Synthesis and Characterisation of Monophosphines and Aminophosphines Bearing Chiral Phosphetane Units

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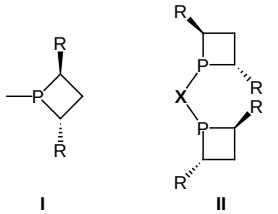
Abstract: Enantiomerically pure monophosphines bearing phosphetane units have been prepared from primary phosphines and the cyclic sulfates of *anti*-1,3-diols. Various substituents have been introduced on both the phosphorus and the ring carbon atoms, thus showing the high flexibility of the synthetic approach. The same synthetic method has been applied to the preparation of P–N heterobidentate ligands bearing phosphetane and azetidine rings. The final products have been characterised by X-ray diffraction studies.

Key words: phosphorus, heterocycles, metallocenes, transition metals, asymmetric catalysis

Structural modularity is a key feature for chiral ligands in order to be broadly useful in enantioselective catalysis. Thus, whenever a new efficient synthon or concept for ligand design has been highlighted, the versatility of the corresponding synthetic approach must be checked in a systematic fashion to ensure optimisation of the properties of these ligands for any given purpose. This is the case for the chiral synthons **I**, namely the 2,4-disubstituted phosphetane moieties, which are easily accessible from enantiomerically pure 1,3-diol derivatives. They have already been used for the synthesis of diphosphine ligands, **II**, highly efficient in enantioselective ruthenium and rhodium catalysed hydrogenations.[1] The nature of the phosphetane-connecting scaffold in **II** modulates the catalyst efficiency and opens, for instance, specific application fields to the bis-phosphetanoferrocenes (**X** = 1,1'-ferrocenediyl) with respect to the bis-phosphetanobenzenes (**X** = 1,2-phenylene) or bis-phosphetanoethanes (**X** = 1,2-ethanediyl) (Figure 1).

Within a single family of bis-phosphetanes **II**, the steric properties of the ligands have been finely tuned by variations of the R substituents, as the chiral *anti*-1,3-diols required for their synthesis are very easily available via asymmetric hydrogenation of the corresponding 1,3-diketones.[2]

As application field for chiral phosphetanes, previous work considered mainly catalytic hydrogenations, which founded the choice of bidentate, C_2-symmetric phosphines as target structures. However, phosphetane-based ligands could also be designed for a number of other catalytic applications and, therefore, new variations of the general structure **I** are highly desirable. In this context we present here the synthesis and characterisation of new monodentate phosphetanes as well as the first examples of P–N heterobidentate phosphetanes.



X = 1,2-phenylene, 1,2-ethanediyl, 1,1'-ferrocenediyl

Figure 1 Structures of model chiral phosphetane units **I** and **II**

Generally speaking, the successful use of bidentate ligands in many asymmetric catalytic reactions obscures the field of chiral monodentate phosphines. Nevertheless, recent literature data provide clear evidence for the specific catalytic applications of monodentate phosphorus ligands and point out the crucial need for efficient chiral phosphines of this family.[3] In this context, monodentate phosphetanes could be interesting tools as they are readily available from virtually any primary phosphine and a number of 1,3-diols, according to the synthetic approach shown in Scheme 1. Consequently, after our initial report on the synthesis of **1a** (R' = Ph, R = Me) and **2** (R' = Mesityl, R = Me),[1a] the general synthetic method has been widely developed and the catalytic potential of monodentate phosphetanes has been proven, as shown hereafter.[4]

The cyclic sulfates of several *anti*-1,3-diols were employed in the reaction with dilithiated phenylphosphine to afford the corresponding phosphetane-borane complexes **8a**–**e** in moderate to good yields (40–80%). Notably, even the highly hindered 2,2,6,6-tetramethylheptane-3,5-diol cyclic sulfate afforded the phosphetane borane **8e** in acceptable yield (46%). However, the attempted synthesis of (*S*,*S*)-1,2,4-triphenylphosphetane from the bis-mesylate of (*R*,*R*)-1,3-diphenylpropane-1,3-diol, led to the undesired *meso*-isomer of the expected phosphetane.[5] Racemisation of the benzylic carbon atoms takes place under basic reaction conditions to afford the more stable

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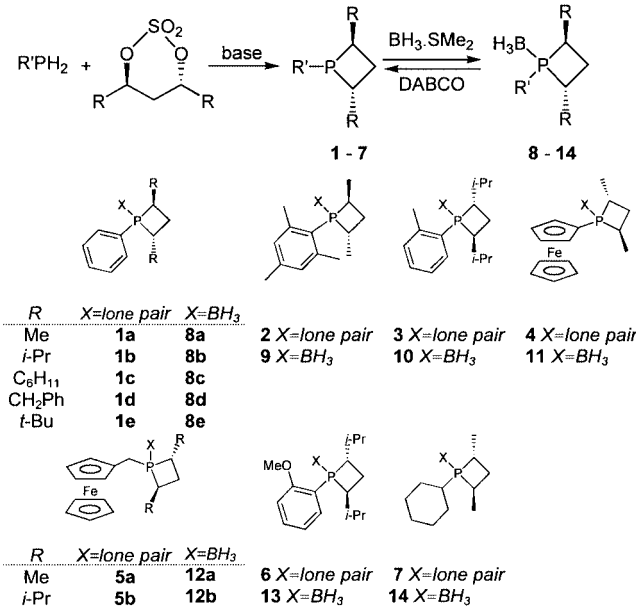


R	X=lone pair	X=BH_3
Me	**1a**	**8a**
i-Pr	**1b**	**8b**
C_6H_{11}	**1c**	**8c**
CH_2Ph	**1d**	**8d**
t-Bu	**1e**	**8e**

2 *X*=lone pair **9** *X*=BH_3 **3** *X*=lone pair **10** *X*=BH_3 **4** *X*=lone pair **11** *X*=BH_3

R	X=lone pair	X=BH_3
Me	**5a**	**12a**
i-Pr	**5b**	**12b**

6 *X*=lone pair **13** *X*=BH_3 **7** *X*=lone pair **14** *X*=BH_3

Scheme 1

anti-anti isomer.[6] Phosphetanes **1a–e** were obtained then quantitatively from their borane complexes **8a–e** by reaction with an excess DABCO in benzene at 40 °C.

Stable rhodium complexes (COD)Rh(L*)$_2^+PF_6^-$ were isolated for L* = **1a–d** by reacting two equivalents of the corresponding phosphetanes with $(COD)_2RhPF_6$ in dichloromethane at room temperature. They proved to be efficient catalyst precursors for hydrogenation reactions of model substrates (see experimental section). Especially, in the hydrogenation of *N*-acetyldehydrophenylalanine, phosphetanes **1a** (R = Me) and **1d** (R = CH_2Ph) afforded enantiomeric excesses of 80% and 86% respectively. These values compare favourably with the ee attained in the hydrogenation of the same acid, or the corresponding ester, by other monodentate phosphines (CAMP: 85% ee;[7] [2-(4-methoxymethyl-1,3-dioxan-2-yl)ferrocenyl]diphenylphosphine: 87% ee;[8] 1,2,5-triphenylphospholane: 82% ee;[6b] 2,5-dimethyl-1-phenylphospholane: 60% ee[9]) and suggest a promising potential for these ligands. Their catalytic efficiency should be related to the relative conformational rigidity of the four-membered ring and to the presence of a chirotopic[10] phosphorus atom. The chirotopic phosphorus centre in **1** creates a highly asymmetric environment around the metal atom – just as if it were stereogenic (see Figure 2) – while avoiding the usual drawbacks of P-chiral ligands, e.g. challenging synthesis and easy racemisation.

Figure 2 also shows that, with monodentate phosphetanes devoid of any functional group, chiral induction should come from the different, relative sterical hindrance of the R and R' substituents. Improvement of their efficiency should result from the choice of phosphorus substituents (R') with suitable steric properties, however in an unpredictable manner. The sterical hindrance of the phosphorus substituent can be increased easily by the use of appropriate, bulky primary phosphines as starting materials. This has been demonstrated in this work by applying both substituted arylphosphines, that is mesityl-, *o*-anisyl- and *o*-tolylphosphine, and very bulky ferrocene-derived phosphines to the synthesis of phosphetanes. In addition, trialkyl phosphetanes have been prepared from ferrocenylmethylphosphine and cyclohexylphosphine.

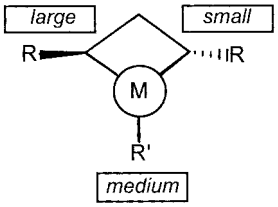


Figure 2 Essential structural features of chiral monodentate phosphetane ligands

Phosphetanes **2–7** have been obtained as their borane complexes **9–14** following a two-steps procedure: the monolithiated phosphine was reacted at –78 °C to 0 °C with the cyclic sulfate of the enantiomerically pure 1,3-diol, then addition of one equivalent of *s*-BuLi allowed deprotonation of the remaining PH function and cyclisation. Complexation of phosphorus with BH_3 was performed by adding an excess $BH_3{\cdot}SMe_2$ to the crude reaction mixture (see experimental section). Yields for all isolated phosphetane borane complexes, including **11** and **12**, were satisfying, thus showing that even monosubstituted ferrocenyl moieties are fully compatible with the phosphetane synthesis above. Other bulky organometallic fragments can also be reasonably envisaged as phosphorus substituents in monodentate phosphetanes.

The trivalent phosphetanes **1–3**,**6**,**7** are air sensitive oils, while **4** and **5** are easy to handle, air stable solids.

