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A Synthetic Approach to Macrocyclic, Chiral Phosphane Derivatives with Crown-Ether-Like Structures

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(*S*,*S*)-Bis(2-hydroxypropyl)(phenyl)phosphane oxide has been prepared, either by ring-opening of (*S*)-propylene oxide with dilithio(phenyl)phosphane or by catalytic hydrogenation of bis(2-oxopropyl)(phenyl)phosphane oxide, promoted by ruthenium/MeO-BIPHEP. Catalytic hydrogenation also allowed the enantioselective synthesis of (*R*,*R*)-bis(2-phenyl-2-hydroxyethyl)(phenyl)phosphane oxide from the corresponding diketone. These bis(β-hydroxyalkyl)phosphane derivatives are suitable chiral starting materials for the synthesis of 1-phospha-10-aza-18-crown-6 derivatives, the first examples of optically pure, crown-ether-like, phosphorus-containing macrocycles. One of them has been characterised by X-ray diffraction study. Complexation of Na^+ by the crown ether moiety of the macrocyclic ring has been observed by ^1H NMR analysis.

Introduction

The point of the use of functionalised phosphorus ligands in enantioselective catalysis is to create secondary interactions between ligands, metal ions and/or substrates during the catalytic cycles. According to Hayashi[1] and Ito,[2] who first proposed and developed the concept, such interactions should affect rates and selectivities, and should also improve enantiocontrol by differentiating one diastereomeric transition state over another. Consequently, a variety of chiral phosphanes have been designed so as to take advantage of hemilabile complexation processes,[3] electrostatic interactions or hydrogen bonding[4,5] and Lewis acid–base interactions.[6]

In this context, there have been reports of chiral phosphorus ligands in which the structural design is based on selectivity-directing secondary interactions between a crown ether function and ammonium or metal cations. Chiral phosphane–crown ether hybrid ligands were first introduced in Ito's work.[7] These are ferrocenyl-based diphosphanes with planar and central chirality, bearing 1-aza-15-crown-5, 1-aza-18-crown-6, 1,10-diaza-18-crown-6, or 1-aza-21-crown-7 units at the ends of their pendant arms. Electrostatic interactions between an encapsulated metal cation and a negatively charged substrate should be expected when such ligands are used in, for instance, enantioselective palladium-catalysed allylic substitution reactions. More recently, 1-aza-15-crown-5-functionalised bis(phosphites)[8] and ferrocenyldiphosphanes[9] have been prepared by Landis. They were evaluated in rhodium-promoted hydroformylation and hydrogenation reactions, with the aim of exploiting hydrogen-bonding interactions with ammonium cations.

Additional examples are bis(phosphinites) bearing carbohydrate-based crown ether moieties, which have been used in asymmetric hydrogenation reactions.[10]

In all the diphosphanes above, the phosphorus centre, usually a diphenylphosphanyl group, is connected to the crown ether moiety through carbon linkers. A conceivable alternate approach to crown-ether-like phosphanes would be to design macrocycles incorporating a phosphorus centre in a polyoxygenated chain.

This unprecedented strategy has been considered here, and this manuscript outlines an enantioselective synthetic approach to macrocyclic chiral phosphanes with crown-ether-like structures.

Results and Discussion

Our synthetic strategy to macrocyclic phosphanes is based on the use of a single, enantiomerically pure phosphorus synthon, easily integrable into a variety of macrocyclic structures (Scheme 1). The pseudo-C_2-symmetric, bis(2-hydroxyethyl)phosphane oxides **1** were therefore chosen as the key starting materials.

The hydroxy groups of **1** should be easily alkylated to introduce oxygen-containing chains of various lengths. The terminal leaving groups X (X = halide) should react with bifunctional nucleophiles in the final cyclisation step to afford the desired macrocyclic phosphane oxides.

