Synthesis of Racemic and Enantiomerically Pure (*R**,*R**,*R**)-Tris(α-methylbenzyl)phosphane − X-ray Crystal Structures of the Phosphane Oxides and Borane Complexes

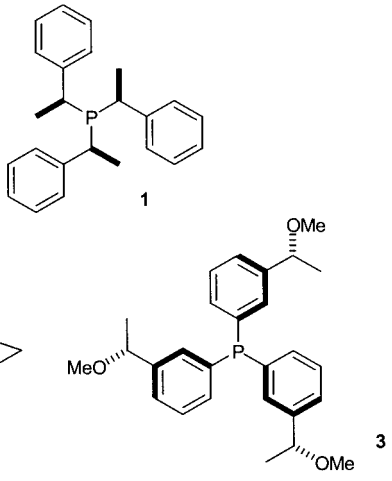
Paul Wyatt,*[a] Helen Eley,[a] Jonathan Charmant,[b] Berian J. Daniel,[b] and Anob Kantacha[b]

Keywords: Phosphanes / Asymmetric synthesis / C_3 symmetry / Boranes

An asymmetric synthesis of C_3-symmetric phosphane **1** has been achieved. Two of the α-methylbenzyl groups were introduced as nucleophiles (using an α-methylbenzyl Grignard reagent), and asymmetry was introduced by resolution using (*R*)-α-methylbenzylamine. The final α-methylbenzyl group was introduced as an electrophile (α-methylbenzyl iodide) in a modestly selective reaction.

Introduction

Monodentate phosphorus ligands are back in vogue.[1−3] Enantiomerically pure C_3-symmetrical phosphanes **2** are known,[4,5] and while transition metal complexes with congested phosphane ligands like tBu$_3$P and Cy$_3$P have been shown to have unusual catalytic properties,[6,7] those of enantiomerically pure C_3-symmetrical phosphanes **3** have shown promise in asymmetric reactions.[8,9] We report here the asymmetric synthesis of a phosphane **1** that is monodentate, C_3 symmetrical and where the chiral centres are as close to phosphorus as possible while avoiding a chiral phosphorus atom itself. We report the X-ray crystal structure of the oxide and borane complex.



Results and Discussion

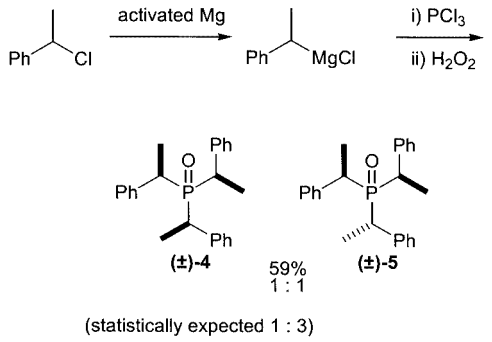
Synthesis of Racemic Phosphane Oxide and Borane

The synthesis of the racemic phosphane oxide **4** was reasonably straightforward; α-methylbenzyl Grignard reagent was reacted with PCl_3 followed by H_2O_2 to give a mixture of the diastereomeric phosphanes **4** and **5** in 59% yield (Scheme 1). The standard difficulties with benzyl Grignard preparation were largely overcome using the method from Brown et al., which involves the mechanical grinding of the magnesium turnings for five days.[10] Although statistics are against us — a purely statistical outcome from this reaction would yield a 3:1 ratio of C_1:C_3 phosphanes — the ratio of diastereomers was 1:1. Therefore, a 1:1 mixture of diastereomers, though a little unusual, actually represents a *stereoselective* reaction. The desired diastereomer was isolated by recrystallisation. As we have found before,[11] C_3-symmetrical compounds have a greater tendency to crystallise than their less symmetrical diastereomers. This was useful for purification purposes for all of the C_3-symmetrical compounds described in this paper.

As is common with phosphane chemistry, our plan was to isolate the corresponding phosphane oxide **4** of the phosphane **1** and our initial plan for an asymmetric route fea-

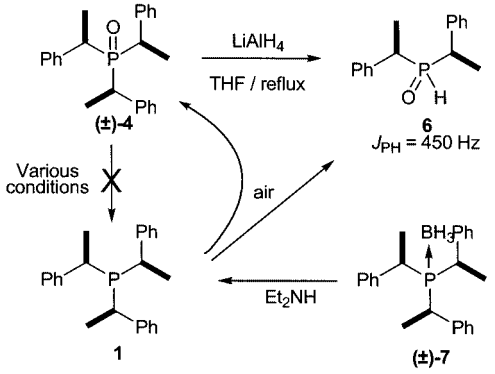
[a] School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, England
Fax: (internat.) +44-(0)117-929-8611
E-mail: paul.wyatt@bristol.ac.uk
[b] Structural Chemistry Laboratory, University of Bristol, Cantock's Close, Bristol, BS8 1TS, England
Fax: (internat.) +44-(0)117-929-050
E-mail: jon.charmant@bristol.ac.uk
Supporting information for this article is available on the WWW under http://www.eurjoc.org or from the author.

  DOI: 10.1002/ejoc.200300396



Scheme 1. Preparation of racemic phosphane oxide **4**

tured phosphane oxide **4** as an intermediate. However, we were unable to reduce the phosphane oxide to its phosphane. The usual conditions of AlH_3,[12] $HSiCl_3$ [13] and $LiAlH_4$ [14,15] (at room temperature) failed to reduce the oxide **4**. The phosphane oxide responded to more persuasive methods ($LiAlH_4$ in refluxing THF) with a debenzylation to give the phosphinous acid **6** (Scheme 2).



Scheme 2. Attempts to form **1** and its reaction products

Clearly the phosphane oxide could not feature as an intermediate in our asymmetric route and we therefore sought an alternative. Reaction of PCl_3 with α-methylbenzyl Grignard reagent followed by BH_3·THF (instead of H_2O_2) gave the phosphane−borane complex **7** (and its diastereomer) in a combined yield of 52%. As would be expected, the diastereomeric ratio was similar to the oxide with a ratio of 1:1. Removal of the borane to reveal the phosphane was easily achieved using Et_2NH in 90% yield (Scheme 2).[16,17]

We then tested the sensitivity of the phosphane **1** in air. Although we had considered its oxidation to oxide **4** in air, we had not expected the alternative debenzylation reaction to the phosphinous acid **6**. It is interesting to note that debenzylation happens under both oxidative (air) and reductive (with $LiAlH_4$) conditions (Scheme 2).

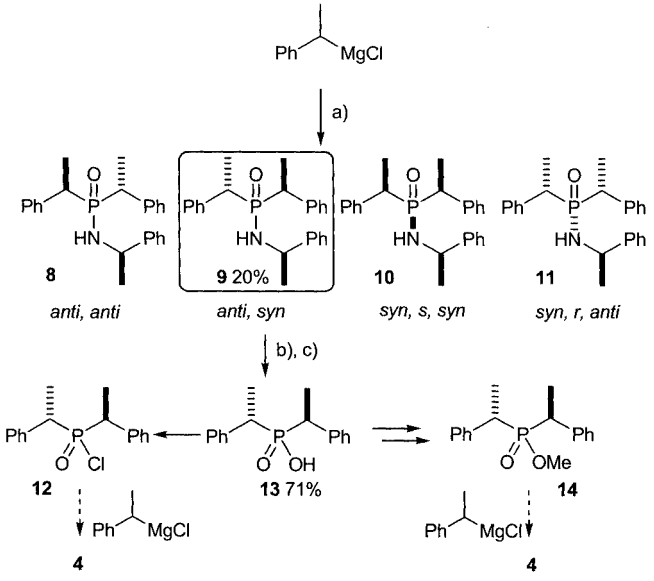
Attempted Resolution

Phosphane oxides can be resolved by a variety of techniques.[18] Most straightforward are those employing acids. We were not successful in any attempt to resolve the phosphane oxide using camphorsulfonic acid or tartrate derivatives. But in any case, success here would have been thwarted when it came to liberating the phosphane due to the reduction difficulties discussed above. Attempted resolution of the phosphane using the asymmetric borane $IpcBH_2$ was also not successful.[19] Any complexes that were formed were too unstable to be useful. Resolution of the completed phosphane was abandoned and alternative asymmetric syntheses were investigated.

Asymmetric Synthesis using Electrophilic Phosphorus

A key intermediate in the strategy for asymmetric synthesis was phosphinic acid **13**, which contains two of the three α-methylbenzyl groups with the correct relative and absolute stereochemistry. Introduction of the final α-methylbenzyl unit to some derivative of this acid (**12** or **14**) was to be done exploiting the electrophilic properties of phosphorus.

Following a procedure outlined by Denmark et al.[20] we reacted PCl_3 with α-methylbenzyl Grignard reagent followed by (*R*)-α-methylbenzylamine and finally H_2O_2 to give all four diastereomers of the phosphinic amide products **8**−**11** (Scheme 3). Two of these diastereomers **10** and **11** contain a stereogenic phosphorus atom while the other two contain a non-stereogenic phosphorus atom (stereochemistry is indicated in Figure 1; the phosphorus atom is, in essence, a pseudoasymmetric centre. Pseudoasymmetric centres are more commonly encountered when they are



Scheme 3. Preparation of four phosphinic amides and the subsequent reaction of **9**; reagents a) i) PCl_3; ii) (*R*)-α-methylbenzylamine; iii) H_2O_2; b) Separation, c) HCl/dioxane reflux

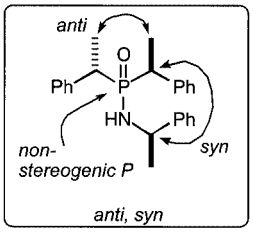
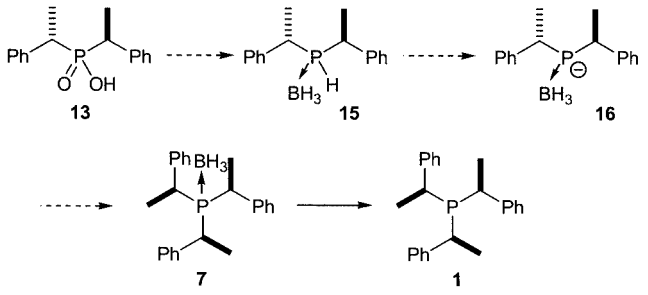


Figure 1. Stereochemistry

stereogenic and achirotopic.[21] Clearly the phosphorus atom is not included by these conditions as it *is* chirotopic by virtue of the α-methylbenzyl group of the phosphinamide. However, there is no link between its stereoisomerism and chirality (it is not a chiral centre as it has two enantiotopic α-methylbenzyl groups attached).[22] The descriptors necessary (*s* and *r*) are also characteristic of a standard pseudoasymmetric centre).[21,22] The diastereomer **9** was the second most abundant from this procedure. Hydrolysis gave the phosphinic acid **13**, which was readily converted into the phosphinic acid chloride **12** or ester **14**. However, reaction of **12** or **14** with α-methylbenzyl Grignard reagent failed. It was at this point that we also learned from our investigation into the racemic material that we were unable to reduce the phosphane oxide **4** anyway. Hence any asymmetric route (or, indeed, any route to racemic materials) would have to exclude the oxide **4** as an intermediate.