The procedures for the preparation of phosphetanes **1–7** are only few, nevertheless representative examples show the high flexibility of the synthetic approach to enantiomerically pure, monodentate phosphetanes. These monophosphines should find specific use in reactions which require monodentate ligands for the generation of catalytically active species (e.g. palladium-promoted hydrosilylation of olefins,[11] reduction of allylic carbonates,[12] ene-type carbocyclisations,[13] nickel promoted hydrovinylation,[14] etc). Moreover, new applications should emerge from recent studies showing the peculiar properties of hindered monophosphines in transition metal catalysis. Notably, tri-*tert*-butylphosphine, tri-*o*-tolylphosphine and their palladacycles, di-*tert*-butylferrocenylphosphine and dicyclohexyl(biaryl)phosphines display very high catalytic activities in various palladium- and rhodium-promoted reactions.[15] Phosphetanes should afford potentially useful, chiral analogues of these species. Studies toward the catalytic applications of chiral monodentate phosphetanes are in progress.

Next in this work, P–N heterobidentate, phosphetane based ligands have been selected as synthetic targets, giv-

en that aminophosphines represent a well established class of chiral auxiliaries with known application fields. For instance, carbon–carbon bond formations via allylic substitutions (Pd) or cross coupling reactions (Ni) should be mentioned as significant applications.[16] Relevant literature reports show that in all current chiral aminophosphines the two coordinating centres have different steric and electronic properties, so that both effects are superimposed and, therefore, not distinguishable.[17] Consequently, it would be worthwhile to prepare and study bidentate P–N ligands having comparable steric environments at the two coordinating centres. Purely electronic effects will be evidenced in catalytic processes by comparing them with the analogous, C_2-symmetrical N–N or P–P bidentate ligands. Following this concept we designed the synthesis of azetidino-phosphetanes with an overall "C_2-symmetric" geometric structure and especially that of **III** and **IV** (Figure 3), which are analogues of the CnrPHOS [chiral bis(phosphetano)benzenes][1a–c] and BPE-4 [1,2-bis(phosphetano)ethanes][1f] ligands previously reported.

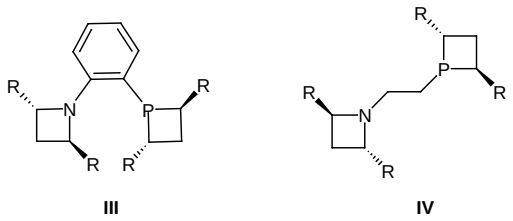
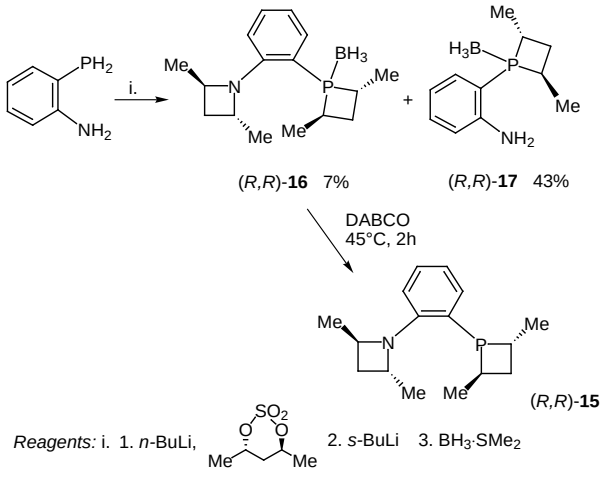


Figure 3 Structures of azetidino-phosphetanes **III** and **IV**

Comparison between the CnrPHOS or BPE-4 ligands and the corresponding azetidino-phosphetanes **III** and **IV**, respectively, would hopefully afford information on the role of electronic effects in selected catalytic reactions.

The first azetidino-phosphetane, **15**, was prepared from (2-aminophenyl)phosphine[18] and the cyclic sulfate of (*S*,*S*)-pentane-2,4-diol, following the usual cyclisation procedure (Scheme 2).



Scheme 2

The yield of borane complex **16** was very low (7%, in the usual conditions of phosphetane synthesis), the major product of the cyclisation reaction being the 1-(2-aminophenyl)phosphetane **17** (43% yield). Nevertheless, complex **16** was isolated and its structure was unambiguously established by X-ray crystallography (Figure 4).

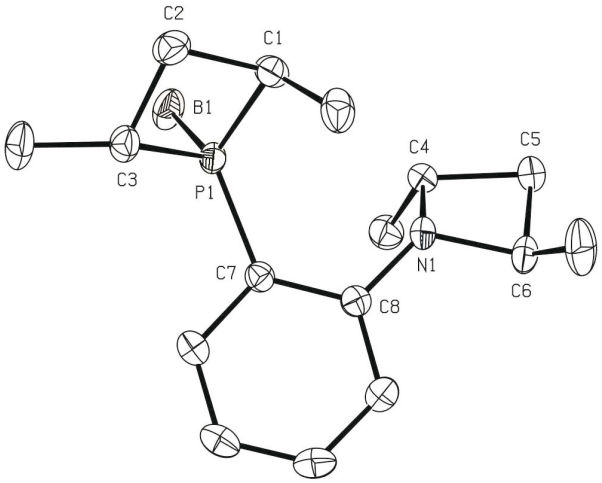
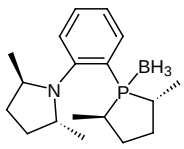


Figure 4 ORTEP drawing of **16**. Selected bond distances (Å): P–C(1) 1.855(2), P–C(3) 1.849(2), C(1)–C(2) 1.561(2), C(2)–C(3) 1.550(2), P–C(7) 1.814(2), N–C(4) 1.504(2), N–C(6) 1.486(2), C(4)–C(5) 1.549(2), C(5)–C(6) 1.545(2), N–C(8) 1.395(2). Selected bond angles (°): C(1)–P–C(3) 78.33(7), P(1)–C(3)–C(2) 87.3(1), P–C(1)–C(2) 86.8(1), C(3)–C(2)–C(1) 97.5(1), C(4)–N–C(6) 91.7(1), N–C(4)–C(5) 87.4(1), N–C(6)–C(5) 88.2(1), C(4)–C(5)–C(6) 87.8(1).

The azetidine ring displays a nearly square-planar geometry with N–C and C–C bond distances varying from 1.48 Å to 1.54 Å and intracyclic bond angles between 87.4° and 91.7°, while the phosphetane ring shows a very distorted geometry with long P–C bonds (1.85 Å, vs. 1.55Å for C–C), acute C–P–C angle (78.3°) and large C–C–C intracyclic angle (97.5°).

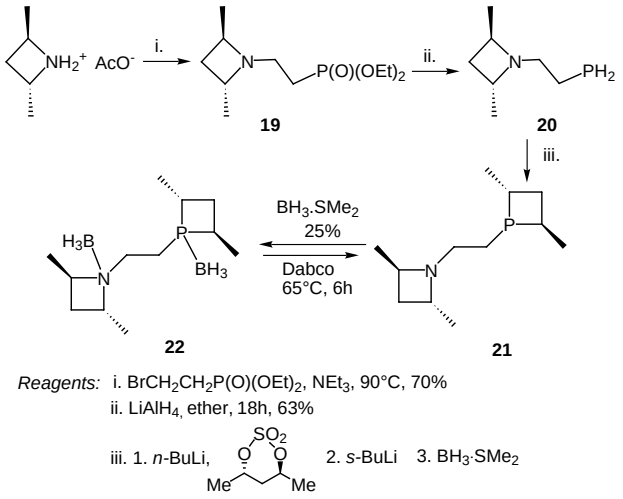
The azetidino-phosphetane **15** was released quantitatively from its borane complex by reaction with 1.5 equivalents of DABCO. It has been unambiguously characterised, but the conditions of its synthesis need to be improved before applications in asymmetric catalysis would be reasonably envisaged. According to the reagents used in Scheme 2, the limiting step is the cyclisation reaction on nitrogen which is impeded by the low nucleophilic character of the lithium arylamide. Incidentally, it must be noted that the attempted synthesis of the analogous pyrrolidine-phospholane by the same approach led to **18** (Figure 5) in equally low yield (less than 5%).



18

Figure 5 Structure of the pyrrolidine analogue **18**

The (2-azetidinoethyl)phosphetanes **IV**, are available through a multistep procedure which avoids the use of the highly volatile and potentially toxic 2-aminoethylphosphine. As shown in Scheme 3, the method implied formation of the azetidine and phosphetane rings in two separate steps. At first, the (*R*,*R*)-2,4-dimethylazetidinium acetate was prepared according to the published procedure[19] and was reacted then with 2-bromoethylphosphonate[20] to afford **19**. The phosphonate function of **19** served as precursor for the primary phosphino group which was required for phosphetane syntheses. The cyclisation reaction between **20** and (*S*,*S*)-2,4-pentanediol cyclic sulfate, followed by borane addition, led to the (azetidinoethyl)phosphetane as its bis-borane complex **22** in acceptable yield (25%, under non-optimised conditions).



Scheme 3

The structure of the (azetidinoethyl)phosphetane **22** was established by X-ray crystallography (see Figure 6).

The phosphetane and azetidine rings in **22** are structurally very similar to the corresponding rings in **16**. In both compounds the structural parameters - bond angles and distances - of the azetidine ring differ significantly from those of the phosphetane unit thus creating a slightly different steric environment around the phosphorus and nitrogen centres respectively. This must be taken into account in further studies, when comparing the catalytic properties of these P–N bidentate ligands with the corresponding, symmetric diphosphines or diamines.