Bis(2-hydroxyethyl)phosphanes of the general formula **1** have been prepared previously, in their racemic forms, by

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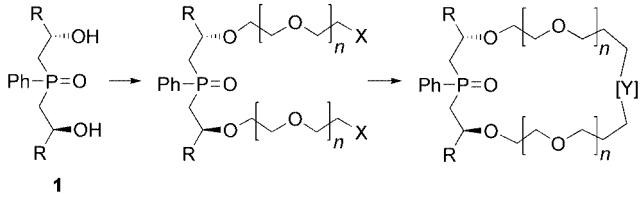
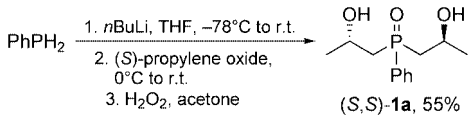


Scheme 1. Synthetic approach to macrocyclic phosphane oxides.

treatment of monosubstituted oxiranes with lithium salts of primary phosphanes.[11] On the other hand, ring-opening reactions of optically pure epoxides with phosphorus nucleophiles have been applied to the synthesis of several enantiomerically pure β-hydroxyphosphane derivatives.[12] The same method has been applied here to the stereoselective synthesis of the phosphane oxide **1a** from (*S*)-propylene oxide and phenylphosphane, as shown in Scheme 2. The reaction proceeds with high regioselectivity, as the lithiated phosphane attacks essentially at the less substituted carbon atom of the epoxide to afford (*S*,*S*)-bis(2-hydroxypropyl)(phenyl)phosphane. For this study, the trivalent phosphane was not isolated but was rather oxidised directly to the corresponding phosphane oxide **1a**.

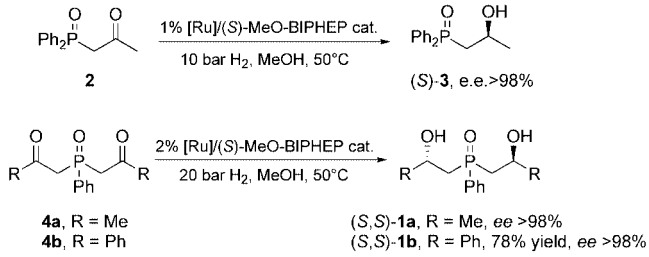


Scheme 2. Synthesis of the bis(2-hydroxypropyl)phosphane oxide **1a** from propylene oxide.

The epoxide ring-opening reaction shown here represents a convenient approach to optically pure bis(β-hydroxyalkyl)-phosphane derivatives, provided that two conditions are fulfilled: the starting oxirane must be easily available, and the ring-opening must be highly regioselective. This is not the case for styrene oxides, ring-openings of which with phosphorus nucleophiles display poor regioselectivity.[12b] An alternative and unprecedented strategy has thus been worked out for the synthesis of the phenyl-substituted phosphane oxide **1b**.

The synthetic approach to **1b** is based on the catalytic enantioselective hydrogenation of the corresponding diketone **4b**, promoted by ruthenium–MeO-BIPHEP complexes (Scheme 3). The catalytic hydrogenation of functionalised ketones, first introduced by Noyori and Takaya with BINAP as the chiral ligand,[13] has become a very powerful and widely used tool for the asymmetric synthesis of chiral alcohols.[14] High enantioselectivities are attained, notably in the hydrogenations of β-functionalised ketones such as β-oxo esters,[13] β-amino ketones[13b] and β-oxo phosphonates[15] and others. According to the stereochemical model proposed by Noyori,[16] the efficient stereochemical control is the result of the ability of these substrates to chelate the ruthenium centre in the enantiodetermining step of the catalytic cycle.

As a general rule, ketones bearing functional groups that would be able to coordinate the metal centre are likely to allow high enantioselectivities in the ruthenium-promoted hydrogenation reactions. β-Oxo phosphane oxides fulfil such structural requirement, as the P=O groups usually display good coordinating properties toward transition metal ions, and should thus be suitable substrates for asymmetric hydrogenation reactions. This hypothesis proved to be correct, as shown in Scheme 3.



Scheme 3. Ruthenium-promoted enantioselective hydrogenation of β-oxo phosphane oxides.