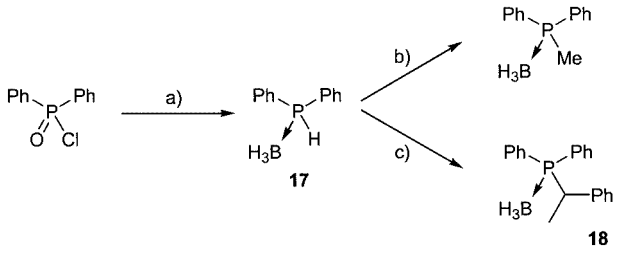


Scheme 4. A strategy based on the nucleophilic phosphorus

Asymmetric Synthesis Using Nucleophilic Phosphorus

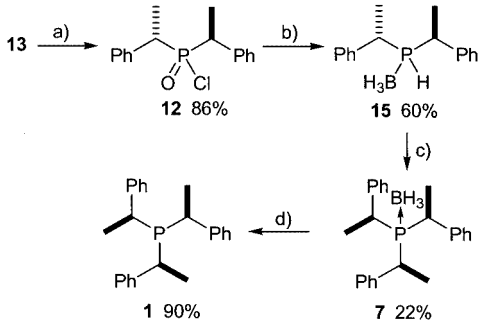
Faced with the difficulties of using an electrophilic phosphorus atom, we decided to change to a strategy using a nucleophilic phosphorus atom. Because we had established that boron could be removed from **7**, the successful formation of a nucleophilic species **16**, followed by alkylation would represent a route to the free phosphane **1**. Thus either bis(α-methylbenzyl)phosphane itself or its boron complex **15**, would be prepared and then alkylated. The method for the introduction of two of the three absolute stereocentres was the same and so phosphinic acid **13** was again a key intermediate.

A method for the conversion of acid **13** to complex **15** was needed as was a method for the alkylation of **15**. Model experiments were conducted with diphenylphosphinic acid to find suitable conditions (Scheme 5). The reduction of Ph_2PCl to its phosphane−borane $Ph_2PH{\cdot}BH_3$ has been reported using a combination of $LiAlH_4$ and $BH_3{\cdot}THF$.[17] We found that the efficacy of this reagent combination extended to Ph_2POCl for the formation of complex **17** (54% yield; Scheme 5). It would have been more convenient to reduce acid **13** directly but conditions effective for reduction of Ph_2POH (i.e. $LiAlH_4/NaBH_4/CeCl_3$) are low yielding for phosphinic acids.[17]



Scheme 5. Model experiments; preparation and alkylation of diphenylphosphane−borane; reagents: a) (i) $LiAlH_4$, (ii) $BH_3{\cdot}$THF; b) (i) KOH/MeOH, (ii) MeI; c) (i) *n*BuLi, (ii) PhCHIMe

The methylation of the borane complex **17** with KOH and MeI is known[23] and was repeated without difficulty, but the reaction with KOH and α-methylbenzyl chloride did not lead to alkylation. After some investigation we determined that successful alkylation (51% yield) could be achieved to give **18** using *n*BuLi as the base and α-methylbenzyl iodide[24] as the electrophile.



Scheme 6. Preparation and alkylation of bis(α-methylbenzyl)phosphane−borane; reagents: a) $SOCl_2$; b) (i) $LiAlH_4$, (ii) $BH_3{\cdot}$THF; c) (i) *n*BuLi, (ii) α-methylbenzyl iodide, iii) separation; d) Et_2NH

These conditions were applied to phosphinic chloride **12** to give complex **15** in 60% yield and the alkylated product **7** in 55% yield in a 2:1 ratio in favour of the C_3 diastereomer. Curiously, reaction of **15** with KOH/MeOH and MeI fails. Separation and purification of the single diastereomer lowered the yield to 22%. The ratio of diastereomers to be expected statistically is 1:1. Initially, we used just over one equivalent of alkyl iodide but, since it is racemic, this would necessarily limit the ratio of products to 1:1. To at least *allow* the possibility of kinetic resolution (where the lithium phosphide can choose to react with the enantiomer it wishes) we used five equivalents of alkyl iodide. Thus the small improvement in selectivity to 2:1 was noted. The final step in the asymmetric synthesis was removal of borane using Et_2NH. This reaction had been established in the racemic sequence and proceeded as expected to give phosphane **1** in 90% yield.

Optically Pure Phosphane-Borane 7

X-ray crystal structure determination was performed on the phosphane−borane complex **7** (Figure 2).

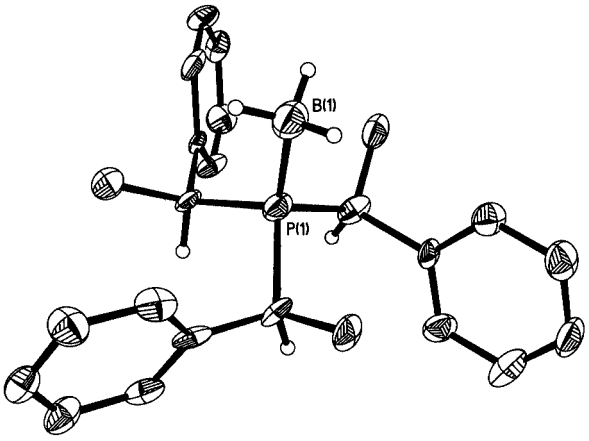


Figure 2. ORTEP drawing of the phosphane−borane **7**

The visually apparent symmetry in the crystal structure is not crystallographic and thus not reflected in the space group. The C−P bond lengths are 1.864(7), 1.847(7) and 1.858(7) Å while the C−P−C bond angles are 105.0(3)°, 105.0(3)° and 102.8(3)°. Most interesting is the cone angle for the phosphane which is estimated from this crystal structure to be 183.4°. This large cone angle is similar to the 182° of tBu$_3$P[25] and a view from the side (Figure 3) shows how well the phosphorus atom is embedded in the structure. A good way to consider the orientation of the α-methylbenzyl groups in the structure is to note that the carbon−benzylic proton bond approaches antiperiplanarity with the P−B bond (the dihedral angles are between 165.7° and 170.4°). This is in stark contrast to the orientation of the benzyl groups in the analogous amine **20**.[11]

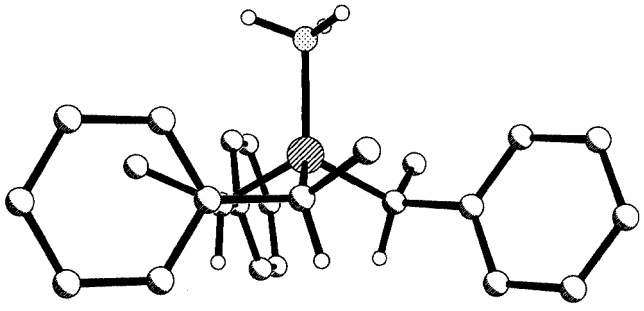


Figure 3. Side view of phosphane−borane **7**

Racemic Phosphane-Borane (±)-7 and Phosphane Oxide (±)-4

The crystal system of the racemic borane complex is monoclinic with a $P2_1/c$ space group.

The appearance of the crystal structure is visually very similar to the optically pure borane. The crystal system of the racemic phosphane oxide is triclinic with a $P\bar{1}$ space group. Again it is very similar to that of the borane com-

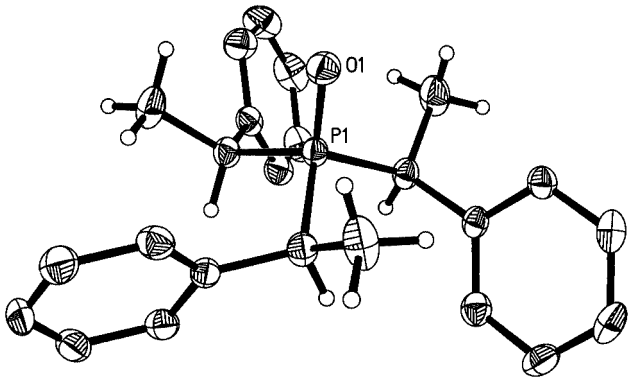


Figure 4. ORTEP drawing of phosphane oxide **4**

plexes but the α-methylbenzyl groups twist slightly further so that the methyl groups are closer to the P=O bond. Thus the dihedral angle between the P=O bond and the benzylic C−H bond varies between 152.0° and 154.8°. The C−P bond lengths are 1.8469(19), 1.848(2) and 1.851(2) Å.

NMR Spectra

It is instructive to compare the expansions of NMR spectra of the C_3-symmetrical phosphane and its diastereomer with the spectra of the C_3-symmetrical amine **20** and its diastereomer **21**.[11] The expansions (δ = 3.5−0.5 ppm for phosphanes and δ = 5.0−0.5 ppm for amines) in the following figures include signals from the benzylic protons and methyl protons. The C_3-symmetrical diastereomer of phosphane−borane **7** contains an unremarkable double doublet corresponding to the three homotopic methyl groups (Figure 5). The other diastereomer **19** contains three diastereotopic methyl groups which are immediately evident in the ^{1}H NMR spectrum (Figure 6).

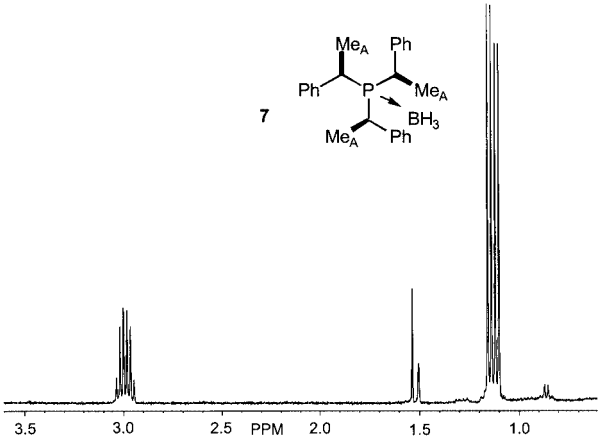


Figure 5. ^{1}H NMR spectrum of phosphane−borane **7**

The C_3-symmetric diastereomer of amine **20** (Figure 7) contains a doublet for the three homotopic methyl groups. But this time in the other diastereomer there are only two diastereotopic methyl groups present in a 2:1 ratio. Once again this is revealed in the ^{1}H NMR spectrum (Figure 8). The difference between the diastereotopic characteristics of

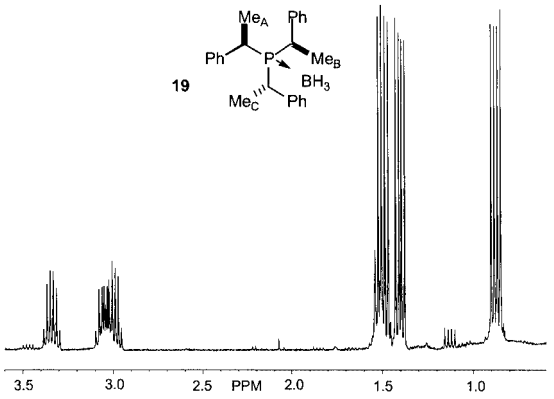


Figure 6. ^{1}H NMR spectrum of phosphane−borane **19**

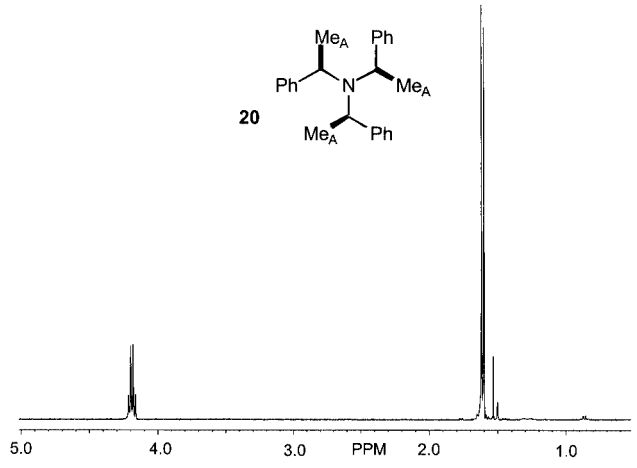


Figure 7. ^{1}H NMR spectrum of amine **20**

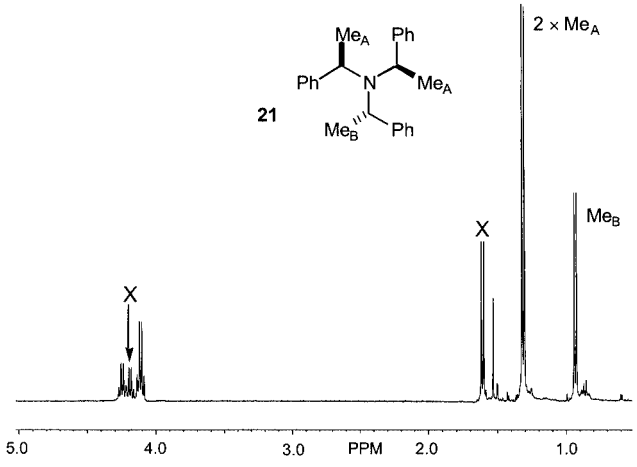


Figure 8. ^{1}H NMR spectrum of amine **21**; 'X' indicates signals from the amine **20**

the two molecules (amine **21** and phosphane−borane **19**) arises because the nitrogen centre inverts whereas the phosphorus centre does not. Working through a standard test for diastereotopicity[26] exposes pseudoasymmetric phosphorus atom (this is pseudoasymmetry of the kind encountered in molecules **10** and **11**)[27] upon replacement of the methyl groups (something that does not occur with nitrogen). Hence, the striking contrast in the NMR spectra.