Decomplexation of **22** was performed in a sealed NMR tube, with an excess DABCO and the final (azetidinoethyl)phosphetane **21** was characterised in the crude mixture. Phosphetane **17** is an extremely air sensitive compound which requires manipulation in a strictly inert atmosphere. Previous experiments on the analogous BPE-4 ligands[1f] suggest that air oxidation should be reduced if the phosphetane ring bears more bulky substituents. Especially, the use of cyclohexyl groups as substituents of the rings is

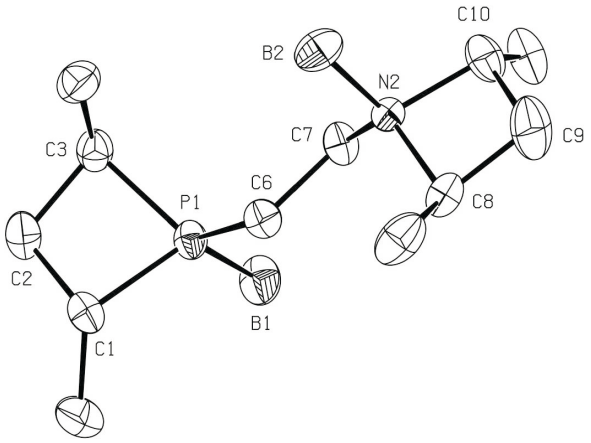


Figure 6 ORTEP drawing of **22**. Selected bond distances (Å): P–C(1) 1.828(2), P–C(3) 1.837(2), C(1)–C(2) 1.550(3), C(2)–C(3) 1.546(3), P–C(6) 1.809(2), N–C(8) 1.536(3), N–C(10) 1.574(2), C(8)–C(9) 1.531(3), C(9)–C(10) 1.530(3), N–C(7) 1.488(2). Selected bond angles (°): C(1)–P–C(3) 79.6(1), P(1)–C(3)–C(2) 87.7(1), P–C(1)–C(2) 87.9(1), C(3)–C(2)–C(1) 98.5(1), C(8)–N–C(10) 88.0(1), N–C(8)–C(9) 90.2(2), N–C(10)–C(9) 88.8(2), C(8)–C(9)–C(10) 89.8(1).

expected to afford air-stable, easy to handle analogues of **21**.

In summary, this work proves the versatility of the synthetic approach to chiral phosphetanes from primary phosphines and enantiomerically pure 1,3-diol derivatives. Especially, its efficiency for the preparation of ferrocenyl substituted phosphetanes with tunable steric properties has been demonstrated. Moreover, the first examples of azetidinophosphetanes have been described, which represent a new class of P–N bidentate ligands. Utility of all these ligands in asymmetric catalysis will be reported later.

All reactions were performed under inert atmosphere (Ar). NMR spectra were recorded on either a Bruker AM 400 or a Bruker AM 200 spectrometer. Selected NMR data are given hereafter for all new compounds. *o*-Tolylphosphine[21] and *o*-anisylphosphine[22] were prepared by reduction of the corresponding diethylphosphonate with a $LiAlH_4$/TMSCl mixture.[23] Diethyl phosphonates were prepared by $NiCl_2$-catalysed coupling of the corresponding aryl bromides with triethyl phosphite.[24,25] Ferrocenylphosphine was obtained from ferrocene in a two-step reaction: ferrocene was lithiated in THF at –78 °C with *t*-BuLi (1 equiv)/*t*-BuOK (0.12 equiv)[26] and reacted then with $ClP(OEt)_2$. The crude ferrocenylphosphonite was reduced then with $LiAlH_4$/TMSCl (THF, 12 h at r.t.) to give the primary phosphine which was purified by filtration on a short alumina column (Et_2O as eluent).[27] Ferrocenylmethylphosphine was prepared according to the literature procedure.[28]

Phosphetane-Borane Complexes 8a–e; General Procedure

A solution of phenylphosphine (0.11 mL, 1.0 mmol) in THF (4 mL) was cooled to –78 °C and BuLi (3.0 mL, 1.6 M solution in hexane, 2.2 mmol) was added. Once warmed to r.t., the mixture was stirred for 1 h to afford dilithiated phenylphosphine. The yellow-orange suspension was added slowly at –40 °C to a solution of cyclic sulfate of the suitable chiral 1,3-diol (1 mmol) in THF (40 mL). After warming to r.t. and stirring for about 30 min, an excess $BH_3{\cdot}Me_2S$ (about 2 mmol) was added. After hydrolysis the solvent was evap-

orated and the residue extracted with Et_2O, washed with H_2O and dried ($MgSO_4$). The final products **8** were purified by chromatography on an alumina column with a 5% Et_2O–cyclohexane mixture as eluent and were obtained as colourless solids.

(*S*,*S*)-2,4-Diisopropyl-1-phenylphosphetane Borane Complex 8b

The (*R*,*R*)-2,6-dimethylheptane-3,5-diol cyclic sulfate[1b] was used in the synthesis; yield: 50%; $[\alpha]_D$ –70 (*c* 0.5, $CHCl_3$).

^{31}P NMR ($CDCl_3$): δ = 43 (br).

^{1}H NMR (C_6D_6): δ = 0.46 (d, *J* = 6.4 Hz, 3 H, CH_3), 0.53 (dd, *J* = 6.5, 0.9 Hz, 3 H, CH_3), 0.78 (dd, *J* = 6.3, 1.2 Hz, 3 H, CH_3), 0.94 (d, *J* = 6.1 Hz, 3 H, CH_3), 7.0 (m, 3 H_{arom}), 7.8 (m, 2 H_{arom}).

^{13}C NMR ($CDCl_3$): δ = 19.9 (d, *J* = 11.8 Hz, CH_3), 20.3 (d, *J* = 13.9 Hz, CH_3), 21.0 (d, *J* = 3.3 Hz, CH_3), 21.8 (d, *J* = 4.6 Hz, CH_3), 29.1 (d, *J* = 5.8 Hz, CH), 29.6 (CH), 30.0 (d, *J* = 15.2 Hz, CH_2) 39.8 (d, *J* = 38.8 Hz, CH), 42.3 (d, *J* = 40.0 Hz, CH), 128.1 (d, *J* = 31.3 Hz, CP).

MS: *m*/*z* = 234 (M – BH_3, 100).

Anal. Calcd for $C_{15}H_{26}BP$: C, 72.60; H, 10.56. Found: C, 72.48; H, 10.74.

(*S*,*S*)-2,4-Dicyclohexyl-1-phenylphosphetane Borane Complex 8c

The (*R*,*R*)-1,3-dicyclohexylpropane-1,3-diol cyclic sulfate[1b] was used in the synthesis; yield: 86%; $[\alpha]_D$ –6 (*c* 1, $CHCl_3$)

^{31}P NMR (C_6D_6): δ = 59 (br).

^{13}C NMR (C_6D_6): δ = 25.7, 25.9, 26.0, 26.2, 26.3, 26.7 (CH_2), 28.4 (d, *J* = 15.6 Hz, CH_2), 30.3 (d, *J* = 11.1 Hz, CH_2), 31.1 (d, *J* = 13.2 Hz, CH_2), 31.7 (CH_2), 32.4 (d, *J* = 4.4 Hz, CH_2), 38.4 (d, *J* = 5.8 Hz, CH), 38.8 (d, *J* = 37.9 Hz, CH), 38.9 (CH), 41.1 (d, *J* = 39.4 Hz, CH), 129.4 (d, *J* = 29.8 Hz, CP).

MS (CI): *m*/*z* = 346 (M + NH_4).

Anal. Calcd for $C_{15}H_{26}BP$: C, 76.83; H, 10.40. Found: C, 76.35; H, 10.13.

(*S*,*S*)-2,4-Dibenzyl-1-phenylphosphetane Borane Complex 8d

The (*R*,*R*)-1,5-diphenylpentane-2,4-diol[1c] cyclic sulfate was used in the synthesis; yield 82%; $[\alpha]_D$ = +75 (c 1, CH_2Cl_2).

^{31}P NMR (C_6D_6): δ = 48.7 (br).

^{1}H NMR (C_6D_6): δ = 2.2–2.6 (m, 4 H), 2.8–3.3 (m, 4 H), 6.83 (d, *J* = 6.5 Hz, 1 H), 7.0–7.5 (m, 14 H).

^{13}C NMR ($CDCl_3$): δ = 31.2 (d, *J* = 14.6 Hz, CH_2), 33.5 (d, *J* = 38.5 Hz, CH), 35.0 (d, *J* = 38.7 Hz, CH), 36.3 (CH_2),127.3 (d, *J* = 32.2 Hz, CP), 138.5 (d, *J* = 9.9 Hz, C), 139.7 (d, *J* = 10.2 Hz, C).

MS: *m*/*z* (%) = 330 (M – BH_3, 80), 91 (100).

Anal. Calcd for $C_{23}H_{26}BP$: C, 80.25; H, 7.61. Found: C, 80.12; H, 7.61.

(*R*,*R*)-2,4-Di-*tert*-butyl-1-phenylphosphetane Borane Complex 8e

The (*S*,*S*)-2,2,6,6-tetramethylheptane-3,5-diol cyclic sulfate[1c] was used in this synthesis; yield: 46%.

^{31}P NMR (C_6D_6): δ = 43 (br).

^{1}H NMR (C_6D_6): δ = 0.61 (s, 9 H, *t*-C_4H_9), 1.09 (s, 9 H, *t*-C_4H_9), 2.0–2.3 (m, 2 H), 2.6–2.8 (m, 2 H), 7.0 (m, 3 H), 7.9 (m, 2 H).

^{13}C NMR (C_6D_6): δ = 25.1 (d, *J* = 12.8 Hz, CH_2), 27.7 [d, *J* = 5.9 Hz, C(*C*H_3)$_3$], 28.2 [d, *J* = 6.2 Hz, C(*C*H_3)$_3$], 33.0 [*C*(CH_3)$_3$], 33.2 [d, *J* = 6.1 Hz, *C*(CH_3)$_3$], 43.6 (d, *J* = 35.0 Hz, CH), 48.8 (d, *J* = 36.5 Hz, CH), 130.1 (d, *J* = 28.4 Hz, CP).