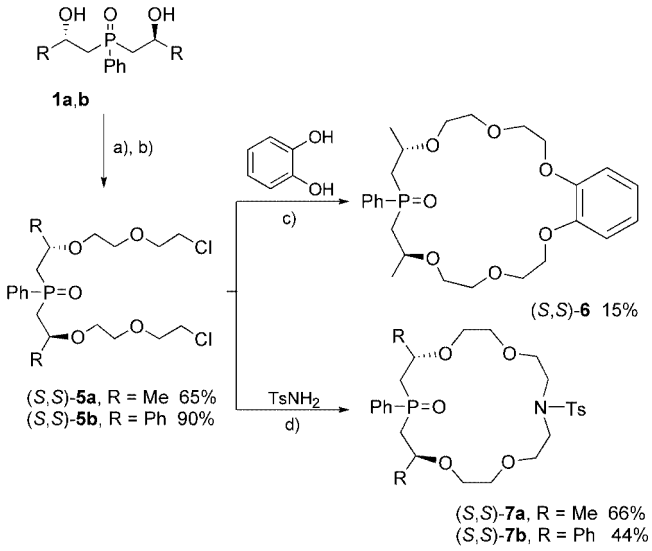
The catalytic hydrogenation of β-oxo phosphane oxides was first tested on a model substrate, (2-oxopropyl)diphenylphosphane oxide (**2**),[17] and was then applied to the phosphane oxides **4a**[18] and **4b**. Compound **4b**[19] has been prepared by treatment of dichloro(phenyl)phosphane with the lithium enolate of acetophenone, as described in the Exp. Sect.

The catalytic hydrogenation of **2** and **4** in the presence of (*S*)-MeO-BIPHEP–ruthenium catalysts allowed quantitative and – for **4a** and **4b** – totally diastereoselective conversions into **3**, **1a** and **1b**, respectively, as confirmed by ^{1}H NMR analysis of the crude reaction mixture. Enantiomeric excesses were established to be higher than 98% by chiral HPLC (see Exp. Sect.). The absolute configurations of the stereogenic centres of **3** and **1a** were assigned as (*S*) by comparison of the retention times and $[\alpha]_D$ values with those of known samples.[20] They are consistent with the predicted stereochemical outcome of the hydrogenation reaction, according to Noyori's model.[16] By analogy, the absolute configuration of **1b** was tentatively assigned as (*S*,*S*).

The few examples given in Scheme 3 indicate that the catalytic hydrogenation of β-oxo phosphane oxides promoted by atropoisomeric phosphane–ruthenium complexes could represent a general and convenient approach for the enantioselective synthesis of phosphorus derivatives. It complements other known methods based on catalytic enantioselective transformations of prochiral phosphorus-containing substrates.[21] For the purposes of this study, it represents a highly convenient procedure for the synthesis of **1a** and **1b**.

The second step of the sequence shown in Scheme 1 is the *O*-alkylation of both hydroxy functions of the phosphane oxides **1** with polyoxygenated electrophiles (Scheme 4), and so 2-(2-chloroethoxy)ethanol and its derivatives were selected as alkylating agents. Only triflate was found to be an acceptable leaving group for this displacement reaction by the sodium salts of **1**. Diethyl ether is the

solvent of choice, while THF undergoes partial ring-opening oligomerisation to afford contaminating side products. In diethyl ether the desired phosphane oxides **5** are obtained at room temperature in moderate to good yields.



Scheme 4. *O*-Alkylation reactions of the phosphane oxides **1** and cyclisation reactions. Reagents and conditions: *a*) NaH, diethyl ether, room temp. *b*) $Cl(CH_2)_2O(CH_2)_2OTf$, room temp. *c*) K_2CO_3, BuOH, 110 °C. *d*) K_2CO_3, DMF, 150 °C.

Macrocyclic phosphane derivatives should be obtainable from compounds **5** through taking advantage of the presence of chloride leaving groups in their reactions with suitable nucleophiles. Catechol was used first in the cyclisation reaction, with the expected macrocyclic phosphane oxide **6** being obtained, albeit in low yields regardless of the reaction conditions applied.

Better results were obtained by treatment of **5** with tosylamine in DMF at reflux in the presence of K_2CO_3 as the base. The 1-phospha-10-aza-18-crown-6 derivatives **7a** and **7b** were isolated in acceptable yields after purification by column chromatography.

Structural characterisation of **7b** was performed by X-ray diffraction studies. An ORTEP drawing and selected bond angles and distances are given in Figure 1; and Table 1, respectively.

Compounds **7** represent a new class of chiral, pseudo-C_2-symmetric, macrocyclic phosphane oxides that are potential receptors for metal ions, ammonium salts and other substrates. Enantiomeric recognition could be expected in such complexation processes.[22]

As far as we are aware, no enantiomerically pure phosphane oxides with crown-ether-like structures have been described before, although several examples of achiral derivatives have been reported.[23]

In order to examine the complexing ability of **7** we compared, in qualitative experiments, the ^{1}H NMR spectra of the macrocyclic phosphane oxides alone and in the presence of potential guests {sodium tetraphenylborate and [1-(1-naphthyl)ethyl]ammonium chloride}.