Conclusion

The asymmetric synthesis of the interesting molecule **1** has proved challenging and the overall yield from α-methylbenzyl alcohol is approximately 1%. The asymmetric part of the synthesis depends upon (*R*)-α-methylbenzylamine as a resolving agent and the three α-methylbenzyl groups themselves are introduced by both nucleophilic and electrophilic methods. Although the free phosphane itself is very air sensitive and resisted our attempts to characterise it thoroughly, the formation of a metal complex can be achieved in situ once the phosphane is liberated from its borane complex. The NMR spectra of rhodium complexes with the phosphanes are included in the Supporting Information (see also footnote on the first page of this article). The application of these complexes is being investigated.

Experimental Section

General Experimental Details: All reactions, unless otherwise stated, were performed under nitrogen in glassware that had been dried overnight in an oven at 150 °C. Reactions were monitored by TLC using glass-backed silica gel F_{254} plates (Merck) and visualised using UV_{254nm} or by iodine adsorption as appropriate. Flash column chromatography[28] was carried out routinely using 60-Å silica gel (Fluorochem). Reagents were used without further purification from commercial sources unless otherwise stated. Petroleum ether refers to the fraction with 40−60 °C boiling point range.

NMR spectra were recorded with a Joel Delta/GX 270, 400, a Lambda 300 or an Eclipse 300 MHz spectrometer. Mass spectra were recorded with a VG analytical autospec mass spectrometer. IR spectra were recorded with a Perkin−Elmer 881 IR spectrometer in the solid state or as a liquid film. $[\alpha]_D$ Values were recorded with a Perkin−Elmer 241 MC polarimeter and are given in 10^{-1} deg·cm^2·g^{-1}.

Anhydrous solvents were obtained by passing HPLC grade solvents through a modified Grubbs system[29] manufactured by anhydrous engineering. De-oxygenated solvents were prepared by passing a stream of N_2 through the solvent of choice at room temperature via a fine capillary for 2 h prior to use.

HPLC measurements were made using Gilson 712 HPLC system controller software, a dynamic absorbance detector (model UV 1), dynamic mixer 811C, manomeric module 806, a Gilson 506C system interface module and Gilson pumps 305 and 303.

Preparation of Racemic Materials

(±)-1-Chloro-1-phenylethane: *sec*-Phenethyl alcohol (20.0 mL, 166 mmol) was dissolved in $CHCl_3$ (100 mL) in a dry three-necked round-bottomed flask and the solution stirred at room temperature. A solution of thionyl chloride (11.0 mL, 151 mmol) in $CHCl_3$ (30 mL) was added dropwise to the mixture over 2 h. The sulfur dioxide evolved was quenched by bubbling through a saturated $NaHCO_3$ solution. The mixture was then stirred overnight at room temperature. Saturated aqueous $NaHCO_3$ solution (150 mL) was added to the reaction mixture and the aqueous layer was extracted with $CHCl_3$ (3 × 100 mL). The organic phases were combined, dried ($MgSO_4$) and concentrated under reduced pressure yielding a crude yellow oil which was purified by distillation under reduced pressure to give the chloride (19.8 g, 85.0%) as a colourless oil (b.p.

95 °C/20 Torr; ref.[30] 29−32 °C/0.6 Torr). R_f(EtOAc/petroleum ether, 1:3) = 0.45. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.85 (d, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH_3), 5.09 (q, $^3J_{H,H}$ = 6.8 Hz, 1 H, CH) and 7.30−7.43 (m, 5 H, 5 × PhH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 26.2 (*C*CH_3), 59.0 (*C*Cl), 126.6 (2 × *o*-PhC), 128.3 (*p*-PhC), 128.7 (2 × *m*-PhC), 142.4 (*i*-PhC) ppm. EI MS: *m*/*z* (%) = 105 (100) [PhCHMe], 125 (8.8) [$M^{35}Cl$ − Me], 127 (2.8) [$M^{37}Cl$ − Me], 140 (15.4) [$M^{35}Cl$], 142 (5) [$M^{37}Cl$].

(*RS*,*RS*,*RS*)-Tris(α-methylbenzyl)phosphane Oxide (4): Freshly prepared (±)-1-phenethylmagnesium chloride[10] (80 mL of a 0.45 M solution in Et_2O, 36 mmol; the solution was titrated with *sec*-butyl alcohol and 1,10-phenanthroline[31]) was added dropwise to a vigorously stirred solution of phosphorus trichloride (0.79 mL, 9.0 mmol) in anhydrous Et_2O (10 mL). A white precipitate formed almost immediately on addition. Once addition was complete, the mixture was heated at reflux for 3 h, then cooled to room temperature and stirred overnight. The mixture was then filtered through a frit under N_2 resulting in a yellow solution. The solvent was quickly evaporated under reduced pressure to give a yellow oil. This oil was redissolved in CH_2Cl_2 (80 mL) and cold H_2O_2 (30%, 80 mL) was added. The biphase was stirred vigorously for 30 min at room temperature prior to the addition of NaOH (2 mL of an aqueous 2 M solution). The resulting mixture was stirred at room temperature for a further 4 h. Water (100 mL) was added and the organics were extracted into $CHCl_3$ (4 × 400 mL). The organic phases were combined, dried ($MgSO_4$) and the solvents evaporated under reduced pressure to give a partially solid crude yellow oil. This crude oil was purified by flash chromatography, eluting with 10% EtOAc/petroleum ether and graduating to 100% EtOAc, to yield a 1:1 mixture, and confirmed by the ^{1}H NMR spectrum of (*RS*,*RS*,*RS*)-tris(α-methylbenzyl)phosphane oxide (**4**) and (*RS*,*RS*,*SR*)-tris(α-methylbenzyl)phosphane oxide (**5**) (1.91 g, 58.5% combined). The two diastereoisomers **4** and **5** were separated by recrystallisation with EtOAc to yield (*RS*,*RS*,*RS*)-**4** as highly crystalline white needles. M.p. 126−128 °C (from EtOAc). R_f (EtOAc/petroleum ether, 1:1) = 0.17. IR (solid state): $\tilde{\nu}$ = 2933 (CH), 1602 (Ar), 1491 and 1450 (CH deformations), and 1153 (P=O) cm^{-1}. MS EI: *m*/*z* = 362 (15) [M^+], 258 (19) [M − $PhCHCH_3^+$], 153 (30) [$PhCHCH_3POH^+$], 105 (100) [$PhCHCH_3^+$]. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.29 (dd, $^3J_{P,H}$ = 14.7, $^3J_{H,H}$ = 7.5 Hz, 9 H, 3 × CH_3), 3.12 (dq, $^2J_{P,H}$ = 10.3, $^3J_{H,H}$ = 7.5 Hz, 3 H, 3 × CH), 7.18−7.27 (m, 15 H, PhH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 15.92 (d, $^2J_{C,P}$ = 3.8 Hz, CH_3), 38.9 ($^1J_{C,P}$ = 56.1 Hz, CH), 126.8 ($^5J_{C,P}$ = 5.4 Hz, *p*-PhC), 128.5 ($J_{C,P}$ = 2.3 Hz, *m*- or *o*-PhC), 128.7 ($J_{C,P}$ = 5.4 Hz, *m*- or *o*-PhC), 139.7 ($^2J_{C,P}$ = 4.6 Hz, *i*-PhC) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): δ = 50.75 ppm. $C_{24}H_{27}OP$ (362.5): calcd. C 79.53, H 7.51; found C 79.62, H 7.87. (*RS*,*RS*,*SR*)-Tris(α-methylbenzyl)phosphane oxide **5** was isolated as a colourless oil. R_f (EtOAc/petroleum ether, 1:1) = 0.23. IR (liquid film): $\tilde{\nu}$ = 2930 (CH), 1602 (Ar), 1492 (Ar) 1452 (CH deformations) and 1153 (P=O) cm^{-1}. MS EI: *m*/*z* = 362 (30) [M^+], 258 (33) [$(PhCHCH_3)_2P(O)H^+$], 153 (38) [$PhCHCH_3P(O)H^+$], 105 (100) [$PhCHCH_3^+$]. HRMS EI (M^+, $C_{24}H_{27}PO^+$): calcd. 362.179954; found 362.178879. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.04 [dd, $^3J_{P,H}$ = 14.7, $^3J_{H,H}$ = 7.3 Hz, 3 H, $(CH_3)_C$], 1.33 [dd, $^3J_{P,H}$ = 14.7, $^3J_{H,H}$ = 7.3 Hz, 3 H, $(CH_3)_B$], 1.36 [dd, $^3J_{P,H}$ = 14.2, $^3J_{H,H}$ = 7.3 Hz, 3 H, $(CH_3)_A$], 3.01 (dq, $^2J_{P,H}$ = 8.3, $^3J_{H,H}$ = 7.3 Hz, 1 H, CH_C), 3.10 (dq, $^2J_{P,H}$ = 10.7, $^3J_{H,H}$ = 7.3 Hz, 1 H, CH_B), 3.30 (dq, $^2J_{P,H}$ = 10.3, $^3J_{H,H}$ = 7.3 Hz, 1 H, CH_A), 7.12−7.35 (m, 15 H, PhH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.79 [$^2J_{C,P}$ = 1.5 Hz, $(CH_3)_C$], 16.10 [$^2J_{C,P}$ = 3.81 Hz, $(CH_3)_B$], 16.31 [$^2J_{C,P}$ = 3.8 Hz, $(CH_3)_A$], 38.16 ($^1J_{C,P}$ = 56.1 Hz, CH_C), 38.20 ($^1J_{C,P}$ = 53.8 Hz, CH_B), 38.77 ($^1J_{C,P}$ = 57.7 Hz, CH_A), 126.67−128.91 (several lines), 138.57 ($^2J_{P,C}$ = 4.6 Hz, *i*-PhC_C), 139.47 ($^2J_{P,C}$ = 4.9 Hz, *i*-PhC_B), 139.98 ($^2J_{P,C}$ = 4.6 Hz, *i*-PhC_A) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): δ = 51.28 ppm.