MS: *m*/*z* (%) = 262 (M – BH_3, 90), 136 (100).

Phosphetane-Borane Complexes 9–14; General Procedure

The primary phosphine (1 mmol) was lithiated at –78 °C in THF (5 mL), by addition of BuLi (1.1 equiv). After addition of the 1,3-diol cyclic sulfate (1.1 equiv, in 20 mL THF), the mixture was warmed up to r.t. and stirred for about 20 min. (For the synthesis of **9** and **10** the lithiated phosphine was added to a cooled THF solution of the cyclic sulfate). *s*-BuLi (1 equiv, 1.3 N solution in hexane) was added then at –78 °C. The mixture was warmed up to r.t. and treated as above for the preparation of **8a**–**e**. The synthesis of **14** was performed at 0–25 °C.

(*S*,*S*)-2,4-Diisopropyl-1-(*o*-tolyl)phosphetane Borane Complex 10

o-Tolylphosphine and (*R*,*R*)-2,2,6,6-tetramethylheptane-3,5-diol cyclic sulfate were used in this synthesis; yield: 36%; $[\alpha]_D$ –13 (*c* 1, $CHCl_3$).

^{31}P NMR ($CDCl_3$): δ = 41 ($J_{P\text{-}B}$ = 55 Hz).

^{1}H NMR ($CDCl_3$): δ = 0.75 (d, *J* = 6.6 Hz, 6 H, CH_3), 0.97 (dd, *J* = 6.6, 1.2 Hz, 3 H, CH_3), 1.02 (d, *J* = 6.6 Hz, 3 H, CH_3),1.8 (m, 1 H), 2.1–2.5 (m, 4 H), 2.56 (s, 3 H, CH_3), 2.8 (m, 1 H), 7.1–7.5 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = 19.0 (d, *J* = 5.7 Hz, CH_3), 19.9 (d, *J* = 14.5 Hz, CH_3), 21.6 (d, *J* = 8.1 Hz, CH_3), 22.4 (d, *J* = 5.3 Hz, CH_3), 22.5 (s, CH_3), 27.0 (d, *J* = 12.5 Hz, CH_2), 28.1 (d, *J* = 7.0 Hz, CH), 29.6 (CH), 41.6 (d, *J* = 36.6 Hz, CH), 42.1 (d, *J* = 38.8 Hz, CH), 125.8 (d, *J* = 8.3 Hz, CH), 128.9 (d, *J* = 26.5 Hz, CP), 130.6 (d, *J* = 6.8 Hz, CH), 130.9 (CH), 131.2 (d, *J* = 8.0 Hz, CH), 141.7 (d, *J* = 9.9 Hz, C).

MS: *m*/*z* (%) = 248 (M – BH_3, 40), 233 (63), 178 (70), 78 (100).

Anal. Calcd for $C_{16}H_{28}BP$: C, 73.30; H, 10.77. Found: C, 71.48; H, 10.52.

(*R*,*R*)-2,4-Dimethyl-1-ferrocenylphosphetane Borane Complex 11

Ferrocenylphosphine and the (*S*,*S*)-pentane-2,4-diol cyclic sulfate were used in this synthesis. The phosphetane borane complex **11** was obtained as a yellow solid in 50% yield; $[\alpha]_D$ +130 (*c* 0.5, CH_2Cl_2).

^{31}P NMR ($CDCl_3$): δ = 49 ($J_{P\text{-}B}$ = 54 Hz).

^{1}H NMR ($CDCl_3$): δ = 0.99 (dd, $J_{H\text{-}P}$ = 15.6 Hz, *J* = 7.4 Hz, 3 H, CH_3), 1.45 (dd, $J_{H\text{-}P}$ = 18.7 Hz, *J* = 7.4 Hz, 3 H, CH_3), 2.1–2.5 (m, 2 H), 2.5–2.7 (m, 1 H), 2.7–2.9 (m, 1 H), 4.27 (s, 5 H, Cp), 4.42 (br, 1 H), 4.53 (br, 2 H), 4.61 (br, 1 H).

^{13}C NMR (C_6D_6): δ = 15.5 (d, *J* = 6.4 Hz, CH_3), 15.7 (CH_3), 28.1 (d, *J* = 46.3 Hz, CH), 28.9 (d, *J* = 43.7 Hz, CH), 35.4 (d, *J* = 15.5 Hz, CH_2), 69.8 (Cp), 70.9 (CH), 72.0 (d, *J* = 5.5 Hz, CH), 72.5 (d, *J* = 7.6 Hz, CH), 75.1 (d, *J* = 14.5 Hz, CH).

MS: *m*/*z* (%) = 300 (M, 17), 286 (M – BH_3, 100).

Anal. Calcd for $C_{15}H_{22}BFeP$: C, 60.06; H, 7.39. Found: C, 59.73; H, 7.38.

(*R*,*R*)-2,4-Dimethyl-1-ferrocenylmethylphosphetane Borane Complex 12a

(Ferrocenylmethyl)phosphine and the (*S*,*S*)-pentane-2,4-diol cyclic sulfate were used in this synthesis. The phosphetane borane complex **12a** was obtained as a yellow solid in 72% yield.

^{31}P NMR (C_6D_6): δ = 55 ($J_{P\text{-}B}$ = 50 Hz).

^{1}H NMR (C_6D_6): δ = 0.81 (dd, $J_{H\text{-}P}$ = 14.6 Hz, *J* = 7.5 Hz, 3 H, CH_3), 1.05 (dd, $J_{H\text{-}P}$ = 17.8 Hz, *J* = 7.3 Hz, 3 H, CH_3), 1.5 (m, 1 H), 1.8 (m, 1 H), 1.9 (m, 1 H), 2.2 (m, 1 H), 2.63 (ABX, $J_{A\text{-}B}$ = 14.5 Hz,

$J_{H\text{-}P}$ = 10.9 Hz, 1 H, PCH_2), 2.69 (ABX, $J_{H\text{-}P}$ = 7.4 Hz, 1 H, PCH_2), 3.7–3.8 (m, 3 H, CH), 3.86 (5 H, Cp), 4.1 (br, 1 H, CH).

^{13}C NMR (C_6D_6): δ = 14.8 (d, *J* = 6.5 Hz, CH_3), 15.2 (CH_3), 25.0 (d, *J* = 13.0 Hz, PCH_2), 26.0 (d, *J* = 39.3, CH), 27.9 (d, *J* = 37.0, CH), 35.6 (d, *J* = 15.6 Hz, CH_2), 68.0 (CH), 68.5 (CH), 69.2 (Cp), 69.3 (d, *J* = 1.5 Hz, CH), 69.8 (d, *J* = 1.9 Hz, CH), 79.5 (C).

MS (CI): *m*/*z* = 332 (M + NH_4).

Anal. Calcd for $C_{16}H_{24}BFeP$: C, 61.20; H, 7.70. Found: C, 61.15; H, 7.83.

(*S*,*S*)-2,4-Diisopropyl-1-ferrocenylmethylphosphetane Borane Complex 12b

(Ferrocenylmethyl)phosphine and the (*R*,*R*)-2,6-dimethylheptane-3,5-diol cyclic sulfate were used in this synthesis. The phosphetane borane complex **12b** was obtained as a yellow solid in 40% yield; $[\alpha]_D$ +35 (*c* 1, $CHCl_3$).

^{31}P NMR (C_6D_6): δ = 53.

^{1}H NMR (C_6D_6): δ = 0.63 (d, *J* = 6.4 Hz, 3 H, CH_3), 0.71 (d, *J* = 6.5 Hz, 3 H, CH_3), 0.85 (d, *J* = 6.5 Hz, 3 H, CH_3), 0.86 (d, *J* = 6.5 Hz, 3 H, CH_3), 1.5–2.1 (m, 6 H), 2.93 (ABX, $J_{A\text{-}B}$ = 14.2 Hz, *J* = 11.2 Hz, 1H, CH_2), 2.98 (ABX, *J* = 7.3 Hz, 1H, CH_2), 3.92 (br, 2H, CH), 3.98 (s, 5H, Cp), 4.01 (br, 1H, CH), 4.32 (br, 1H, CH).

^{13}C NMR (C_6D_6): δ = 20.3 (d, *J* = 11.9 Hz, CH_3), 20.7 (d, *J* = 12.5 Hz, CH_3), 22.2 (d, *J* = 4.2 Hz, CH_3), 22.4 (CH_3), 25.4 (d, *J* = 15.4 Hz, PCH_2), 29.5 (CH), 29.9 (CH), 30.4 (d, *J* = 12.6 Hz, CH_2), 38.5 (d, *J* = 36.3 Hz, CH), 41.2 (d, *J* = 37.5 Hz, CH), 68.1 (CH), 68.7 (CH), 69.4 (Cp), 69.7, CH), 70.5 (CH), 79.8 (C).

Anal. Calcd for $C_{20}H_{32}BFeP$: C, 64.91; H, 8.71. Found: C, 64.96; H, 8.79.

(*S*,*S*)-1-(*o*-Anisyl)-2,4-diisopropylphosphetane Borane Complex 13

o-Anisylphosphine and the (*R*,*R*)-2,6-dimethylheptane-3,5-diol cyclic sulfate were used in this synthesis. The phosphetane borane complex **13** was obtained as a colourless solid in 58% yield; $[\alpha]_D$ –43 (*c* 1, $CHCl_3$).

^{31}P NMR (C_6D_6): δ = 43 ($J_{P\text{-}B}$ = 62 Hz).