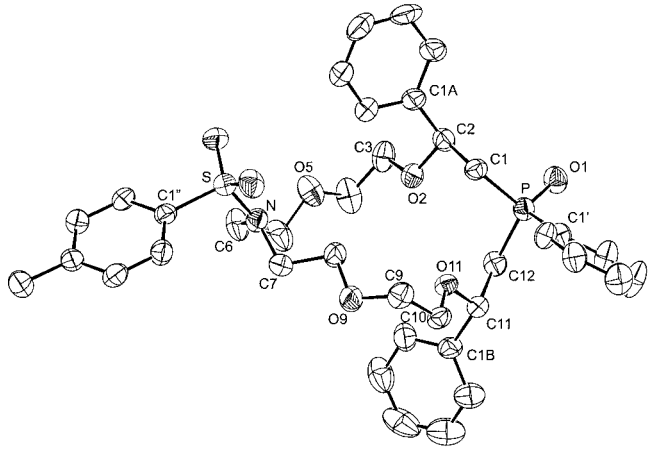


Figure 1. ORTEP drawing of the crystal structure for compound **7b**, showing 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths [Å] and bond angles [°] for compound **7b**.

P–C(1)	1.805(6)	P–C(12)	1.808(6)
C(1)–C(2)	1.529(8)	C(12)–C(11)	1.514(9)
C(2)–O(2)	1.429(7)	C(11)–O(11)	1.426(7)
C(6)–N	1.492(8)	C(7)–N	1.468(8)
C(2)–C(1A)	1.508(9)	C(11)–C(1B)	1.510(8)
P–O(1)	1.494(5)	P–C(1′)	1.795(6)
N–S	1.606(5)	S–C(1′′)	1.772(6)
C(1)–P–C(12)	110.5(3)	C(6)–N–C(7)	117.8(6)
P–C(1)–C(2)	114.4(4)	O(1)–P–C(1′)	112.2(3)
C(1)–C(2)–O(2)	106.7(5)	C(12)–C(11)–O(11)	107.1(5)
C(1)–C(2)–C(1A)	109.9(5)	C(12)–C(11)–C(1B)	112.7(5)
C(2)–O(2)–C(3)	115.3(5)	C(11)–O(11)–C(10)	112.2(4)

The most marked shifts of the NMR signals were observed when $NaBPh_4$ was added to $CDCl_3$/MeOD solutions of the macrocyclic hosts **7a** or **7b**, which is indicative of efficient bonding of sodium cations (see Figure 2).

All signals in the δ = 2–5 ppm region of the ^{1}H NMR spectrum (i.e., signals for the CH_2 and CH protons of the macrocyclic ring) are shifted by up to 0.4 ppm when 1 equiv. of $NaBPh_4$ is added. The methyl substituent in the *N*-tosyl moiety also experiences a slight downfield shift, from δ = 2.40 to 2.45 ppm. The ^{31}P NMR chemical shift of **7b** is not significantly affected by addition of the sodium salt, with a $\Delta\delta$ of only 0.3 ppm. As a $\Delta\delta$ of about 8 ppm was observed previously upon coordination of a P(O) function to a sodium salt,[23e] it may be assumed that the P(O) function of **7b** does not contribute to the coordination process here.

Addition of (*R*)- and (*S*)-[1-(1-naphthyl)ethyl]ammonium chloride induces only very small changes in the NMR spectrum of **7b**, while the spectroscopic data of **7a** remain almost unchanged in the presence of these ammonium salts. In the case of **7b**, in which signals on the "left-side", aromatic portion of the spectrum are the most affected, it may be tentatively assumed that π-stacking between aromatic rings is the main host–guest interaction taking place here,

