7.4 Hz, 6 H), 0.91–0.00 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.00 (C), 137.98 (C), 133.53 (dd, J = 2.3, 5.4 Hz), 131.87 (pseudo t, J = 4.2 Hz), 128.84 (m), 128.36, 128.30 (m), 127.75, 127.66, 73.13 (CH_2), 71.23 (m, CH_2), 29.32 (d, J = 28.2 Hz, CH_2), 28.42 (d, J = 30.0 Hz), 28.02 (d, J = 29.5 Hz), 12.56 (d, J = 1.5 Hz, CH_3), 12.42 (d, J = 2.0 Hz, CH_3).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 31.27 (m).

MS (EI, 50 eV, 260 °C): *m*/*z* (%) = 790 (1) [M^+].

ESI-HRMS: *m*/*z* calcd for $C_{48}H_{66}B_2NaO_4P_2$: 813.4520; found: 813.4549.

(2*R*,5*R*)-2,5-Bis{(*R*,*R*)-bis[2-(benzyloxy)-1-methylethyl]phosphanyl}hexane–Bis(borane) Complex (17)

Borane complex **5** (230 mg, 0.67 mmol) was dissolved in anhyd THF (4 mL) and the soln was cooled to 0 °C. A soln of 2.5 M *n*-BuLi in hexane (0.3 mL, 0.75 mmol) was added dropwise over 15 min and the soln was stirred for 30 min at 0 °C. This was followed by slow addition of (2*S*,5*S*)-hexane-2,5-diyl dimesylate (88 mg, 0.32 mmol) in THF (2 mL) and once addition was complete, the reaction mixture was heated to 55 °C for 3 h. The cooled reaction mixture was added dropwise to ice-cold 1 M aq HCl (5 mL) and the aqueous phase was extracted with Et_2O (2 × 25 mL) and the organic layers were combined, dried ($MgSO_4$), and filtered. The solvent was evaporated to give a colorless oil, which was purified by flash chromatography (silica gel, Et_2O–PE, 50:50).

Yield: 111 mg (45%); colorless oil; $[\alpha]_D^{20}$ +17.3 (*c* 2.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.23 (m, 20 H), 4.42 (m, 4 H), 4.39 (br s, 4 H), 3.69 (m, 4 H), 3.52 (m, 4 H), 2.39 (m, 2 H), 2.24

(m, 2 H), 1.82 (m, 2 H), 1.73 (m, 2 H), 1.37 (m, 2 H), 1.24 (dd, J = 7.0, 12.5 Hz, 6 H), 1.19 (dd, J = 7.0, 13.0 Hz, 6 H), 1.07 (dd, J = 7.0, 13.9 Hz, 6 H), 0.90–0.00 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.99 (C), 128.37, 128.35, 127.79, 127.76, 127.69, 127.67, 73.14 (CH_2), 73.09 (CH_2), 71.47 (d, J = 4.2 Hz, CH_2), 71.39 (d, J = 3.8 Hz, CH_2), 29.46 (d, J = 11.2 Hz, CH_2), 27.42 (d, J = 28.1 Hz), 27.02 (d, J = 28.1 Hz), 25.93 (d, J = 30.0 Hz), 13.91 (d, J = 3.3 Hz, CH_3), 13.06 (d, J = 3.3 Hz, CH_3), 12.76 (d, J = 2.2 Hz, CH_3).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 36.28 (m).

MS (EI, 50 eV, 260 °C): m/z (%) = 756 (1) [$M^+ - BH_3$].

ESI-HRMS: m/z calcd for $C_{46}H_{70}B_2NaO_4P_2$: 793.4833; found: 793.4860.

1,3-Bis({(*S*,*S*)-bis[2-(1-ethoxyethoxy)propyl]phosphanyl}methyl)benzene–Bis(borane) Complex (19)

Preparation of **19** was by Method A. Chromatography (silica gel, EtOAc–PE, 5:95 to 10:90); yield: 88% (mixture of diastereomers); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.05 (m, 4 H), 4.88 (m, 1 H), 4.75 (m, 2 H), 4.66 (m, 1 H), 4.33–3.91 (m, 4 H), 3.71–3.05 (m, 11 H), 2.29–1.85 (m, 5 H), 1.70 (m, 2 H), 1.51 (m, 2 H), 1.39–1.10 (m, 36 H), 0.9–0.0 (m, 6 H).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 15.01 (m).

1,3-Bis{(*S*,*S*)-bis[(2-hydroxypropyl)phosphanyl]methyl}benzene–Bis(borane) Complex

For characterization of **19**, a sample was deprotected by stirring with a catalytic amount of *p*-TsOH in EtOH for 30 h at r.t. Neutralization with $NaHCO_3$ and extractive workup with Et_2O was followed by chromatography (EtOAc–PE, 70:30); this gave the tetrol.