^{1}H NMR ($CDCl_3$): δ = 0.61 (d, *J* = 6.5 Hz, 3 H, CH_3), 0.79 (d, *J* = 6.6 Hz, 3 H, CH_3), 0.90 (d, *J* = 6.5 Hz, 3 H, CH_3), 0.91 (dd, *J* = 6.5, 1.3 Hz, 3 H, CH_3), 1.9–2.0 (m, 1 H), 2.1–2.2 (m, 1 H), 2.3–2.6 (m, 3 H), 2.8–2.9 (m, 1 H) 3.91 (s, 3 H, OCH_3), 6.94 (dd, *J* = 8.1 Hz, $J_{H\text{-}P}$ = 3.2 Hz, 1 H), 7.05 (tt, *J* = 7.4, 1.4 Hz, 1 H), 7.49 (tm, *J* = 7.4 Hz, 1 H), 7.84 (ddd, $J_{H\text{-}P}$ = 12.7 Hz, *J* = 7.6 Hz, *J* = 1.7 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 20.1 (d, *J* = 10.9 Hz, CH_3), 20.4 (d, *J* = 15.4 Hz, CH_3), 21.6 (d, *J* = 5.2 Hz, CH_3), 22.1 (d, *J* = 4.4 Hz, CH_3), 29.6–29.9 (CH, CH_2), 40.4 (d, *J* = 39.5 Hz, PCH), 43.0 (d, *J* = 40.9 Hz, CH), 55.2 (OCH_3), 110.9 (d, *J* = 3.6 Hz, CH), 117.0 (d, *J* = 26.5 Hz, C), 121.2 (d, *J* = 1.5 Hz, CH), 133.5 (CH), 135.6 (d, *J* = 11.5 Hz, CH), 161.5 (C).

MS: *m*/*z* (%) = 264 (M – BH_3, 48), 138 (AnisylP, 100).

Anal. Calcd for $C_{16}H_{28}BOP$: C, 69.08; H, 10.15. Found: C, 68.94; H, 10.22.

(*R*,*R*)-1-Cyclohexyl-2,4-dimethylphosphetane Borane Complex 14

Cyclohexylphosphine and the (*S*,*S*)-pentane-2,4-diol cyclic sulfate were used in this synthesis. The deprotonation steps were performed at 0–25 °C. The reaction mixture was stirred overnight at r.t. before addition of the BH_3·SMe_2 complex. The phosphetane borane complex **14** was obtained as a colourless solid in 73% yield; $[\alpha]_D$ +6 (*c* 0.5, $CHCl_3$).

^{31}P NMR ($CDCl_3$): δ = 57 ($J_{P\text{-}B}$ = 49 Hz).

^{1}H NMR ($CDCl_3$): δ = 1.22 (dd, $J_{H\text{-}P}$ = 17.4 Hz, *J* = 7.2 Hz, 3 H, CH_3), 1.28 (dd, $J_{H\text{-}P}$ = 14.1, 7.5 Hz, 3 H, CH_3), 1.2–1.9 (m, 9 H), 2.0–2.4 (m, 3 H), 2.5 (m, 2 H).

^{13}C NMR (C_6D_6): δ = 15.3 (d, *J* = 6.5 Hz, CH_3), 15.6 (CH_3), 25.1 (CH_2), 25.8 (CH_2), 26.1 (d, *J* = 41.4, PCH), 26.3 (d, *J* = 11.1 Hz, CH_2), 26.6 (d, *J* = 11.2 Hz, CH_2), 26.8 (CH_2), 27.2 (d, *J* = 39.0 Hz, PCH), 32.8 (d, *J* = 18.0, PCH), 35.8 (d, *J* = 15.5 Hz, CH_2).

MS: *m*/*z* (%) = 184 (M – BH_3, 44), 142 ($C_8H_{15}P$, 100).

Anal. Calcd for $C_{11}H_{24}BP$: C, 66.69; H, 12.21. Found: C, 66.76; H, 12.22.

Displacement of Phosphetanes 1–9 from Their Borane Complexes; General Procedure

The phosphine-borane complex (0.5 mmol) was treated with DABCO (1.1 equiv) in benzene (2 mL) at 45 °C for about 3 h. According to ^{31}P NMR of the reaction mixture, phosphetanes were displaced quantitatively from their complexes. They were purified by filtration under argon on a short alumina column with a cyclohexane–Et_2O mixture (1–2%) as eluent. Note: in a few cases prolonged contact with alumina induced formation of byproducts.

(*S*,*S*)-2,4-Diisopropyl-1-phenylphosphetane (1b)

Colourless oil; $[\alpha]_D$ –26 (*c* 0.5, CH_2Cl_2).

^{31}P NMR (C_6D_6): δ = 21.6.

^{1}H NMR (C_6D_6): δ = 0.61 (d, *J* = 6.5 Hz, 3 H, CH_3), 0.67 (d, *J* = 6.4 Hz, 3 H, CH_3), 0.97 (d, *J* = 6.0 Hz, 3 H, CH_3), 1.09 (d, *J* = 6.2 Hz, 3 H, CH_3), 1.3 (m, 1 H), 1.7–2.1 (m, 3 H), 2.3–2.7 (m, 2 H), 7.0 (3 H), 7.6 (2 H).

^{13}C NMR (C_6D_6): δ = 19.4 (d, *J* = 4.6 Hz, CH_3), 20.7 (d, *J* = 6.1 Hz, CH_3), 20.8 (d, *J* = 6.8 Hz, CH_3), 21.2 (d, *J* = 12.4 Hz, CH_3), 30.3 (d, *J* = 3 Hz, CH), 31.7 (d, *J* = 19.0 Hz, CH), 33.8 (d, *J* = 2.7 Hz, CH_2), 35.7 (d, *J* = 8.0 Hz, CH), 37.9 (d, *J* = 5.0 Hz, CH), 137.3 (d, *J* = 34.2 Hz, CP).

(*S*,*S*)-2,4-Dicyclohexyl-1-phenylphosphetane (1c)

Colourless solid.

^{31}P NMR (C_6D_6): δ = 21.5.

^{13}C NMR (C_6D_6): δ = 26.0, 26.2, 26.69, 26.72, 26.8, 27.2 (CH_2), 30.0 (d, *J* = 4.6 Hz, CH_2), 31.45, 31.48, 31.51, 31.61, 31.64, 31.77 (CH_2), 32.67 (d, *J* = 2.4Hz, CH_2), 35.0 (d, *J* = 7.8 Hz, CH), 36.7 (d, *J* = 4.9 Hz, CH), 39.7 (d, *J* = 3.4 Hz, CH), 41.2 (d, *J* = 17.2 Hz, CH), 137.6 (d, *J* = 34.6 Hz, CP).

(*S*,*S*)-2,4-Dibenzyl-1-phenylphosphetane (1d)

Colourless oil; $[\alpha]_D$ +75 (*c* 0.5, CH_2Cl_2).

^{31}P NMR (C_6D_6): δ = 21.2.

^{1}H NMR (C_6D_6): δ = 2.3 (m, 2 H), 2.5 (m, 1 H), 2.6 (m, 1 H), 2.7–2.8 (m, 2 H), 2.9–3.1 (m, 2 H), 6.9–7.4 (C_6H_5).

^{13}C NMR (C_6D_6): δ = 30.0 (CH), 32.6 (d, *J* = 10.0 Hz, CH), 34.0 (CH_2), 38.1 (d, *J* = 3.6 Hz, CH_2), 40.9 (d, *J* = 20.7 Hz, CH_2), 137.9 (d, *J* = 34.3 Hz, C), 140.8 (d, *J* = 3.5 Hz, C), 141.4 (d, *J* = 8.3 Hz, C).

(*R*,*R*)-2,4-Di-*tert*-butyl-1-phenylphosphetane (1e)

Colourless oil; $[\alpha]_D$ –98 (*c* 0.5, CH_2Cl_2).

^{31}P NMR (C_6D_6): δ = 17.4.

^{1}H NMR (C_6D_6): δ = 0.68 [s, 9 H, *t*-C_4H_9], 1.09 (s, 9 H, *t*-C_4H_9), 2.3–2.5 (m, 3 H), 2.6–2.8 (m, 1 H), 7.1 (m, 3 H, C_6H_5), 7.7 (m, 2 H, C_6H_5).

^{13}C NMR (C_6D_6): δ = 27.7 [C(*C*H$_3$)$_3$], 27.8 [C(*C*H$_3$)$_3$], 28.3 (CH$_2$), 32.3 [d, *J* = 13.9 Hz, *C*(CH$_3$)$_3$], 34.3 [d, *J* = 3.8 Hz, *C*(CH$_3$)$_3$], 39.1 (d, *J* = 7.0 Hz, CH), 42.3 (CH), 138.1 (d, *J* = 37.0 Hz, C).

MS: *m*/*z* (%) = 262 (M, 60), 247 (M – Me, 100).

(*S*,*S*)-2,4-Diisopropyl-1-(*o*-tolyl)phosphetane (3)
Colourless oil; [α]$_D$ –89 (*c* 0.5, CH_2Cl_2).

^{31}P NMR (C_6D_6): δ = 2.4.

^{1}H NMR (C_6D_6): δ = 0.61 (d, *J* = 6.5 Hz, 3 H, CH$_3$), 0.76 (d, *J* = 6.6 Hz, 3 H, CH$_3$), 1.03 (d, *J* = 6.6 Hz, 3 H, CH$_3$), 1.07 (d, *J* = 6.6 Hz, 3 H, CH$_3$), 1.6 (m, 1 H), 1.9–2.5 (m, 5 H), 2.61 (Ar-C*H*$_3$), 7.0–7.2 (m, 3 H), 7.7 (m, 1 H).