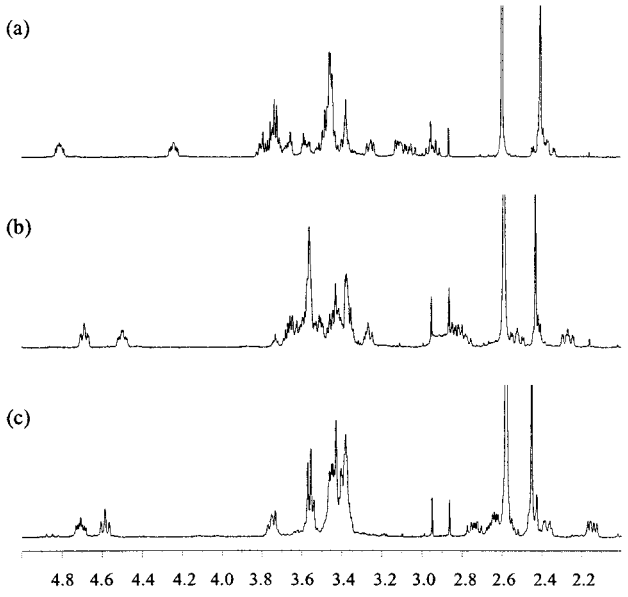
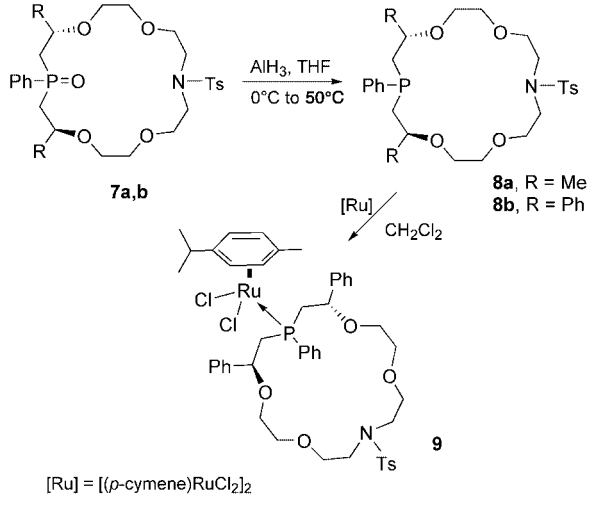


Figure 2. ^{1}H NMR spectra of the aza-phospha-crown ether **7b**: at 4×10^{-3} mmol mL^{-1} in $CDCl_3$/MeOH (95:5) (a), after addition of 0.5 equiv. of $NaBPh_4$ (b), and after addition of 1 equiv. of $NaBPh_4$ (c).

while hydrogen-bonding interactions are comparatively weak. If it is assumed that the P(O) group does not intervene in the complexation process, inducing a break in the crown ether structure, compounds **7** may be compared to 18-crown-5 derivatives, which usually display moderate affinities to ammonium salts through hydrogen bonding.[24]

Phosphane oxides **7a** and **7b** have been converted into the corresponding trivalent phosphanes **8a** and **8b** by reduction with AlH_3 under mild conditions (0 °C to 50 °C), according to the reported method (Scheme 5).[25]



Scheme 5. Synthesis of trivalent macrocyclic phosphanes and coordination to ruthenium.

Finally, the coordinating ability of **8b** toward transition metals has been observed through its reaction with the [(*p*-cymene)$RuCl_2$]$_2$ complex, which quantitatively affords the expected complex **9** as an air-stable, yellow-orange compound.

Conclusions

This report describes a convenient approach to the enantiomerically pure, phosphorus-containing diols **1**, by catalytic asymmetric hydrogenation of the corresponding diketones. Diols **1** have been shown to be suitable starting materials for the synthesis of chiral phosphorus-containing macrocycles with crown-ether-like structures. The phosphane oxides **6** and **7**, and the corresponding trivalent phosphanes, are representative examples of this new class of chiral phosphorus derivatives.

To the best of our knowledge, a single family of chiral macrocyclic phosphanes had been prepared previously with the purpose of studying their catalytic properties in transition-metal-promoted reactions,[26] so very little information on the effects of the macrocyclic structure of phosphorus ligands on catalysis is so far available. Consequently, in the next step of this work we intend to examine the catalytic applications of selected transition metal complexes of phosphanes **8**, with the aim of identifying how their macrocyclic crown ether structures affect rates and selectivities through secondary interactions.

Experimental Section

General: The phosphane oxide **4a** was prepared by ozonolysis of 3,4-dimethyl-1-phenyl-3-phospholene oxide[27] as described in ref.[18] Aluminium hydride solutions were prepared from $LiAlH_4$ and sulfuric acid, or from $LiAlH_4$ and $AlCl_3$, according to reported methods.[28] All reactions were performed under argon.