HPLC analysis of oxide **4** using a Chiracel OD column and eluting with *i*PrOH/heptane (1:99) at 1 mL·min^{-1} gave retention times of 28.3 min and 43.6 min for the two enantiomers.

Attempted Reduction of Phosphane Oxide 4:[14] Phosphane oxide (*RS*,*RS*,*RS*)-**4** (50 mg, 0.138 mmol) was dissolved in anhydrous THF and the solution was cooled to 0 °C. A solution of $LiAlH_4$ (0.152 mL of a 1.0 M solution in THF, 0.152 mmol) was added dropwise and the mixture was stirred at room temperature overnight. No reaction was evident by TLC analysis (EtOAc/petroleum ether, 1:1). Water (10 mL) was added to the organic phase followed by the addition of aqueous NaOH (5 mL, 20%). The organics were extracted into EtOAc (20 mL), dried ($MgSO_4$) and the solvents evaporated to dryness to give pure starting material **4** (50 mg, 100%). In other experiments using $HSiCl_3$ or AlH_3 as the reducing agents, starting material was also recovered.

Another reaction was conducted as above except the mixture was heated at reflux with $LiAlH_4$ for 2 h before being quenched by the addition of water (10 mL) and aqueous NaOH (10 mL of a 1.5 M aqueous solution). A 1:1 mixture of starting material plus another product was evident by TLC and ^{1}H NMR spectroscopy. The crude mixture was purified by flash chromatography, eluting with 50% EtOAc/petroleum ether and graduating to 100% EtOAc to yield the decomposition product (*RS*,*RS*)-bis(α-methylbenzyl)phosphane oxide (**6**, 34.2 mg, 48%) as a yellow oil. R_f(EtOAc, 100%) = 0.15. IR (liquid film): $\tilde{\nu}$ = 2968, 2930, 2873 (CH), 2308 (PH), 1605 (Ar), 1582 (Ar), 1492, 1451 (P−O) and 1165 (P=O) cm^{-1}. MS EI: *m*/*z* = 258 (15) [M^+], 274 (9.5) [M + O^+], 153 (5) [$PhCH(CH_3)POH^+$], and 105 (100) [$PhCHCH_3^+$]. HRMS EI [M^+, $C_{16}H_{19}PO^+$]: calcd. 258.117354; found 258.117004. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.54 [dd, $^3J_{P,H}$ = 15.6, $^3J_{H,H}$ = 7.3 Hz, 3 H, $(CH_3)_A$], 1.59 [dd, $^3J_{P,H}$ = 17.1, $^3J_{H,H}$ = 7.8 Hz, 3 H, $(CH_3)_B$], 2.79 (quin, $^2J_{P,H}$ = $^3J_{H,H}$ = 7.8 Hz, the other 3*J*H,H coupling constant = 0, 1 H, CH_B), 2.92 (dquin, $^2J_{P,H}$ = 14.2, $^3J_{H,H}$ = $^3J_{H,H}$ = 7.3 Hz, 1 H, CH_A), 6.79 ($^1J_{P,H}$ = 450, $^3J_{H,H}$ = 5.1 Hz, 1 H, P-H) 7.06−7.38 (m, 10 H, PhH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 15.43 [$^2J_{C,P}$ = 3.1 Hz, $(CH_3)_B$], 16.95 [$^2J_{C,P}$ = 2.3 Hz, $(CH_3)_A$], 37.81 ($^1J_{C,P}$ = 60.0 Hz, CH_B), 38.18 ($^1J_{C,P}$ = 60.0 Hz, CH_A), 127.43 ($^5J_{C,P}$ = 2.3 Hz, *p*-PhC_B), 127.52 ($^5J_{C,P}$ = 3.1 Hz, *p*-PhC_A), 128.44 (2 × *o*-PhC_B), 128.86 ($^3J_{C,P}$ = 1.5 Hz, 2 × *o*-PhC_A), 128.92 ($^4J_{C,P}$ = 2.3 Hz, 2 × *m*-PhC), 129.04 ($^4J_{C,P}$ = 2.3 Hz, 2 × *m*-PhC_A), 137.37 ($^2J_{C,P}$ = 5.4 Hz, *i*-PhC_B), 138.29 ($^2J_{C,P}$ = 3.8 Hz, *i*-PhC_A) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): δ = 50.43 ($^1J_{P,H}$ = 440 Hz) ppm. (*RS*,*RS*,*RS*)-**4** (45 mg, 45.0%) was also recovered.

(*RS*,*RS*,*RS*)-Tris(α-methylbenzyl)phosphane−Borane (7): Phosphorus trichloride (0.35 mL, 4.0 mmol) was suspended in anhydrous Et_2O (10 mL) in a three-necked flask equipped with a dropping funnel and reflux condenser and stirred vigorously. Freshly prepared (±)-1-phenethylmagnesium chloride (40 mL of a 0.50 M solution in Et_2O, 20 mmol) was added dropwise with vigorous stirring to the solution. A white precipitate formed immediately on addition of the Grignard. Once addition was complete, the solution was heated at reflux (45 °C) for 3 h and then stirred overnight at room temperature. The mixture was filtered through a frit under N_2 to give a pale yellow solution and was cooled to 0 °C. A solution of BH_3·THF (6 mL of a 1 M solution in THF, 6.0 mmol) was added dropwise to the vigorously stirred solution and the resulting mixture was stirred for a further 1 h at 0 °C. A white precipitate formed gradually which became yellow during this time. Cautiously the

solution was added dropwise to ice-cold aqueous HCl (50 mL of an aqueous 2 M solution) with vigorous stirring.[32] The organic layer was extracted with Et_2O (3 × 50 mL), dried ($MgSO_4$) and the solvents evaporated to dryness under reduced pressure yielding a partially solid yellow oil. This crude mixture was purified using flash chromatography, eluting with petroleum ether-EtOAc 20:1, to give a 3:4 mixture of (*RS*,*RS*,*RS*)-tris(α-methylbenzyl)phosphane−borane (**7**) and (*RS*,*RS*,*SR*)-tris(α-methylbenzyl)phosphane−borane (**19**; 750 mg, 52.1%) and confirmed by ^{1}H NMR spectroscopy. Recrystallisation with Et_2O/heptane gave pure (*RS*,*RS*,*RS*)-**7** as highly crystalline white needles. R_f(Et_2O/petroleum ether, 1:20) = 0.20. M.p. 162−164 °C (from Et_2O/heptane). IR (solid state): $\tilde{\nu}$ = 2924 and 2872 (C−H), 2385 (B−H), 1602 (Ar), 1491 and 1450 (CH deformations), 1377 (PB) cm^{-1}. MS EI: *m*/*z* (%) = 360 (14) [M], 346 (42) [M $-^{11}BH_3$], 241 (40) [$PhCHCH_3)_2P$], 105 (100) [$PhCHCH_3$]. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.30−0.90 (v br. q, 3 H, BH_3), 1.13 (dd, $^3J_{P,H}$ = 14.7, $^3J_{H,H}$ = 7.3 Hz, 9 H, 3 × CH_3), 2.99 (dq, $^2J_{P,H}$ = 13.7, $^3J_{H,H}$ = 6.8 Hz, 3 H, 3 × CH) 7.19−7.31 (m, 15 H, PhH) ppm. ^{11}B NMR (96 MHz, $CDCl_3$, ^{1}H decoupled, 25 °C): δ = −45.6 (dm, J_{PB} = 45.3 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 18.03 ($^2J_{C,P}$ = 2.3 Hz, 3 × CH_3), 36.15 ($^1J_{C,P}$ = 25.4 Hz, 3 × CH), 127.18 ($^5J_{C,P}$ = 2.3 Hz, *p*-PhC), 128.56 ($J_{C,P}$ = 1.54 Hz, *m*- or *o*-PhC), 128.99 ($J_{C,P}$ = 3.8 Hz, *m*- or *o*-PhC) 140.32 ($^2J_{C,P}$ = 3.9 Hz, *i*-PhC) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): δ = 41.0 (q, J_{PB} = 46 Hz) ppm. $C_{24}H_{30}BP$ (360.2): calcd. C 80.01, H 8.39; found C 79.88, H 8.59. (*RS*,*RS*,*SR*)-Tris(α-methylbenzyl)phosphane−borane (**19**) was isolated as a colourless oil; R_f(Et_2O/petroleum ether, 1:20) = 0.15. IR (liquid film): $\tilde{\nu}$ = 2974 and 2927, 2871 (CH), 2387 (B−H), 1601 (Ar), 1492 (Ar), 1450 (Ar), 1384 (PB) cm^{-1}. MS EI: *m*/*z* (%) = 346 (4) [M − BH_3], 241 (24) [$P(CHCH_3Ph)_2$], 105 (100) [$PhCHCH_3$]. HRMS EI [M^+, $C_{24}H_{30}BP^+$]: calcd. 360.217186; found 360.217820. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.30−0.75 (v br. q, 3 H, BH_3), 0.85 [dd, $^3J_{P,H}$ = 14.2, $^3J_{H,H}$ = 7.3 Hz, 3 H, $(CH_3)_C$], 1.40 [dd, $^3J_{P,H}$ = 12.7, $^3J_{H,H}$ = 7.3 Hz, 3 H, $(CH_3)_B$], 1.49 [dd, $^3J_{P,H}$ = 14.7, $^3J_{H,H}$ = 7.4 Hz, 3 H, $(CH_3)_A$], 3.00 (dq, $^2J_{P,H}$ = 14.2, $^3J_{H,H}$ = 7.4 Hz, 1 H, CH_C), 3.05 (dq, $^2J_{P,H}$ = 11.2, $^3J_{H,H}$ = 6.8 Hz, 1 H, CH_B), 3.34 (dq, $^2J_{P,H}$ = 13.7, $^3J_{H,H}$ = 7.3 Hz, 1 H, CH_A), 7.18−7.37 (m, 15 H, Ph-H) ppm. ^{11}B NMR (400 MHz, $CDCl_3$, ^{1}H decoupled, 25 °C): δ = −43.36 ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 15.82 [$(CH_3)_C$], 18.18 [$^2J_{C,P}$ = 2.3 Hz, $(CH_3)_B$], 18.76 [$(CH_3)_A$], 34.80 ($^1J_{C,P}$ = 23.8 Hz, CH_C), 35.38 ($^1J_{C,P}$ = 15.4 Hz, CH_B), 35.62 ($^1J_{C,P}$ = 14.6 Hz, CH_A), 126.98 ($^5J_{C,P}$ = 1.5 Hz, *p*-PhC_C), 127.05 ($^5J_{C,P}$ = 2.3 Hz, *p*-PhC_B), 127.38 ($^5J_{C,P}$ = 2.3 Hz, *p*-PhC_A), 128.10−129.18 (several lines), 139.20 ($^2J_{P,C}$ = 3.9 Hz, *i*-PhC_C), 139.93 ($^2J_{P,C}$ = 3.1 Hz, *i*-PhC_B) 140.70 ($^2J_{P,C}$ = 1.5 Hz,, *i*-PhC_A) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): δ = 41.95 (q, $^1J_{PB}$ = 49.9 Hz) ppm.