^{13}C NMR (C_6D_6): δ = 19.9 (d, *J* = 3.2 Hz, CH$_3$), 20.6 (d, *J* = 10.7 Hz, CH$_3$), 21.1 (d, *J* = 10.3 Hz, CH$_3$), 21.4 (Ar-*C*H$_3$), 21.5 (d, *J* = 23.4, CH$_3$), 29.6 (d, *J* = 4.1 Hz, CH), 31.1 (CH$_2$), 33.2 (d, *J* = 19.5 Hz, CH), 37.5 (CH), 37.9 (d, *J* = 7.4 Hz, CH), 136.4 (d, *J* = 37.2 Hz, C), 142.8 (d, *J* = 24.5, C).

(*R*,*R*)-2,4-Dimethyl-1-ferrocenylphosphetane (4)
Yellow-orange solid; [α]$_D$ +33 (*c* 1, $CHCl_3$).

^{31}P NMR (C_6D_6): δ = 18.4.

^{1}H NMR (C_6D_6): δ = 0.88 (dd, $J_{H\text{-}P}$ = 8.2 Hz, *J* = 6.9 Hz, 3 H, CH$_3$), 1.42 (dd, $J_{H\text{-}P}$ = 17.9 Hz, *J* = 7.2 Hz, 3 H, CH$_3$), 2.3–2.5 (m, 4 H), 4.06 (5 H, Cp), 4.17 (br, 3 H), 4.30 (br, 1 H).

^{13}C NMR (C_6D_6): δ = 17.3 (d, *J* = 3.9 Hz, CH$_3$), 20.8 (d, *J* = 24.1 Hz, CH$_3$), 23.3 (d, *J* = 6.9 Hz, CH), 24.6 (d, *J* = 11.7 Hz, CH), 39.6 (CH$_2$), 69.0 (Cp), 70.7 (CH), 70.8 (CH), 71.5 (d, *J* = 7.0 Hz, CH), 74.6 (d, *J* = 32.4 Hz, CH), 76.5 (d, *J* = 32.6 Hz, CH).

(*R*,*R*)-2,4-Dimethyl-1-ferrocenylmethylphosphetane (5a)
Yellow-orange solid.

^{31}P NMR (C_6D_6): δ = 25.5.

^{1}H NMR (C_6D_6): δ = 1.02 (dd, $J_{H\text{-}P}$ = 10.4 Hz, *J* = 7.5 Hz, 3 H, CH$_3$), 1.22 (dd, $J_{H\text{-}P}$ = 16.5, *J* = 7.4 Hz, 3 H, CH$_3$), 1.85 (m, 1 H), 2.1–2.4 (m, 3 H), 2.76 (AB, 2 H, CH$_2$), 3.95 (m, 2 H, CH), 4.0 (m, 2 H, CH), 4.06 (5 H, Cp).

^{13}C NMR (C_6D_6): δ = 16.2 (d, *J* = 3.8 Hz, CH$_3$), 20.4 (d, *J* = 21.4 Hz, CH$_3$), 21.8 (d, *J* = 4.2 Hz, CH), 24.8 (d, *J* = 30.1 Hz, PCH$_2$), 25.4 (d, *J* = 8.0 Hz, CH), 39.2 (CH$_2$), 67.6, 67.8 (CH), 69.1 (Cp), 85.7 (d, *J* = 13.0 Hz, C).

(*S*,*S*)-2,4-diisopropyl-1-ferrocenylmethylphosphetane (5b)
Yellow-orange solid; [α]$_D$ +116 (*c* 0.5, CH_2Cl_2).

^{31}P NMR (C_6D_6): δ = 22.2.

^{1}H NMR (C_6D_6): δ = 0.76 (d, *J* = 6.2 Hz, 3 H, CH$_3$), 0.84 (d, *J* = 6.2 Hz, 3 H, CH$_3$), 0.92 (d, *J* = 6.5 Hz, 3 H, CH$_3$), 1.05 (d, *J* = 6.6 Hz, 3 H, CH$_3$), 1.7–1.9 (m, 4 H), 2.4–2.5 (m, 1 H), 2.6–2.7 (m, 1 H), 2.96 (2 H, CH$_2$), 3.96 (br, 2 H, CH), 4.08 (?, 5 H, Cp), 4.12 (br, 1 H, CH), 4.16 (br, 1 H, CH).

^{13}C NMR (C_6D_6): δ = 19.8 (d, *J* = 4.6 Hz, CH$_3$), 20.9 (d, *J* = 8.8 Hz, CH$_3$), 21.2 (d, *J* = 4.6 Hz, CH$_3$), 21.3 (d, *J* = 4.2 Hz, CH$_3$), 24.1 (d, *J* = 28.2 Hz, PCH$_2$), 30.4 (d, *J* = 2.3 Hz, CH), 31.4 (d, *J* = 16.4 Hz, CH), 33.8 (d, *J* = 2.7 Hz, CH$_2$), 35.8 (d, *J* = 5.7 Hz, CH), 36.5 (d, *J* = 6.5 Hz, CH), 67.5, 67.8, 69.0 (CH), 69.1 (Cp), 69.3 (CH), 85.9 (d, *J* = 13.7 Hz, C).

Anal Calcd for $C_{20}H_{29}FeP$: C, 67.43; H, 8.20. Found: C, 66.06; H, 8.32.

(*S*,*S*)-1-(*o*-Anisyl)-2,4-diisopropylphosphetane (6)
[α]$_D$ –240 (*c* 0.5, CH_2Cl_2).

^{31}P NMR (C_6D_6): δ = 9.1.

^{1}H NMR (C_6D_6): δ = 0.69 (d, *J* = 6.6 Hz, 3 H, CH$_3$), 0.83 (d, *J* = 6.4 Hz, 3 H, CH$_3$), 0.97 (d, *J* = 6.3 Hz, 3 H, CH$_3$), 1.07 (d, *J* = 6.5 Hz, 3 H, CH$_3$), 1.5–1.6 (m, 1 H), 1.9–2.2 (m, 3 H), 2.3–2.4 (m, 1 H), 2.4–2.6 (m, 1 H), 3.30 (s, 3 H, OCH$_3$), 6.50 (ddd, *J* = 8.2, 3.9, 0.7 Hz, 1 H, CH), 6.94 (td, *J* = 7.4, 1.1 Hz, 1 H, CH), 7.14 (td, *J* = 7.8, 1.5 Hz, 1 H, CH), 7.53 (ddd, *J* = 7.4, 3.4, 1.7 Hz, 1 H, CH).

^{13}C NMR (C_6D_6): δ = 19.8 (d, *J* = 3.4 Hz, CH$_3$), 20.8 (d, *J* = 10.2 Hz, CH$_3$), 21.5 (d, *J* = 11.2 Hz, CH$_3$), 21.8 (CH$_3$), 30.1 (d, *J* = 3.9 Hz, CH), 31.8 (CH$_2$), 32.4 (d, *J* = 20.1 Hz, CH), 36.6 (d, *J* = 6.9 Hz, CH), 38.4 (CH), 54.8 (OCH$_3$), 110.1 (CH), 121.0 (CH), 126.6 (d, *J* = 39.6 Hz, PC), 129.7 (CH), 132.1 (CH), 161.8 (d, *J* = 13.8 Hz, CH).

(*R*,*R*)-1-Cyclohexyl-2,4-dimethylphosphetane (7)
[α]$_D$ +18 (*c* 1, CH_2Cl_2).

^{31}P NMR ($CDCl_3$): δ = 28.1.

^{1}H NMR (C_6D_6): δ = 1.07 (t, $J_{H\text{-}P}$ = *J* = 6.9 Hz, 3 H, CH$_3$), 1.24 (dd, $J_{H\text{-}P}$ = 16.0, *J* = 7.2 Hz, 3 H, CH$_3$).

^{13}C NMR (C_6D_6): δ = 15.4 (d, *J* = 4.3 Hz, CH$_3$), 20.2 (d, *J* = 20.1 Hz, CH$_3$), 20.6 (d, *J* = 2.9 Hz, CH), 24.2 (d, *J* = 8.0 Hz, CH), 25.6 (d, *J* = 8.0 Hz, CH$_2$), 25.8 (CH$_2$), 26.1 (d, *J* = 9.1 Hz, CH$_2$), 27.4 (d, *J* = 14.1 Hz, CH$_2$), 30.2 (d, *J* = 18.0 Hz, CH$_2$), 33.3 (d, *J* = 24.2, PCH), 38.0 (CH$_2$).

(COD)Rh(L*)$_2$PF$_6$ complexes (L* = 1a–d); General Procedure
The rhodium complexes were prepared by adding (COD)$_2$RhPF$_6$ (0.5 equiv) to a solution of phosphetane (0.5 mmol) in CH_2Cl_2 (2 mL). The pure complexes were recovered after crystallisation from CH_2Cl_2–Et_2O mixtures and fully characterised. Some selected data are given below.

(COD)Rh[(*S*,*S*)-1a]$_2$PF$_6$
[α]$_D$ +66 (*c* 0.2, $CHCl_3$).

^{31}P NMR ($CDCl_3$): δ = 67.4 (d, $J_{P\text{-}Rh}$ = 144 Hz).

(COD)Rh[(*S*,*S*)-1b]$_2$PF$_6$
[α]$_D$ = +134 (*c* 0.2, $CHCl_3$).

^{31}P NMR ($CDCl_3$): δ = 53.6 (d, $J_{P\text{-}Rh}$ = 145 Hz).

(COD)Rh[(*S*,*S*)-1c]$_2$PF$_6$
[α]$_D$ +123 (*c* 1, $CHCl_3$).