(*S*,*S*)-Bis(2-hydroxypropyl)(phenyl)phosphane Oxide (1a). Method A (from Propylene Oxide): *n*BuLi (7.5 mL, 2.5 M solution in hexane) was added at –78 °C to a solution of phenylphosphane (1.0 g, 9 mmol) in THF (30 mL). The mixture was allowed to warm to room temperature and stirring was maintained for 1 h. After the system had been cooled to 0 °C, (*S*)-propylene oxide (1,32 mL, 18.9 mmol) was added. The reaction mixture was stirred at about 25–30 °C for 2 h, during which time the yellow-orange solid ($PhPLi_2$) dissolved to afford a yellow solution. Water (1 mL) was added and THF was removed. The residue was taken up in a diethyl ether/water mixture. The aqueous layer was extracted successively with diethyl ether and dichloromethane. After drying ($MgSO_4$) and evaporation of the solvents, the residue containing the trivalent phosphane [$\delta(^{31}P)$ = –38 ppm] and its oxide **1a** was dissolved in acetone (10 mL) and then cooled to 0 °C. The phosphane was oxidised by addition of H_2O_2 (30% solution, 1.5 mL) and stirring at room temperature for about 30 min. An aqueous solution of sodium thiosulfate was added and the reaction mixture was then extracted with dichloromethane. The organic extracts were dried with $MgSO_4$ and solvents were removed to afford the crude oxide **1**, which was purified by column chromatography on silica gel (diethyl ether/methanol, 90:10). Compound **1** was obtained in 55% yield (1.2 g), as a colourless oil. **Method B (by Catalytic Hydrogenation):** The ruthenium catalyst was prepared by addition of a methanolic HBr solution (0.19 M, 0.11 mL) to a mixture of (cod)Ru(2-methylallyl)$_2$ (3.2 mg, 0.01 mmol) and (*S*)-MeO-BI-

PHEP (6.4 mg, 0.011 mmol, Aldrich) in anhydrous acetone.[29] After the mixture had been stirred at room temperature for 40 min, the solvent was removed under vacuum and the residue was taken up in methanol (1 mL). Bis(2-oxopropyl)(phenyl)phosphane oxide (**4a**, 0.12 g, 0.5 mmol) was added to the reaction vessel, which was then placed in a stainless steel autoclave. The argon was replaced by hydrogen, at a pressure of 20 bar, and the reaction was allowed to proceed at 50 °C for 24 h. Complete conversion into the diol **1a** was confirmed by NMR spectroscopy. After evaporation of the solvent, the phosphane oxide **1a** was purified by column chromatography as above. The enantiomeric excess was >98%. **1a:** $[\alpha]_D$ = +42 (*c* = 1, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ = 1.23 (dd, ^3J = 6.1, ^4J = 1.7 Hz, 3 H, Me), 1.29 (dd, ^3J = 6.2, ^4J = 1.7 Hz, 3 H, Me), 1.96 (ddd, $^2J_{AB}$ = 14.8, *J* = 8.3, *J* = 1.8 Hz, 1 H, PCH_2), 2.18 (m, 2 H, PCH_2), 2.37 (dt, $^2J_{AB}$ = 14.8, *J* = 10.2 Hz, 1 H, PCH_2), 3.9 (br., 1 H, OH), 4.1 (br., 1 H, C*H*OH), 4.4 (br., 2 H), 7.5 (3 H, Ph), 7.6–7.8 (2 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.06 (Me), 25.22 (Me), 38.6 (d, $^1J_{C,P}$ = 67.8 Hz, PCH_2), 39.8 (d, $^1J_{C,P}$ = 67.0 Hz, PCH_2), 62.8 (d, $^2J_{C,P}$ = 5.2 Hz, CH), 63.3 (d, $^2J_{C,P}$ = 5.3 Hz, CH), 128.8, 129.0, 129.9, 130.1, 132.2 (CH_{Ph}), 132.1 (d, $^1J_{C,P}$ = 94.9 Hz, C_{ipso}) ppm. ^{31}P NMR ($CDCl_3$): δ = 43 ppm. EI MS: *m*/*z* (%) = 242 (2) $[M]^+$, 227 (18) $[M - Me]^+$, 209 (20) $[M - 2\times Me]^+$, 184 (46), 140 (100). $C_{12}H_{19}O_3P$ (242.11): calcd. C 59.99, H 7.13; found C 59.13, H 7.77. HPLC assay: Chiralcel AS-H, 9:1 hexane/*i*PrOH, flow 1 mL min^{-1}, detection by UV at 544 nm, retention times 16.4 min (*R*,*R*) and 24.0 min (*S*,*S*).