Yield: 83%; $[\alpha]_D^{20}$ +32.8 (c 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (t, J = 7.6 Hz, 1 H), 7.14 (br s, 1 H), 7.08 (dd, J = 1.0, 7.6 Hz, 2 H), 4.29–4.11 (m, 4 H), 3.20 (pseudo t, J = 13.8 Hz, 2 H), 3.11 (dd, J = 10.7, 14.0 Hz, 2 H), ~2.70 (br s, 4 H), 2.02–1.80 (m, 6 H), 1.67 (ddd, J = 2.2, 9.9, 14.8 Hz, 2 H), 1.27 (dd, J = 1.4, 6.1 Hz, 6 H), 1.24 (dd, J = 1.4, 6.1 Hz, 6 H), 1.0–0.1 (br m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.06 (dd, J = 2.3, 6.8 Hz, C), 131.67 (pseudo t, J = 4.0 Hz), 128.73 (m), 64.02, 64.02 (d, J = 5.3 Hz), 33.14 (d, J = 32.6 Hz, CH_2), 32.64 (d, J = 34.0 Hz, CH_2), 32.61 (d, J = 32.0 Hz, CH_2), 25.78 (d, J = 11.5 Hz, CH_3), 25.71 (d, J = 11.9 Hz, CH_3).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 13.41 (m).

MS (EI, 70 eV, 170 °C): m/z (%) = 430 (0.8) [M^+].

HRMS (EI): calcd for $C_{20}H_{42}O_4B_2P_2$: 430.2752; found: 430.2757.

(*S*,*S*,*S*)-Tris[2-(1-ethoxyethoxy)propyl]phosphane–Borane Complex (20)

Borane complex **6** (1.20 g, 3.9 mmol) was dissolved in anhyd THF (15 mL) and cooled to 0 °C. A 1.6 M soln of *n*-BuLi in hexane (2.5 mL, 4 mmol) was added dropwise and the mixture was stirred at 0 °C for 1 h. (*S*)-2-(1-Ethoxyethoxy)propyl methanesulfonate (1.15 g, 5 mmol) dissolved in THF (10 mL) was introduced dropwise, and once the addition was complete the mixture was stirred overnight at 30 °C. H_2O (5 mL) was added slowly and the mixture was diluted with Et_2O (50 mL). The organic layer was separated, the aqueous layer was extracted with Et_2O (2 × 25 mL), and the combined organic phases were washed with brine (1 × 50 mL) and dried ($MgSO_4$). Evaporation of solvents afforded a colorless oil, which was subjected to column chromatography (silica gel deactivated with 13% (w/w) of H_2O, Et_2O–PE, 15:85); this yielded **20** (1.26 g, 74%) as a mixture of diastereomers.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.82–4.66 (m, 3 H), 4.19–3.95 (m, 3 H), 3.65–3.42 (m, 6 H), 2.18–1.76 (m, 6 H), 1.31–1.13 (m, 27 H), 0.91–0.20 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 100.82–97.45 (7 signals), 71.88–67.19 (7 signals), 61.53–59.54 (7 signals, CH_2), 34.46–32.60 (16 signals), 23.97–20.40 (15 signals, CH_3), 15.34 (CH_3).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 12.55 (br m).

(*S*,*S*,*S*)-Tris(2-hydroxypropyl)phosphane–Borane Complex

For characterization, a sample of **20** was deprotected by stirring with a catalytic amount of *p*-TsOH in EtOH for 30 h at r.t. Neutralization with $NaHCO_3$ and extractive workup with Et_2O gave the crude product, which crystallized from $CHCl_3$ to afford the triol.

Yield: 93%; mp 126–130 °C; $[\alpha]_D^{20}$ +55.6 (c 1.0, EtOH).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.73 (d, J = 5.1 Hz, 3 H), 3.98 (m, 3 H), 1.89 (m, 6 H), 1.14 (dd, J = 6.1, 1.2 Hz, 9 H), 0.9–0.2 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 64.03, 34.19 (d, J = 34.2 Hz, CH_2), 25.99 (d, J = 12.1 Hz, CH_3).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 9.87 (br m).

MS (EI, 70 eV, 90 °C): m/z (%) = 221 (95) [$M - H^+$].

HRMS (EI): m/z calcd for $C_9H_{23}BO_3P$: 221.1480; found: 221.1478.

Acknowledgment

P.K. is grateful for a grant provided by the Fonds zur Förderung der wissenschaftlichen Forschung in Österreich (Lise Meitner grant Nr. M852-N11).

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