(*RS*,*RS*,*RS*)-Tris(α-methylbenzyl)phosphane (1): (*RS*,*RS*,*RS*)-Tris-(α-methylbenzyl)phosphane−borane (**7**, 50.0 mg, 0.139 mmol) was dissolved in freshly distilled anhydrous diethylamine (1 mL, 9.65 mmol) and heated at reflux (65 °C) under N_2 for 2 h.[16,33] The mixture was cooled to room temperature and de-oxygenated HCl (5 mL of an aqueous 2 M solution) was added cautiously, followed by de-oxygenated Et_2O (5 mL). The mixture was stirred vigorously for 5 min to ensure complete extraction of the organics and the aqueous layer was then decanted using a pipette. A portion of the organic phase (0.5 mL) was removed and oxidised by the addition of H_2O_2 (2 mL, 30%) and aqueous NaOH (0.1 mL of a 1.5 M aqueous solution). This mixture was shaken vigorously and analysed for the presence of (*RS*,*RS*,*RS*)-oxide **4** which was confirmed by NMR spectroscopy. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.29 (dd, $^3J_{P,H}$ = 14.7, $^3J_{H,H}$ = 7.5 Hz, 9 H, 3 × CH_3), 3.12 (dq, $^2J_{P,H}$ = 10.3, $^3J_{H,H}$ = 7.5 Hz, 3 H, 3 × CH), 7.18−7.27 (m, 15 H, PhH) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): δ = 50.75 ppm. The solvent was removed under vacuum via the manifold to give (*RS*,*RS*,*RS*)-tris(α-methylbenzyl)phosphane (**1**) as a white solid that was stored and analysed under N_2; R_f(Et_2O/petroleum ether, 1:9) = 0.43. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.22 (dd, $^3J_{P,H}$ = 11.5, $^3J_{H,H}$ = 7.3 Hz, 9 H, 3 × CH_3), 2.95 (dq, $^3J_{H,H}$ = 7.1, $^2J_{P,H}$ = 3.9 Hz, 3 H, 3 × CH) 7.25 (m, 15 H, PhH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 19.10 ($^2J_{P,C}$ = 14.9 Hz, 3 × CH_3), 35.76 ($^1J_{P,C}$ = 22.4 Hz, 3 × CH), 125.6 ($J_{P,C}$ = 2.3 Hz, *p*-ArC), 127.9 ($J_{P,C}$ = 6.2 Hz, *o*-ArC), 128.2 (*m*-ArC), 144.5 ($J_{P,C}$ = 6.9 Hz, *p*-ArC) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): δ = 32.76 ppm. The instability of phosphane **1** in air prevented further characterisation.

Reactions Towards Asymmetric Materials

Synthesis of Phosphinamide Diastereomers; (*R*)-(*anti*,*anti*)-*N*-α-Methylbenzylbis(α-methylbenzyl)phosphinic Amide (8), (*R*)-(*anti*,-*syn*)-*N*-α-Methylbenzylbis(α-methylbenzyl)phosphinic Amide (9), (*R*)-(*syn*-*s*-*syn*)-*N*-α-Methylbenzylbis(α-methylbenzyl)phosphinic Amide (10) and (*R*)-(*syn*-*r*-*anti*)-*N*-α-Methylbenzylbis(α-methylbenzyl)phosphinic Amide (11): Phosphorus trichloride (1.71 mL, 19.6 mmol) was transferred via syringe to a dry three-necked flask and dissolved in anhydrous Et_2O (30 mL). The solution was stirred vigorously at room temperature. (±)-1-Phenethylmagnesium chloride (81.5 mL of a 0.60 M solution in Et_2O, 48.9 mmol) was added dropwise to the ethereal solution resulting in the immediate formation of a white precipitate. Once addition was complete the solution was heated at reflux for 1 h, cooled to room temperature and filtered through a frit into a dry 3-necked flask to give a pale yellow solution. Anhydrous triethylamine (3.28 mL, 23.5 mmol) and anhydrous (*R*)-α-methylbenzylamine (99.6% *ee*), (2.62 mL, 20.6 mmol) were dissolved in anhydrous Et_2O (25 mL) and the mixture was added dropwise to the pale yellow solution at room temperature resulting in the gradual formation of a white precipitate. The solution was stirred overnight, filtered and concentrated under reduced pressure to give a yellow oil. The oil was dissolved in CH_2Cl_2 (100 mL). Cold hydrogen peroxide (100 mL, 30%) was added and the biphase was stirred vigorously for 30 min. Aqueous sodium hydroxide (1.8 mL of a 3 M solution) was added and the solution stirred vigorously for a further 4 h at room temperature. Water (100 mL) was added and the aqueous layer was extracted with CH_2Cl_2 (3 × 100 mL). The organics were combined, dried ($MgSO_4$) and concentrated under reduced pressure to yield a crude mixture of the four diastereoisomers **8−11** (4.65 g, 62.9%) as a yellow-white solid. The crude solid was purified by flash chromatography eluting with petroleum ether/EtOAc (1:1) to remove baseline material. [Crude material gave four signals; ^{31}P{^{1}H} NMR (123 MHz, $CDCl_3$, 25 °C): δ = 45.25, 44.66, 44.60, 43.99 ppm with an integral ratio of 9:1:17:11.5 for **8/11/10/9**]. Flash column chromatography eluting with 50% EtOAc/petroleum ether and graduating to 100% EtOAc yielded the major isomer, pure (*R*)-(*syn*-*s*-*syn*)-**10** (250 mg isolated as pure material) as a white solid. M.p. 147−149 °C (from EtOAc/petroleum ether), (ref.[20] 147.5−148 °C from EtOAc/hexane). R_f (EtOAc, 100%) = 0.18. IR (solid state): $\tilde{\nu}$ = 3255 (NH), 2990 (CH_3), 2972 (CH_3), 2930 (CH), 1599 (Ar), 1208 (P=O) cm^{-1}. MS EI: *m*/*z* (%) = 377 (7) [M], 272 (38) [M − $CH(CH_3)Ph$], 168 (48), 120 (10) [$PhCH(CH_3)NH$] and 105 (100) [$PhCH(CH_3)$]. ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C): δ = 0.96 [d, $^3J_{H,H}$ = 6.9 Hz, 3 H, $NHCH(CH_3)Ph$], 1.40 [dd, $^3J_{P,H}$ = 15.5, $^3J_{H,H}$ = 7.6 Hz, 3 H, $PCH(CH_3)_BPh$], 1.63 [dd, $^3J_{P,H}$ = 15.8, $^3J_{H,H}$ = 7.3 Hz, 3 H, $PCH(CH_3)_APh$], 1.80 (br. t, $^3J_{H,H}$ = 9.6 Hz,

1 H, NH), 2.96 [dq, $^2J_{P,H}$ = 10.5, $^3J_{H,H}$ = 7.3 Hz, 1 H, PCH_B(CH$_3$)Ph], 3.15 [dq, $^2J_{P,H}$ = 12.9, $^3J_{H,H}$ = 7.3, 1 H, PCH_A(CH$_3$)Ph], 4.25 [dq, $^2J_{P,H}$ = 15.0, $^3J_{H,H}$ = 6.9 Hz, 1 H, NHCH(CH$_3$)Ph], 7.02 (m, 2 H, PhH), 7.24 (m, 13 H, PhH) ppm. ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 14.78 [PCH(*C*H$_3$)$_B$Ph], 15.29 [PCH(*C*H$_3$)$_A$Ph], 25.77 [NHCH(*C*H$_3$)Ph], 38.80 [$^1J_{C,P}$ = 76.4 Hz, P*C*H$_B$(CH$_3$)Ph], 39.84 [$^1J_{C,P}$ = 77.4 Hz, P*C*H$_A$(CH$_3$)Ph], 49.88 [NH*C*H(CH$_3$)Ph], 125.84, 126.76, 126.87, 127.06, 128.22, 128.35, 128.47, 128.60, 128.64, 129.12, 139.39, 139.45, 139.50, 145.85 ppm. ^{31}P{^{1}H} NMR (122 MHz, CDCl$_3$, 25 °C): δ = 44.6 ppm. Fractional recrystallisation with EtOAc yielded pure (*R*)-(*anti*,*syn*)-**9** (600 mg) as a white solid. M.p. 210−212 °C (from EtOAc), (ref.[20] 202−205 °C from EtOAC/hexane). R_f(EtOAc, 100%) = 0.32. IR (solid state): ṽ = 3265 (NH), 3027 (CH$_3$), 2966 (CH$_3$), 2928 (CH), 2871 (CH), 1602 (Ar) and 1170 (P=O) cm^{-1}. MS CI: *m*/*z* (%) = 378 (50) [M + H], 272 (7) [M − PhCHMe], 120 (14) [PhCHMeNH], 105 (100) [PhCHMe]. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 1.25 [d, $^3J_{H,H}$ = 6.8 Hz, 3 H, NHCH(C*H*$_3$)Ph], 1.33 [dd, $^3J_{P,H}$ = 15.6, $^3J_{H,H}$ = 7.3 Hz, 3 H, PCH(C*H*$_3$)$_B$Ph], 1.49 [dd, $^3J_{P,H}$ = 15.2, $^3J_{H,H}$ = 7.3 Hz, 3 H, PCH(C*H*$_3$)$_A$Ph], 1.99 [br. t, $^3J_{H,H}$ = 10.35 Hz, 1 H, N*H*CH(CH$_3$)Ph], 2.86 [dq, $^2J_{P,H}$ = 12.7, $^3J_{H,H}$ = 7.8 Hz, 1 H, PCH_B(CH$_3$)Ph], 2.99 [dq, $^2J_{P,H}$ = 11.2, $^3J_{H,H}$ = 7.3 Hz, 1 H, PCH_A(CH$_3$)Ph], 4.42 [dq, $^2J_{P,H}$ = 16.4, $^3J_{H,H}$ = 7.1 Hz, 1 H, NHCH(CH$_3$)Ph], 7.16−7.34 (m, 15 H, 15 × PhH) ppm. ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 15.1 [PCH(*C*H$_3$)Ph], 16.0 [PCH(*C*H$_3$)Ph], 26.4 [NHCH(*C*H$_3$)Ph], 39.1 [$^1J_{C,P}$ = 78.8 Hz, P*C*H$_B$(CH$_3$)Ph], 41.0 [$^1J_{C,P}$ = 83.0 Hz, P*C*H$_A$(CH$_3$)Ph], 49.76 [NH*C*H(CH$_3$)Ph], 126.8, 126.9, 127.1, 128.5, 128.7 ($J_{C,P}$ = 6.3 Hz), 129 ($J_{C,P}$ = 7.4 Hz), 139.4 ($J_{C,P}$ = 4.2 Hz), 139.5 ($J_{C,P}$ = 6.3 Hz), 145.8 ($J_{C,P}$ = 5.3 Hz) ppm. ^{31}P{^{1}H} NMR (123 MHz, CDCl$_3$, 25 °C): δ = 44.0 ppm.[20] The third most abundant isomer (*R*)-(*anti*,*anti*)-**8** was successfully recrystallised from mixed column fractions of the crude mixture, using EtOAc/petroleum ether and isolated as a white solid. M.p. 161−163 °C (from EtOAc/petroleum ether) (ref.[20] 161−162 °C). R_f (EtOAc) = 0.24. IR (solid state): ṽ = 2978 (CH) 2933 (CH), 1492, 1451 and 1601 (Ar), 1169 (P=O) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 1.17 [dd, $^3J_{P,H}$ = 15.6, $^3J_{H,H}$ = 7.3 Hz, 3 H, PCH(C*H*$_3$)$_B$Ph], 1.35 [d, $^3J_{H,H}$ = 6.8 Hz, 3 H, NHCH(C*H*$_3$)Ph], 1.49 [dd, $^3J_{P,H}$ = 15.6, $^3J_{H,H}$ = 7.8 Hz, 3 H, PCH(C*H*$_3$)$_A$Ph], 2.07 [br. t, $^3J_{H,H}$ = 8.8 Hz, 1 H, N*H*CH(CH$_3$)Ph], 2.78 [dq, $^2J_{P,H}$ = 11.2, $^3J_{H,H}$ = 7.3 Hz, 1 H, PCH_B(CH$_3$)Ph], 2.92 [dq, $^2J_{P,H}$ = 12.2, $^3J_{H,H}$ = 7.8 Hz, 1 H, PCH_A(CH$_3$)Ph], 4.43 [br. dq, $^3J_{P,H}$ = 9.8, $^3J_{H,H}$ = 6.8 Hz, 1 H, NHCH(CH$_3$)Ph], 6.90 (m, 2 H, PhH), 7.30 (m, 13 H, PhH) ppm. ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 15.04 [$^3J_{C,P}$ = 4 Hz, PCH(*C*H$_3$)$_B$Ph], 16.20 [$^3J_{C,P}$ = 4 Hz, PCH(*C*H$_3$)$_A$Ph], 25.95 [NHCH(*C*H$_3$)Ph], 39.60 [$^2J_{C,P}$ = 57 Hz, P*C*H$_B$(CH$_3$)Ph], 40.10 [$^2J_{C,P}$ = 64 Hz, P*C*H$_A$(CH$_3$)Ph], 50.09 [NH*C*H(CH$_3$)Ph], 125.89, 126.08, 126.76, 126.92, 127.06, 128.42, 128.44, 128.53, 128.62, 128.76, 128.81, 129.16, 129.22, 139.5, 139.6, 145.9 ppm. ^{31}P{^{1}H} NMR (CDCl$_3$; 121 MHz; 25 °C): δ = 45.19 ppm.