Catalytic Hydrogenation of (2-Oxopropyl)diphenylphosphane Oxide (2): The hydrogenation reaction was performed on a 1 mmol scale, with 1% ruthenium catalyst, at 50 °C, under 10 bar of H_2, as described above. Both (*R*)- and (*S*)-MeO-BIPHEP were used in successive experiments. Total conversion was observed by ^1H NMR spectroscopy. The enantiomeric excesses were determined by HPLC assay. The absolute configurations were assigned by comparison of the retention times with that of a known sample prepared from (*S*)-propylene oxide.[30]

(2-Hydroxypropyl)diphenylphosphane Oxide (3): ^1H NMR (400 MHz, $CDCl_3$): δ = 1.28 (dd, ^3J = 6.2, ^4J = 1.8 Hz, 3 H, Me), 2.36 (ddd, $^2J_{AB}$ = 14.8, $^2J_{H,P}$ = 7.4, ^3J = 2.1 Hz, 1 H, PCH_2), 2.48 (ddd, $^2J_{AB}$ = 14.8, $^2J_{H,P}$ = 11.7, ^3J = 9.9 Hz, 1 H, PCH_2), 4.2–4.3 (m, 1 H, C*H*OH), 4.5 (br., OH), 7.5 (m, 3 H, Ph), 7.7 (m, 2 H, Ph) ppm. ^{31}P NMR ($CDCl_3$): δ = 35 ppm. HPLC assay: Chiralcel OD-H, 9:1 hexane/*i*PrOH, flow 1 mL min^{-1}, retention times 15.8 min (*R*) and 24.2 min (*S*).