^{31}P NMR ($CDCl_3$): δ = 54.8 (d, $J_{P\text{-}Rh}$ = 143 Hz).

Anal. Calcd for $C_{50}H_{74}F_6P_3Rh$: C, 60.97; H, 7.57. Found: C, 60.97; H, 7.40.

(COD)Rh[(*S*,*S*)-1d]$_2$PF$_6$
^{31}P NMR (CD_2Cl_2): δ = 65.3 (d, $J_{P\text{-}Rh}$ = 147 Hz).

Anal. Calcd for $C_{54}H_{58}F_6P_3Rh$: C, 63.78; H, 5.75. Found: C, 60.47; H, 6.18.

Rhodium Complexes as Catalysts in Model Hydrogenation Experiments; General Procedure
Hydrogenations of α-acetamido cinnamic acids were performed an a 1 mmol scale, in MeOH at r.t., with 1% rhodium catalyst under 3–5 bar of H_2. Reactions were allowed to proceed overnight. Quantitative conversions were obtained. Enatiomeric excesses (80% with phosphetane **1a**, 10% with **1b** and 86% with **1d**) were measured on the corresponding methyl esters by HPLC (OD-H column).

Aminophosphetane Borane Complexes 16 and 17
To a solution of 2-(aminophenyl)phosphine (510 mg, 4 mmol) in THF (8 mL) cooled to –78 °C was added BuLi (2.5 N in hexane, 3.6 mL, 2.2 equiv). After warming to r.t. and stirring for 30 min, the resulting solution was added to a solution of (*S*,*S*)-pentane-2,5-diol

cyclic sulfate (1.3 g, 2 equiv) in THF (150 mL) at –78 °C. After 3 h at r.t., *s*-BuLi (1.3 N in hexane, 6.9 mL) was added at –78 °C. The mixture was stirred overnight at r.t., then an excess of $BH_3{\cdot}SMe_2$ (4 equiv) was added. After hydrolysis, evaporation and extraction with Et_2O, the mixture was separated by column chromatography on alumina with a cyclohexane–Et_2O gradient.

(*R,R*)-1-{2-[(*R,R*)-2,4-Dimethylazetidino]phenyl}-2,4-dimethylphosphetane Borane Complex 16

Colourless solid; yield: 83 mg (7%); R_f 0.7 (cyclohexane–Et_2O, 90:10); $[\alpha]_D$ –234 (*c* 1, $CHCl_3$).

^{31}P NMR ($CDCl_3$): δ = 48 ($J_{P\text{-}B}$ = 53 Hz).

^{1}H NMR ($CDCl_3$, at 55 °C): δ = 1.19 (d, *J* = 6.1 Hz, 6 H, 3 H, CH_3), 1.40 (dd, $J_{H\text{-}P}$ = 17.4 Hz, *J* = 6.9 Hz, 3 H, CH_3), 1.42 (dd, $J_{H\text{-}P}$ = 14.8 Hz, *J* = 7.4 Hz, 3 H, CH_3), 2.0 (br, 2 H), 2.06 (dt, $J_{H\text{-}P}$ = 47.2 Hz, *J* = 10.7 Hz, 1 H, CH_2), 2.5 (m, 1 H, CH_2), 2.63 (m, *J* = 6.4 Hz, 1 H), 2.98 (m, 1 H), 4.42 (m, *J* = 6.2 Hz, 2 H, NCH), 6.71 (dd, *J* = 7.4, 4.0 Hz, 1 H), 6.93 (t, *J* = 7.4 Hz, 1 H), 7.11 (1 H), 7.30 (1 H).

^{13}C NMR ($CDCl_3$): δ = 14.3 (CH_3), 16.4 (d, *J* = 8.0 Hz, CH_3), 18.9 (br, 2 CH_3), 30.6 (d, *J* = 37.7, CH), 32.2 (d, *J* = 42.6 Hz, CH), 32.5 (CH_2), 35.6 (d, *J* = 12.5 Hz, CH_2), 116.1 (d, *J* = 5.6 Hz, CH), 120.3 (d, *J* = 9.2, CH), 122.9 (d, *J* = 26.9 Hz, C), 130.8 (CH), 131.4 (d, *J* = 8.4 Hz, CH), 148.8 (d, *J* = 3.2 Hz, C).

MS: *m*/*z* = 261 (M – BH_3, 25), 190 (100).

Anal. Calcd for $C_{16}H_{27}BNP$: C, 69.84; H, 9.89; N, 5.09. Found: C, 69.74; H, 9.94; N, 5.09.

(*R,R*)-1-(2-Aminophenyl)-2,4-dimethylphosphetane Borane Complex 17

Colourless solid; yield: 360 mg (43%); R_f 0.25 (cyclohexane–Et_2O, 90:10); $[\alpha]_D$ –93 (*c* 1, $CHCl_3$).

^{31}P NMR (C_6D_6): δ = 45 ($J_{P\text{-}B}$ = 39 Hz).

^{1}H NMR ($CDCl_3$, at 55 °C): δ = 0.79 (dd, *J* = 15.1, 7.3 Hz, 3 H, CH_3), 1.20 (dd, *J* = 18.5, 7.0 Hz, 3 H, CH_3), 1.6 (ddt, $J_{H\text{-}P}$ = 36.4 Hz, *J* = 9.9 Hz, *J* = 3.1 Hz, 1 H, CH_2), 2.2 (m, 1 H), 2.4 (m, 1 H), 2.6 (m, 1 H), 4.04 (br, 2 H, NH_2), 6.1 (m, 1 H), 6.6 (m, 1 H), 6.9 (m, 1 H), 7.0 (m, 1 H).

^{13}C NMR (C_6D_6): δ = 14.6 (CH_3), 15.4 (d, *J* = 7.2 Hz, CH_3), 26.6 (d, *J* = 41.6 Hz, CH), 28.8 (d, *J* = 38.9 Hz, CH), 35.0 (d, *J* = 14.1 Hz, CH_2), 112.0 (d, *J* = 31.2 Hz, C), 116.7 (d, *J* = 5.7 Hz, CH), 118.3 (d, *J* = 8.0 Hz, CH), 131.3 (d, *J* = 4.6 Hz, CH), 132.3 (d, *J* = 2.3 Hz, CH), 150.3 (d, *J* = 6.9 Hz, C).

MS: *m*/*z* (%) = 193 (M – BH_3, 85), 136 (100).

Anal. Calcd for $C_{11}H_{19}BNP$: C, 63.81; H, 9.25; N, 6.76. Found: C, 64.10; H, 9.44; N, 6.39.

X-Ray Structure Determination of 16

Molecular formula: $C_{16}H_{27}BNP$. Molecular weight 275.17. Colourless cube, dimensions: 0.20 × 0.20 × 0.20 mm; crystal system: triclinic, space group: P21. a(Å) = 8.251(4), b(Å) = 9.481(2), c(Å) = 11.121(2), a(°) = 90.001(10), b(°) = 104.992(15) g(°) = 90.073(15), V(Å^3) = 840.4(4), Z = 2; d (gcm^{-3}) = 1.087. Diffractometer KappaCCD, X-Ray source Mo Ka (λ = 0.71070 Å), graphite monochromator. T(K) 150.0(1). Reflections measured: 4971. Independent reflections: 3096. Refinement type Fsqd. Hydrogen atoms mixed Parameters refined 176. *w*R2 0.0811; R1 0.0287; GoF 1.041. D peak/hole (e Å^{-3}) 0.259/–0.175.

(*R,R*)-1-{2-[(*R,R*)-2,4-Dimethylazetidino]phenyl}-2,4-dimethylphosphetane (15)

Displacement of phosphetane **15** from its borane complex was achieved by reacting **16** with DABCO (1.5 equiv) in benzene solution at 45 °C for 2 h. The crude mixture was purified by filtration on a short alumina column under argon with Et_2O as eluent; colourless oil.

^{31}P NMR (C_6D_6): δ = 19.0.

^{1}H NMR (C_6D_6, at 55 °C): δ = 1.11 (d, *J* = 6.0 Hz, 6 H, CH_3), 1.12 (t, $J_{H\text{-}P}$ = *J* = 7.1 Hz, 3 H, CH_3), 1.31 (dd, $J_{H\text{-}P}$ = 16.7 Hz, *J* = 7.0 Hz, 3 H, CH_3), 1.7 (br, 2 H, CH_2), 2.07 (dt, $J_{H\text{-}P}$ = 33.4 Hz, *J* = 9.5 Hz, 1 H, CH_2), 2.3 (m, 1 H), 2.4 (m, 1 H), 2.8 (m, 1 H), 4.3 (br, 2 H, NCH), 6.53 (dd, *J* = 8.0, 3.2 Hz, 1 H, CH), 6.92 (t, *J* = 7.3 Hz, 1 H, CH), 7.15 (1H), 7.24 (m, 1H).

^{13}C NMR (C_6D_6): δ = 15.9 (d, *J* = 5.3 Hz, CH_3), 18 (br, CH_3), 19.3 (d, *J* = 21.4 Hz, CH_3), 24.0 (d, *J* = 2.3 Hz, CH), 27.4 (d, *J* = 7.6 Hz, CH), 31.1 (CH_2), 35.9 (CH_2), 54.0 (br, NCH), 146.8 (d, *J* = 10.7 Hz, CN).

(*R,R*)-1-{2-[(*R,R*)-2,5-Dimethylpyrrolidino]phenyl}-2,5-dimethylphospholane Borane Complex 18

^{31}P NMR (C_6D_6): δ = 42 ($J_{P\text{-}B}$ = 65 Hz).