(*S*,*S*)-Bis(α-methylbenzyl)phosphinic Acid (13):[20] (*R*)-(*anti*,*syn*)-*N*-α-Methylbenzylbis(α-methylbenzyl)phosphinic amide (**9**; 100 mg, 0.265 mmol) was suspended in HCl (10 mL, of a 2 M solution in 35% dioxane/water) and the mixture was heated at reflux for 2 days. The reaction mixture was allowed to cool to room temperature and then water (10 mL) was added. The organics were then extracted into CH_2Cl_2 (3 × 50 mL) and the solvents evaporated under reduced pressure to give a yellow oil. The crude product was washed with cold (0 °C) pentane (2 mL) and the resulting white solid (51.6 mg, 71.0%) was filtered and dried under vacuum to give the pure acid **13**. IR (solid state): ṽ = 2978 (CH), 1492 (Ar), 1451 (Ar) and 1147 (P=O) cm^{-1}. MS EI: *m*/*z* (%) = 274 (8.5) [M], 105 (100) [PhCHCH$_3$].[20] ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 1.44 (dd, $^3J_{P,H}$ = 15.6, $^3J_{H,H}$ = 7.3 Hz, 6 H, 2 × CH$_3$), 2.80 (dq, $^2J_{P,H}$ = 12.7, $^3J_{H,H}$ = 6.8 Hz, 2 H, 2 × PCH), 7.16 (m, 4 H, PhH), 7.27 (m, 6 H, PhH), 13.30 (POO*H*) ppm. ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$, 25 °C): δ = 58.46 ppm.

(*S*,*S*)-Bis(α-methylbenzyl)phosphinic Chloride (12):[20] (*S*,*S*)-Bis(α-methylbenzyl)phosphinic acid (**13**; 50.0 mg, 0.183 mmol) was dissolved in a 1:1 mixture of thionyl chloride and dichloromethane (4 mL). The reagents were heated at reflux for 3 h. The reaction was cooled and the excess thionyl chloride and CH_2Cl_2 were removed under reduced pressure. Residual solvents and water were removed as an azeotrope with toluene (2 × 10 mL) to give the product **12** (45.7 mg, 85.6%) as a yellow oil. R_f(Et$_2$O/petroleum ether, 1:1) = 0.50. B.p. 240 °C/0.5 Torr.[20] ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 1.59 [dd, $^3J_{P,H}$ = 18.6, $^3J_{H,H}$ = 7.3 Hz, 3 H, PCH(C*H*$_3$)$_B$], 1.66 [dd, $^3J_{P,H}$ = 18.6, $^3J_{H,H}$ = 7.4 Hz, 3 H, PCH(C*H*$_3$)$_A$], 3.12 (dq, $^2J_{P,H}$ = 8.8, $^3J_{H,H}$ = 7.3 Hz, 1 H, PCH_B), 3.30 (dq, $^2J_{P,H}$ = 10.3, $^3J_{H,H}$ = 7.4 Hz, 1 H, PCH_A), 7.09 (m, 2 H, 2 × PhH), 7.27−7.35 (m, 8 H, 8 × PhH) ppm.[20] ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 136.9, 136.5, 129.32, 129.23, 129.17, 128.93, 128.5, 127.91, 127.77, 44.26 ($^1J_{C,P}$ = 66.1 Hz, PCH$_A$), 44.73 ($^1J_{C,P}$ = 67.7 Hz, PCH$_B$), 16.88 [$^2J_{C,P}$ = 5.4 Hz, (CH$_3$)$_B$], 15.37 [$^2J_{C,P}$ = 3.8 Hz, (CH$_3$)$_A$] ppm. ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$, 25 °C): δ = 76.11 ppm.

Methyl (*S*,*S*)-Bis(α-methylbenzyl)phosphinate (14): Anhydrous triethylamine (0.024 mL, 0.171 mmol) was added to a stirred solution of (*S*,*S*)-**13** (50 mg, 0.171 mmol) in anhydrous methanol (5 mL). The reaction was stirred vigorously and heated at reflux for 2 h. Water (10 mL) was added and the organics were extracted into CH_2Cl_2 (2 × 20 mL), dried and the solvents evaporated to dryness under reduced pressure to give a crude yellow oil. The crude mixture was purified by quick flash chromatography, eluting with 10% EtOAc/petroleum ether and graduating to 70% EtOAc/petroleum ether to give (*S*,*S*)-methylbis(α-methylbenzyl)phosphinate (**14**) (39.0 mg, 79.2%) as a yellow oil. R_f(EtOAc/petroleum ether, 1:1) = 0.26. IR (liquid film): ṽ = 3061 and 2877 (CH), 1255 (P=O), 1022 (P−O), 799 and 764 (Ph) cm^{-1}. MS EI: *m*/*z* (%) = 288 (3) [M$^+$], 105 (100) [PhCHCH$_3$]. HRMS EI [M$^+$, $C_{17}H_{21}PO_2^+$]: calcd. 288.127919; found 288.127777. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 1.39 [dd, $^3J_{P,H}$ = 16.1, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH(C*H*$_3$)$_B$], 1.50 [dd, $^3J_{P,H}$ = 15.6, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH(C*H*$_3$)$_A$], 2.95 (m, 2 H, 2 × CH), 3.57 (d, $^2J_{P,H}$ = 9.8 Hz, 3 H, OC*H*$_3$), 7.13−7.31 (m, 10 H, PhH) ppm. ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 16.23 [$^2J_{C,P}$ = 3.1 Hz, (CH$_3$)$_B$], 16.25 [$^2J_{C,P}$ = 2.3 Hz, (CH$_3$)$_A$], 41.18 ($^1J_{C,P}$ = 41.2 Hz, CH$_B$), 41.60 ($^1J_{C,P}$ = 43.2 Hz, CH$_A$), 127.15 (*p*-PhC$_B$), 127.49 (*p*-PhC$_A$), 128.47 (2 × *o*-PhC$_B$), 128.88 (2 × *o*-PhC$_A$), 128.95 ($^4J_{C,P}$ = 3.1 Hz, 1 × *m*-PhC$_B$), 128.98 ($^4J_{C,P}$ = 3.1 Hz, 1 × *m*-PhC$_B$), 129.17 ($^4J_{C,P}$ = 3.1 Hz, 1 × *m*-PhC$_A$), 129.20 ($^4J_{C,P}$ = 3.1 Hz, 1 × *m*-PhC$_A$), 138.21 (*i*-PhC$_B$), 138.64 (*i*-PhC$_A$) ppm. ^{31}P NMR (121 MHz, CDCl$_3$, 25 °C): δ = 52.58 ppm.

Diphenylphosphinic Acid:[34] Chlorodiphenylphosphane (1.23 g, 5.52 mmol) was added to water (10 mL) at room temperature with vigorous stirring. Crushed sodium hydroxide pellets (468 mg, 11.7 mmol) were added at a rate that maintained the temperature of the reaction below 50 °C. Immediately after the addition was complete, aqueous hydrogen peroxide solution (0.70 mL, 30%) was added and the mixture was stirred at 50 °C for 1 h. The mixture was allowed to cool to room temperature and HCl (5 mL of a 2 M aqueous solution) was added. The resulting white solid was filtered. The crude white solid was recrystallised from hot ethanol to give pure diphenylphosphinic acid (1.03 g, 85.0%). MS EI: *m*/*z* (%) =

218 (9) [M], 217 (23) [M − H], 77 (100) [Ph]. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.26−7.75 (m, 10 H, ArH) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 33.78 ppm.[35]

Diphenylphosphinoyl Chloride:[36] Diphenylphosphinic acid (100 mg, 0.458 mmol) was suspended in toluene (2 mL) and thionyl chloride (0.067 mL, 0.916 mmol) was added. The mixture was heated at reflux for 2 h, cooled to room temperature and the solvent was removed under reduced pressure. Excess thionyl chloride was removed as an azeotrope with fresh toluene (2 × 2 mL) to yield diphenylphosphinoyl chloride (108.3 mg, 100%) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.50−7.62 (m, 6 H, 6 × PhH), 7.91−7.85 (m, 4 H, 4 × PhH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 128.85 ($^3J_{P,C}$ = 14.6 Hz, *m*-PhC), 131.14 ($^2J_{P,C}$ = 12.3 Hz, *o*-PhC), 133.13 ($^4J_{P,C}$ = 3.1 Hz, *p*-PhC) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$; 25 °C): δ = 45.17 ppm.

Diphenylphosphane−Borane (17). Method 1:[17] Chlorodiphenylphosphane (1.00 mL, 5.57 mmol) was suspended in anhydrous Et_2O (20 mL) and the solution was cooled to 0 °C. The complex BH_3·THF (6.13 mL of a 1.0 M in THF, 6.13 mmol) was added followed by $LiAlH_4$ (6.13 mL of a 1.0 M solution in THF, 6.13 mmol) and the mixture was stirred at 0 °C for 2 h. The solution was quenched by addition to ice-cold aqueous HCl (25 mL of an aqueous 2 M solution) and the organic phase was separated. The aqueous layer was extracted with Et_2O (3 × 50 mL), the organic phases were combined, dried ($MgSO_4$) and the solvents evaporated to dryness yielding a crude white solid. The solid was purified by flash chromatography, eluting with 5% EtOAc/petroleum ether to give the phosphane−borane **17** (0.85 g, 76.3%) as a colourless oil. R_f(EtOAc/petroleum ether, 1:9) = 0.18. MS EI: *m*/*z* (%) = 186 (93) [M − BH_3], 108 (100) [PhP]. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.70−1.40 (br. q, $^1J_{B,H}$ = 84 Hz, 3 H BH_3), 6.31 (dq, $^1J_{P,H}$ = 378.6, $^3J_{H,H}$ = 6.8 Hz, 1 H, P*H*) and 7.44−7.70 (m, 10 H, PhH) ppm.[17] ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$, 25 °C): δ = −41.3 (br. d, $^1J_{P,B}$ = 57 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 126.4 ($^1J_{C,P}$ = 55.2 Hz, *i*-PhC), 129.13 ($^2J_{C,P}$ = 9.9 Hz, 2 × *o*-PhC), 129.20 (*p*-PhC), 133.05 ($^3J_{CP}$ = 9.2 Hz, 2 × *m*-PhC) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): δ = 2.02 (br. q, $^1J_{P,B}$ = 52 Hz) ppm.