^{1}H NMR (C_6D_6): δ = 0.60 (d, *J* = 6.5 Hz, 3 H, CH_3), 0.68 (dd, $J_{H\text{-}P}$ = 13.5 Hz, *J* = 7.3 Hz, 3 H, CH_3), 0.92 (d, *J* = 6.0 Hz, 3 H, CH_3), 1.42 (dd, $J_{H\text{-}P}$ = 15.3 Hz, *J* = 7.0 Hz, 3 H, CH_3), 1.2–1.8 (6 H), 2.0 (m, 1 H), 2.2 (m, 1 H), 2.5 (m, 1 H), 3.0 (m, 1 H), 3.3 (m, 1 H), 4.2 (m, 1 H), 6.9 (m, 2 H), 7.0 (m, 1 H), 7.7 (m, 1 H).

^{13}C NMR (C_6D_6): δ = 14.9 (d, *J* = 3.4 Hz, CH_3), 15.8 (d, *J* = 4.5 Hz, CH_3), 17.0 (CH_3), 19.3 (CH_3), 30.1 (d, *J* = 34.9 Hz, PCH), 30.8 (CH_2), 32.4 (CH_2), 32.9 (d, *J* = 7.8 Hz, CH_2), 33.5 (d, *J* = 4.2 Hz, CH_2), 35.5 (d, *J* = 36.4 Hz, PCH), 53.0 (NCH), 60.2 (NCH), 123.8 (d, *J* = 9.5 Hz, CH), 125.4 (d, *J* = 5.3 Hz, CH), 130.9 (d, *J* = 1.5 Hz, CH), 136.0 (d, *J* = 9.1 Hz, CH), 151.8 (C).

MS (CI): *m*/*z* = 304 (M + H, 100%).

2-[(*R,R*)-2,4-Dimethylazetidino]ethylphosphine (20)

A solution containing (*R,R*)-2,4-dimethylazetidinium acetate[19] (2.1g, 14 mmol), diethyl 2-bromoethylphosphonate (5.1g, 21 mmol), Et_3N (4 mL) and toluene (4 mL) was heated overnight at 80 °C. The crude mixture was diluted with Et_2O and the ammonium salt was removed by filtration. After evaporation, the residue was distilled at 60 °C (2 mbar) to remove the excess of diethyl 2-bromoethylphosphonate and the main side-product, diethyl vinylphosphonate. The residue (2.5 g) contained mainly **19**, which was used for the next step without further purification.

19

^{31}P NMR ($CDCl_3$): δ = 30.2.

^{1}H NMR ($CDCl_3$): δ = 1.29 (t, *J* = 6.5 Hz, 6 H, CH_2CH_3), 1.29 (d, *J* = 6.5 Hz, 6 H, CH_3), 2.0 (m, 4 H), 2.9 (m, 2 H), 3.83 (m, *J* = 6.7 Hz, 2 H, NCH), 4.06 (m, *J* = 7.0 Hz, 4 H, OCH_2).

^{13}C NMR ($CDCl_3$): δ = 16.2 (d, *J* = 5.9 Hz, CH_3), 17.3 (CH_3), 23.6 (d, *J* = 139.3 Hz, CH_2P), 32.2 (CH_2), 42.2 (CH_2), 57.2 (NCH), 61.7 (d, *J* = 6.2 Hz, OCH_2).

An Et_2O solution of the crude phosphonate **19** was added to a cooled (–78 °C) suspension of $LiAlH_4$ (2.3 g, 6 equiv) in Et_2O (40 mL). The mixture was warmed up, stirred overnight at r.t., then hydrolysed with H_2O and NaOH (20% aq solution) until a colourless solid separated from the organic phase. The organic phase was transferred under argon in a round bottomed flask, dried successively with $MgSO_4$ and CaH_2, filtered on a Celite pad and distilled in a Kugelrohr apparatus (70 °C, 0.3 bar) to afford 0.91 g (63%) of **20** containing small amounts (<10%) of side products; colourless oil.

^{31}P NMR ($CDCl_3$): δ = –143.9.

^{1}H NMR ($CDCl_3$): δ = 1.15 (d, *J* = 6.4 Hz, 6 H, CH_3), 1.5 (m, 2 H, PCH_2), 1.81 (t, *J* = 6.4 Hz, 2 H, CH_2-azet), 2.5–2.7 (m, 2 H), 2.60 (m, $J_{H\text{-}P}$ = 195.0 Hz, *J* = 7.1 Hz, 2 H, PH_2), 3.5 (m, 2 H, NCH).

^{13}C NMR ($CDCl_3$): δ = 13.1 (d, *J* = 8.4 Hz, PCH_2), 18.3 (CH_3), 32.9 (CH_2), 52.8 (NCH_2), 56.5 (NCH).

MS: *m*/*z* (%) = 145 (M, 19), 98 (100).

(*R*,*R*)-1-{2-[(*R*,*R*)-2,4-Dimethylazetidino]ethyl}-2,4-dimethylphosphetane Bis-borane Complex 22

The cyclisation reaction between **20** (2.8 mmol) and (*S*,*S*)-pentane-2,4-diol cyclic sulfate affording **22**, was performed as described above for the synthesis of the phosphetane borane complexes **9**–**14**. The final product was purified by column chromatography on alumina with cyclohexane–Et_2O (80:20) as eluent; R_f 0.4; yield: 0.16g (25%); colourless solid; $[\alpha]_D$ –38 (*c* = 1, $CHCl_3$).

^{31}P NMR ($CDCl_3$): δ = 55 ($J_{P\text{-}B}$ = 53 Hz).

^{1}H NMR (C_6D_6): δ = 1.25 (dd, $J_{H\text{-}P}$ = 7.5 Hz, *J* = 5.1 Hz, 3 H, CH_3), 1.29 (t, $J_{H\text{-}P}$ = *J* = 7.5 Hz, 3 H, CH_3), 1.40 (d, *J* = 7.2 Hz, 3 H, CH_3), 1.41 (d, *J* = 6.5 Hz, 3 H, CH_3), 1.80 (m, 1 H, CH_2-azet), 2.13 (qd, *J* = 7.0, 4.7 Hz, 1 H, CH_2P), 2.3–2.5 (m, 5 H), 2.6 (m, 1 H, PCH), 2.8–3.0 (m, 2 H, NCH_2), 3.8 (m, 1 H, NCH), 3.9 (m, 1 H, NCH).

^{13}C NMR ($CDCl_3$): δ = 15.0 (d, *J* = 6.5 Hz, CH_3), 15.4 (CH_3), 16.0 (CH_3), 17.1 (CH_3), 18.3 (d, *J* = 17.7 Hz, PCH_2), 26.5 (d, *J* = 40.1 Hz, PCH), 27.1 (d, *J* = 39.3 Hz, PCH), 30.9 (CH_2), 36.3 (d, *J* = 16.9 Hz, CH_2), 51.3 (d, *J* = 5.5 Hz, NCH_2), 63.7 (NCH), 66.1 (NCH).

MS (CI): *m*/*z* = 259 (M + NH_4, 100%).

Anal. Calcd for $C_{12}H_{30}B_2NP$: C, 59.81; H, 12.55; N, 5.81. Found: C, 59.91; H, 12.69; N, 5.65;

X-Ray Structure Determination of 22

Molecular formula: $C_{12}H_{30}B_2NP$. Molecular weight 240.96. Colourless cube, dimensions: 0.24 × 0.24 × 0.24 mm; crystal system: monoclinic, space group: C2: a(Å) = 21.586(5) b(Å) = 6.896(5), c(Å) = 13.923(5), a(°) = 90.000(5), b(°) = 129.060(5) g(°) = 90.000(5), V($Å^3$) = 1609.3(14), Z = 4; d (gcm^{-3}) = 0.995. Diffractometer KappaCCD, X-Ray source MoKa (λ = 0.71069 Å), graphite monochromator. T(K) 150.0(1). Reflections measured: 5362. Independent reflections: 3974. Refinement type Fsqd. Hydrogen atoms mixed. Parameters refined 151. wR2 0.1118; R1 0.0402; GoF 1.056. D peak/hole (e $Å^{-3}$) 0.262/–0.263.

(*R*,*R*)-1-{2-[(*R*,*R*)-2,4-Dimethylazetidino]ethyl}-2,4-dimethylphosphetane (21)

The azetidine-phosphetane **21** was released from its bis-borane complex by heating with an excess DABCO in C_6D_6 at 65 °C for 6 h. The trivalent phosphetane is an extremely air sensitive compound, consequently the decomplexation reaction was performed in a sealed NMR tube and the final product was characterised by NMR of the crude reaction mixture.

^{31}P NMR (C_6D_6): δ = 21.1.

^{1}H NMR (C_6D_6): δ (selected data) = 1.11 (t, $J_{H\text{-}P}$ = *J* = 7.3 Hz, 3 H, CH_3), 1.17 (d, *J* = 6.3 Hz, 6 H, CH_3), 1.39 (dd, $J_{H\text{-}P}$ = 16.8 Hz, *J* = 7.3 Hz, 3 H, CH_3), 1.73 (t, *J* = 6.3 Hz, 2 H, CH_2-azet), 3.50 (m, *J* = 6.3 Hz, 1 H, NCH).

^{13}C NMR (C_6D_6): δ = 16.2 (d, *J* = 3.8 Hz, CH_3), 18.3 (CH_3), 20.5 (d, *J* = 22.0 Hz, CH_3), 21.1 (d, *J* = 6.4 Hz, CH), 24.3 (d, *J* = 27.6 Hz, PCH_2), 26.2 (d, *J* = 9.1 Hz, CH), 33.4 (CH_2), 39.5 (CH_2), 46.9 (d, *J* = 20.5 Hz, NCH_2), 56.3 (NCH).

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