Diphenylphosphane−Borane (17). Method 2: In a variation of the above method, diphenylphosphinoyl chloride (108.3 mg, 0.458 mmol) was dissolved in anhydrous Et_2O (5 mL) and the solution was cooled to 0 °C. $LiAlH_4$ (0.450 mL of a 1 M solution in THF, 0.450 mmol) was added slowly and the mixture was heated at reflux for 1 h,[15] cooled to room temperature, then 0 °C and the complex BH_3·THF (0.504 mL of a 1.0 M solution in THF, 0.504 mmol) was added. The mixture was stirred at room temperature for 1 h and was then quenched by addition to ice-cold aqueous HCl (10 mL of an aqueous 2 M solution). The organic phase was separated and the aqueous phase was extracted with Et_2O (3 × 25 mL). The organic phases were combined, dried ($MgSO_4$) and the solvents evaporated to dryness under reduced pressure yielding a crude white oil. This oil was purified by flash chromatography, eluting with 2% EtOAc/petroleum ether and graduating to 5% EtOAc/petroleum ether to give pure diphenylphosphane−borane (**17**) (50 mg, 54%) as a colourless oil; R_f(EtOAc/petroleum ether, 1:9) = 0.18; data as above.

(*S*,*S*)-Bis(α-methylbenzyl)phosphane−Borane (15): (*S*,*S*)-Bis(α-methylbenzyl)phosphinoyl chloride (**12**; 117 mg, 0.401 mmol) was dissolved in anhydrous Et_2O (5 mL) in a dry 3-neck round bottomed flask. The solution was cooled to 0 °C and stirred vigorously. $LiAlH_4$ (0.401 mL of a 1.0 M in THF, 0.401 mmol) was added dropwise to the solution and once addition was complete, the ice bath was removed. The mixture was then heated at reflux for 1 h,[15] cooled to room temperature and BH_3·THF (0.441 mL of a 1.0 M solution in THF, 0.441 mmol) was added. The resulting mixture was stirred at room temperature overnight before being quenched by the dropwise addition of the solution to ice-cold aqueous HCl (10 mL of an aqueous 2 M solution). The organic phase was collected and the aqueous phase was further extracted with Et_2O (3 × 25 mL). The organic portions were combined, dried ($MgSO_4$) and the solvents evaporated to dryness yielding a crude white oil. The crude oil was purified by flash chromatography, eluting with 2% EtOAc/petroleum ether to give (*S*,*S*)-bis(α-methylbenzyl)phosphane−borane (**15**) as a white solid (53.0 mg, 51.4%). R_f(EtOAc/petroleum ether, 1:9) = 0.35. M.p. 101−103 °C from Et_2O/petroleum ether. IR (solid state): $\tilde{\nu}$ = 2970, 2931 (CH stretch), 2399, 2386 (BH), 1599, 1489 and 1450.9 (Ar), 1375 (PB) cm^{-1}. $[\alpha]_D^{25}$ = −160 (*c* = 1.03, CH_2Cl_2). MS EI: *m*/*z* = 256 (4.8) [M$^+$], 242 (12.8) [M − BH_3], 105 (100) [PhCHCH$_3$]. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.42−1.20 (br. q, $^1J_{B,H}$ = 80 Hz, 3 H, BH_3), 1.45 [dd, $^3J_{P,H}$ = 16.9, $^3J_{H,H}$ = 7.5 Hz, 3 H, $(CH_3)_B$], 1.55 [dd, $^3J_{P,H}$ = 16.3, $^3J_{H,H}$ = 7.5 Hz, 3 H, $(CH_3)_A$], 2.92 (d-quin, $^2J_{P,H}$ = 10.1, $^3J_{H,H}$ = $^3J_{H,H}$ = 7.4 Hz, 1 H, CH_B), 3.15 (d-q-d, $^2J_{P,H}$ = 14.7, $^3J_{H,H}$ = 7.1 Hz and $^3J_{H,H}$ = 3.3 Hz, 1 H, CH_A), 4.71 (d-quin-d, $^1J_{P,H}$ = 357.9, $^3J_{H,H}$ = $^3J_{H,H}$ = 6.8 Hz and 2.9 Hz, 1 H, PH) and 7.09−7.37 (m, 10 H, ArH) ppm. ^{11}B NMR (96 MHz, $CDCl_3$, ^{1}H decoupled, 25 °C): δ = −44.94 (br. d, $^1J_{P,B}$ = 51.2 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 17.77 [$^3J_{C,P}$ = 3.1 Hz, $(CH_3)_A$], 18.21 [$^3J_{C,P}$ = 1.5 Hz, $(CH_3)_B$], 32.67 ($^2J_{C,P}$ = 38.4 Hz, CH_B), 33.37 ($^2J_{C,P}$ = 40.0 Hz, CH_A), 127.36 ($^5J_{C,P}$ = 1.5 Hz, *p*-PhC_B), 127.49 ($^5J_{C,P}$ = 2.3 Hz, *p*-PhC_A), 127.78 ($J_{C,P}$ = 3.8 Hz, *o*- or *m*-PhC_B), 128.52 ($J_{C,P}$ = 5.4, *o*- or *m*-PhC_A), 128.61 (*o*- or *m*-PhC_B), 128.96 (*o*- or *m*-PhC_A), 140.78 (*i*-PhC_B), 140.85 (*i*-PhC_A) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): δ = 29.8 (br. q, $^1J_{P,B}$ = 51.2 Hz) ppm. $C_{16}H_{22}BP$ (256): calcd. C 75.3, H 8.3; found C 75.3, H 8.6.

Investigating the Addition of the Third α-Methylbenzyl Unit onto the Phosphorus Centre

Diphenylmethylphosphane−Borane:[17,37] Diphenylphosphane−borane (100 mg, 0.50 mmol) and methyl iodide (0.030 mL, 0.55 mmol) were dissolved in methanol (10 mL) and the solution was stirred at 0 °C. A solution of potassium hydroxide (0.55 mL of a 1 M solution in MeOH, 0.55 mmol) was added and the mixture was stirred at 0 °C for 1 h followed by 1 h at room temperature. The reaction mixture was slowly added to ice-cold aqueous HCl (50 mL of an aqeuous 2 M solution) and the organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 50 mL), the organic phases were combined, dried ($MgSO_4$) and the solvents evaporated to dryness yielding a crude yellow oil. The oil was purified by flash chromatography, eluting with 5% EtOAc/petroleum ether and graduating to 10% EtOAc/petroleum ether to give diphenylmethylphosphane−borane[37] (69 mg, 64.5%) as a white solid. R_f(EtOAc/petroleum ether, 1:9) = 0.19. MS EI: *m*/*z* (%) = 215 (25) [M + H], 200 (100) [MH − BH_3]. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.48−1.48 (br. q, $^1J_{B,H}$ = 88.8 Hz, 3 H, BH_3), 1.86 (d, $^2J_{P,H}$ = 10.1 Hz, 3 H, PCH_3), 7.50 (m, 10 H, ArH) ppm. ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$, 25 °C): δ = −39.29 ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 12.0 ($^1J_{C,P}$ = 41.2 Hz, PCH_3), 128.85 ($^3J_{P,C}$ = 14.6 Hz, *m*-PhC), 130.65 ($^1J_{P,C}$ = 56.9 Hz, *i*-PhC), 131.17 ($^4J_{P,C}$ = 3.1 Hz, *p*-PhC), 131.81 ($^2J_{P,C}$ = 10.0 Hz, *o*-PhC) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): δ = 10.69 (br. q, $^1J_{PB}$ = 56.6 Hz) ppm.

(±)-1-Iodo-1-phenylethane: *sec*-Phenethyl alcohol (10.0 mL, 82.9 mmol) was suspended in anhydrous dioxane (150 mL) and the solution was vigorously stirred. Freshly distilled borontrifuoride-diethyl etherate (10.5 mL, 82.9 mmol) was added to the solution followed by potassium iodide (41.3 g, 248 mmol) and the mixture was stirred at 25 °C for 3 h. The mixture was then added to ice cold water (100 mL) and the organics were extracted into Et_2O (3 × 250 mL). The organic phases were combined, dried ($MgSO_4$) and the solvents evaporated to dryness to yield a crude brown oil. This oil was immediately purified by flash chromatography, eluting with 1% EtOAc/petroleum ether and graduating to 2% EtOAc/petroleum ether. The resulting oil was washed with a solution of sodium thiosulfate to remove iodine residues, giving the iodide (11.4 g, 59.2%) as a pale yellow oil. R_f(EtOAc/petroleum ether, 1:9) = 0.78. MS EI: *m*/*z* (%) = 105 (100) [M − I]. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.22 (d, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH_3), 5.41 (q, $^3J_{H,H}$ = 7.4 Hz, 1 H, CH; by contrast, the methyl and benzylic signals are reported at 2.68 and 4.8 ppm in ref. 24.) and 7.22−7.46 (m, 5 H, ArH) ppm.[24] ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 20.02 (CH_3), 26.15 (CH), 126.61 (2 × *o*-PhC), 127.99 (*p*-PhC), 128.75 (2 × *m*-PhC), 145.44 (*i*-PhC) ppm.

(α-Methylbenzyl)diphenylphosphane−Borane (18): Diphenylphosphane−borane (100 mg, 0.50 mmol) was dissolved in anhydrous THF (5 mL) and the solution was cooled to −78 °C. *n*BuLi (0.21 mL of a 2.5 M solution in hexanes, 0.525 mmol) was added dropwise and the solution was stirred at −78 °C for 10 min. The solution was allowed to warm to room temperature before the addition of 1-iodo-1-phenylethane (0.13 mL, 0.55 mmol). The mixture was subsequently heated at reflux for 1 h. After cooling to room temperature, the reaction was quenched by addition to ice-cold aqueous HCl (10 mL, 2 M). The organic phase was separated and the aqueous phase was extracted with Et_2O (2 × 25 mL). The organic phases were combined, dried ($MgSO_4$) and the solvents evaporated to dryness yielding a crude yellow oil. This oil was purified by flash chromatography, eluting with 2% EtOAc/petroleum ether and graduating to 5% EtOAc/petroleum ether, giving diphenyl-(α-methylbenzyl)phosphane−borane (**18**) (77 mg, 51%) as a colourless oil. R_f(EtOAc/petroleum ether, 1:9) = 0.19. IR (solid state): $\tilde{\nu}$ = 2973, 2931, 3058, (CH), 2377 (BH stretch), 1436 (BP stretch) 733, 773, 680 (ArH) cm^{-1}. MS EI: *m*/*z* (%) = 290 (75) [M $-{}^{11}BH_3$], 186 (51) [M − $PhCHCH_3BH_3$], 291 (24) [M $-{}^{10}BH_3$], 105 (100) [$PhCHCH_3$]. HRMS EI [M^+, $C_{20}H_{22}BP^+$]: calcd. 290.122439; found 290.122177. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.61−1.82 (br. q, $^1J_{B,H}$ = 76 Hz, 3 H, BH_3), 1.58 (dd, $^3J_{P,H}$ = 16.6, $^3J_{H,H}$ = 7.3 Hz, 3 H, C*H*$_3$CH), 3.81 (dq, $^2J_{P,H}$ = 14.7, $^3J_{H,H}$ = 7.4 Hz, 1 H, CH_3C*H*) and 7.07−7.90 (m, 15 H, ArH) ppm. ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$; 25 °C): δ = −42.62 (br. d, $^1J_{P,B}$ = 53 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 16.41 (CH*C*H_3), 37.52 ($^2J_{C,P}$ = 30.3 Hz, *C*HCH$_3$), 127.12 ($^5J_{C,P}$ = 2.3 Hz, *p*-PhC_{Bn}), 127.89 ($J_{C,P}$ = 2.3, *o*- or *m*-PhC_{Bn}), 128.15 ($^3J_{C,P}$ = 10.0 Hz, *m*-Ph$_A$C), 128.82 ($^3J_{C,P}$ = 10.0 Hz, *m*-Ph$_B$C), 129.32 ($J_{C,P}$ = 4.6 Hz, *o* or *m*-PC_{Bn}), 129.70 ($^1J_{C,P}$ = 58.0 Hz, *i*-Ph$_B$C), 130.20 ($^1J_{C,P}$ = 50.0 Hz, *i*-Ph$_A$C), 130.81 ($^4J_{C,P}$ = 2.3 Hz, *p*-Ph$_B$C), 131.36 ($^4J_{C,P}$ = 2.3 Hz, *p*-Ph$_A$C), 132.87 ($^2J_{C,P}$ = 8.5 Hz, *o*-Ph$_B$C), 133.10 ($^2J_{C,P}$ = 8.5 Hz, *o*-Ph$_A$C), 137.9 (*i*-PhC_{Bn}) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): δ = 26.24 (br. q, $^1J_{B,P}$ = 53 Hz) ppm. Another reaction involving KOH in methanol and 1-chloro-1-phenylethane was attempted and found to be unsuccessful.

(*S*,*S*,*S*)-Tris(α-methylbenzyl)phosphane−Borane (7): (*S*,*S*)-Bis(α-methylbenzyl)phosphane−borane (**7**) (45.0 mg, 0.177 mmol) was dissolved in anhydrous THF (5 mL) and the solution was cooled to −78 °C. *n*BuLi (0.074 mL of a 2.5 M solution in hexanes, 0.185 mmol) was added dropwise and the solution was stirred at −78 °C for 10 min. The dry ice-acetone bath was removed and the solution was allowed to warm to room temperature before 1-iodo-1-phenylethane (61.7 mg, 0.266 mmol) was added dropwise. Once addition was complete, the reaction mixture was heated at reflux for 1 h. The mixture was allowed to cool to room temperature and was then quenched by the dropwise addition of it to ice-cold aqueous HCl (10 mL, 2 M). The organic phase was separated and the aqueous phase was extracted with Et_2O (2 × 25 mL). The organic portions were combined, dried ($MgSO_4$) and the solvents evaporated to dryness yielding a crude yellow oil. This oil was purified by flash chromatography, eluting with 1% EtOAc/petroleum ether to give a 1:1 mixture, by ^{1}H NMR of the (*S*,*S*,*S*)- and (*S*,*S*,*R*)-tris(α-methylbenzyl)phosphane−borane*s* (**7**) and (**19**) (35.0 mg, 54.9%) as a partially crystalline colourless oil. Flash chromatography eluting with 1% EtOAc/petroleum ether gave pure (*S*,*S*,*S*)-tris(α-methylbenzyl)phosphane−borane (**7**) (15.0 mg, 22.2%) as white needles; R_f(Et_2O/petroleum ether, 1:20) 0.20. Characterisation data were identical to the racemic compound except; m.p. 146−148 °C (from Et_2O/petroleum ether). $[\alpha]_D^{23}$ = −277.1 (*c* = 1.0, CH_2Cl_2). $C_{24}H_{30}BP$ (360.2) calcd. C 79.8, H 8.6; found C 79.6, H 8.2%. (*S*,*S*,*R*)-Tris(α-methylbenzyl)phosphane−borane (**19**) was isolated as a colourless oil; All data as for *rac*-**19**, except HRMS EI [M^+, $C_{24}H_{30}PB^+$]: calcd. 360.217186; found 360.217820. Other reactions that featured butyllithium and 1-phenylethyl triflate or NaH and 1-chloro-1-phenylethane failed to give any desired product. A reaction in which the methylation of **7** was attempted using KOH in MeOH and methyl iodide was not successful.

(*S*,*S*,*S*)-Tris(α-methylbenzyl)phosphane (1): Synthesis as for (±)-**1**, except enantiomerically pure (*S*,*S*,*S*)-tris(α-methylbenzyl)-phosphane−borane **7** (50.0 mg, 0.139 mmol) was used, giving (*S*,*S*,*S*)-tris(α-methylbenzyl)phosphane as confirmed by ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): δ = 32.76 ppm. Characterisation data were identical to (±)-**1**.

Crystal Data for (−)-7: $C_{24}H_{30}BP$, *M* = 360.26, orthorhombic, *a* = 6.5095(7) Å, *b* = 12.5383(13) Å, *c* = 25.999(3) Å, *V* = 2122.0(4) Å^3, *T* = 100(2) K, space group $P2_12_12_1$, *Z* = 4 , μ = 1.150 mm^{-1}; 4249 reflections collected, 1625 [*R*(int) = 0.1309] independent reflections, R_1 = 0.0566 [$I > 2\sigma(I)$], wR_2 = 0.1271. With a Flack parameter of −0.09(7), the absolute stereochemistry is clearly established and is in accord with the configuration of the starting material. CCDC-208440 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Crystal Data for (±)-7: $C_{24}H_{30}BP$, *M* = 360.26, monoclinic, *a* = 14.3470(3) Å, *b* = 12.4544(2) Å, *c* = 12.9509(3) Å, *V* = 2093.35(7) Å^3, *T* = 150(2) K, space group $P2_1/c$, *Z* = 4 , μ = 1.165 mm^{-1}; 12324 reflections collected, 2869 [*R*(int) = 0.0295] independent reflections, R_1 = 0.0424 [for 2541 reflections with $I > 2\sigma(I)$], wR_2 = 0.1368. CCDC 211488 contains the supplementary crystallographic data for this structure.

Crystal Data for (±)-4: $C_{24}H_{27}OP$, *M* = 362.43, triclinic, *a* = 5.7141(11) Å, *b* = 10.803(2) Å, *c* = 16.485(3) Å, *V* = 984.5(3) Å^3, *T* = 173(2) K, space group $P\bar{1}$, *Z* = 2 , μ = 0.149 mm^{-1}; 10045 reflections collected, 4465 [*R*(int) = 0.0495] independent reflections, R_1 = 0.0475 [for 2859 reflections with $I > 2\sigma(I)$], wR_2 = 0.0954. CCDC-211487 contains the supplementary crystallographic data for this structure.

Acknowledgments

The generous support of the School of Chemistry is gratefully acknowledged. H. E. is supported by the EPSRC.

[1] F. Lagasse, H. B. Kagan, *Chem. Pharm. Bull.* **2000**, *48*, 315−324.
[2] M. T. Reetz, T. Sell, A. Meiswinkel, G. Mehler, *Angew. Chem.* **2003**, *115*, 814−817; *Angew. Chem. Int. Ed.* **2003**, *42*, 790−792.
[3] I. V. Komarov, A. Börner, *Angew. Chem.* **2001**, *113*, 1237−1240; *Angew. Chem. Int. Ed.* **2001**, *40*, 1197−1200.
[4] C. Bolm, K. B. Sharpless, *Tetrahedron Lett.* **1988**, *29*, 5101−5104.
[5] C. Bolm, W. M. Davis, R. L. Halterman, K. B. Sharpless, *Angew. Chem.* **1988**, *100*, 882; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 835.
[6] A. F. Littke, G. C. Fu, *J. Org. Chem.* **1999**, *64*, 10−11.
[7] M. R. Netherton, C. Dai, K. Neuschütz, G. C. Fu, *J. Am. Chem. Soc.* **2001**, *123*, 10099−10100.
[8] M. T. Powell, A. M. Porte, K. Burgess, *Chem. Commun.* **1998**, 2161.
[9] M. T. Powell, A. M. Porte, J. Reibenspies, K. Burgess, *Tetrahedron* **2001**, *57*, 5027.
[10] K. V. Baker, J. M. Brown, N. Hughes, A. J. Skarnulis, A. Sexton, *J. Org. Chem.* **1991**, *56*, 698.
[11] P. Wyatt, C. P. Butts, V. Patel, B. Voysey, *J. Chem. Soc., Perkin Trans. 1* **2000**, 4222−4223.
[12] A. Bootle-Wilbraham, S. Head, J. Longstaff, P. Wyatt, *Tetrahedron Lett.* **1999**, 5267−5270.
[13] L. Horner, W. D. Balzer, *Tetrahedron Lett.* **1965**, 1157.
[14] I. G. M. Campbell, J. K. Way, *J. Chem. Soc.* **1961**, *2*, 2133.
[15] L. Horner, H. Hoffmann, P. Beck, *Chem. Ber.* **1958**, *91*, 1583.
[16] J. M. Brunel, B. Faure, M. Maffei, *Coord. Chem. Rev.* **1998**, *178−180*, 665.
[17] T. Imamoto, T. Oshiki, T. Onozawa, T. Kusumoto, K. Sato, *J. Am. Chem. Soc.* **1990**, *112*, 5244−5252.
[18] K. M. Pietrusiewicz, M. Zablocka, *Chem. Rev.* **1994**, *94*, 1375−1411.
[19] H. C. Brown, J. R. Schwier, B. Singaram, *J. Org. Chem.* **1978**, 4395.
[20] S. E. Denmark, R. L. Dorow, *J. Org. Chem.* **1989**, *54*, 5−6.
[21] E. L. Eliel, S. H. Wilen, L. N. Mander, *Stereochemistry of Organic Compounds*, John Wiley & Sons, New York, **1994**, p. 484.
[22] K. Mislow, J. Siegel, *J. Am. Chem. Soc.* **1984**, *106*, 3319−3328.
[23] T. Imamoto, T. Kusumoto, N. Suzuki, K. Sato, *J. Am. Chem. Soc.* **1985**, *107*, 5301−5303.
[24] B. P. Bandgar, V. S. Sadavarte, L. S. Uppalla, *Tetrahedron Lett.* **2001**, *42*, 951.
[25] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313.
[26] E. L. Eliel, S. H. Wilen, L. N. Mander, *Stereochemistry of Organic Compounds*, John Wiley & Sons, New York, **1994**, p. 470.
[27] E. L. Eliel, S. H. Wilen, L. N. Mander, *Stereochemistry of Organic Compounds*, John Wiley & Sons, New York, **1994**, p. 479.
[28] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923.
[29] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosa, F. J. Timmers, *Organometallics* **1996**, *15*, 1518.
[30] Z. Goren, M. J. Heeg, S. Mobashery, *J. Org. Chem.* **1991**, *56*, 7187.
[31] S. C. Watson, J. F. Eastham, *J. Organomet. Chem.* **1967**, *9*, 165.
[32] I. D. Gridnev, Y. Yamanoi, N. Higashi, H. Tsuruta, M. Yasutake, T. Imamoto, *Adv. Synth. Catal.* **2001**, *343*, 118−136.
[33] B. Carboni, L. Monnier, *Tetrahedron* **1999**, *55*, 1197.
[34] L. R. Ocone, C. W. Schaumann, B. P. Block, *Inorganic Syntheses* **1966**, *8*, 71.
[35] I. Lukes, M. Barbaruah, L. D. Quin, *J. Am. Chem. Soc.* **1994**, *116*, 1737.
[36] W. B. Jennings, C. J. Lovely, *Tetrahedron* **1991**, *47*, 5561.
[37] M. A. Mathur, *Inorganic Syntheses* **1974**, *15*, 128.

Received June 27, 2003