(*S*,*S*)-Bis(2-hydroxy-2-phenylethyl)(phenyl)phosphane Oxide (1b): Compound **1b** was obtained by catalytic hydrogenation of **4b**. **(a):** Acetophenone (60 mmol) was added to a cooled solution (–78 °C) of LiHMDS (66 mmol) in THF (80 mL). After the mixture had been allowed to stand at –78 °C for 1 h, a THF solution of dichloro(phenyl)phosphane (4.1 mL, 30 mmol) was added dropwise. The mixture was allowed to warm to room temperature and stirred for 14 h. Hydrolysis was performed at 0 °C, by pouring the reaction mixture into HCl solution (5%, 120 mL). After evaporation of the THF, the residue was taken up in CH_2Cl_2. The organic layer was dried and then stirred in air for about 12 h, which allows oxidation of the bis(2-oxo-2-phenylethyl)(phenyl)phosphane under mild conditions. The final product was purified by chromatography on silica gel with cyclohexane/ethyl acetate (3:7) as the eluent. Compound **4b**[19] was obtained in 42% yield (1.5 g): colourless solid, m.p. 132 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.08 (*A*BX, $^2J_{AB}$ = 15.0, $^2J_{H,P}$ = 15.0 Hz, 2 H, PCH_2), 4.13 (A*B*X, $^2J_{AB}$ = 15.0, $^2J_{H,P}$ = 15.0 Hz, 2 H, PCH_2), 7.4–7.6 (9 H, Ph), 7.86 (2 H, Ph), 7.94 (4 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 42.0 (d, $^1J_{C,P}$ = 62.8 Hz, PCH_2), 128.6, 128.7, 128.7, 128.9, 130.7, 130.9, 132.0, 132.4, 133.8, 136.9 (C_{Ph})193.6 (d, $^2J_{C,P}$ = 5.8 Hz, C_{Ph}) ppm. ^{31}P NMR ($CDCl_3$): δ = 32 ppm. $C_{22}H_{19}O_3P$ (362.11): calcd. C 72.92, H 5.29; found C 71.73, H 5.21. **(b):** The hydrogenation reaction was performed as described above for the synthesis of **1a**. The reaction was performed on a 12 mmol scale (4.5 g), under 20 bar H_2, at 50 °C for 4 d. After chromatography on silica gel with diethyl ether/methanol (97:3) as the eluent, the final product was obtained in 78% yield (1.4 g) as a colourless solid, m.p. 171 °C. $[\alpha]_D$ = +49 (*c* = 1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.26 (ddd, $^2J_{AB}$ = 15.0, $^2J_{H,P}$ = 9.1, ^3J = 2.0 Hz, 1 H, PCH_2), 2.40 (ddd, $^2J_{AB}$ = 15.1, $^2J_{H,P}$ = 10.6, ^3J = 2.7 Hz, 1 H, PCH_2), 2.57 (dt, $^2J_{AB}$ = 15.1, *J* = 10.6 Hz, 1 H, PCH_2), 2.68 (ddd, $^2J_{AB}$ = 15.0, ^3J = 10.7, $^2J_{H,P}$ = 8.7 Hz, 1 H, PCH_2), 4.18 (1 H, OH), 4.50 (1 H, OH), 5.15 (t, *J* = 10.0 Hz, 1 H, C*H*OH), 5.26 (t, *J* = 9.8 Hz, 1 H, C*H*OH), 7.2–7.3 (10 H, Ph), 7.5 (3 H, Ph), 7.7 (2 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.1 (d, $^1J_{C,P}$ = 64.9 Hz, PCH_2), 40.8 (d, $^1J_{C,P}$ = 64.3 Hz, PCH_2), 68.6 (d, $^2J_{C,P}$ = 4.5 Hz, CH), 69.0 (d, $^2J_{C,P}$ = 3.6 Hz, CH), 125.5, 127.6, 128.5, 128.7, 128.9, 130.0, 130.1, 132.0, 132.4 (d, $^1J_{C,P}$ = 94.8 Hz, C_{ipso}), 144.1 (d, $^3J_{C,P}$ = 15.2 Hz, C_{Ph}), 144.3 (d, $^3J_{CP}$ = 13.1 Hz, C_{Ph}) ppm. ^{31}P NMR ($CDCl_3$): δ = 43 ppm. EI-MS: *m*/*z* (%) = 366 (17) $[M]^+$, 348 (13) $[M - 18]^+$, 216 (93), 140 (100). $C_{22}H_{23}O_3P$ (366.14): calcd. C 72.12, H 6.33; found C 71.95, H 6.48. HPLC assay: Chiralcel OD-H, 9:1 hexane/*i*PrOH, flow 1 mL min^{-1}, detection by UV at 544 nm, retention times 13.7 min (*S*,*S*) and 19.0 min (*R*,*R*).

(*S*,*S*)-Bis{2-[2-(2-chloroethoxy)ethoxy]propyl}(phenyl)phosphane Oxide (5a). (a): 2-(2-Chloroethoxy)ethyl trifluoromethanesulfonate was prepared from 2-(2-chloroethoxy)ethanol: a mixture containing 2-(2-chloroethoxy)ethanol (8.5 mL, 80 mmol) and triethylamine (11.5 mL, 82 mmol) in dichloromethane (50 mL) was added slowly at 0 °C to a CH_2Cl_2 solution (120 mL) of triflic anhydride (25 g, 88 mmol). The mixture was stirred at room temperature for 6 h and was then hydrolysed with cold water. The organic layer was washed with cold water and dried with $MgSO_4$. Evaporation of the solvent afforded 18.8 g (92% yield) of crude triflate,[31] which was used without further purification. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.64 (m, 2 H, CH_2Cl), 3.79 (m, 2 H, CH_2O), 3.85 (m, 2 H, CH_2O), 4.64 (m, 2 H, CH_2OTf) ppm. **(b):** NaH (0.84 g, 21 mmol, 60% in mineral oil) was added portionwise to a solution of **1a** (2.4 g, 10 mmol) in diethyl ether (130 mL). The mixture was heated at 30 °C for about 1 h and was then cooled to 0 °C. A solution of 2-(2-chloroethoxy)ethyl trifluoromethanesulfonate (5.6 g, 22 mmol) in diethyl ether (5 mL) was added. After 24 h of stirring at room temperature, the mixture was hydrolysed with water (10 mL). After extraction of the aqueous layer with dichloromethane, the organic layers were dried with $MgSO_4$ and the solvents were evaporated. The crude product was purified by column chromatography on silica gel, with a diethyl ether/MeOH gradient (from 95:5 to 90:10) as the eluent, to yield **5a** (2.9 g, 65%) as a colourless oil. **5a**: $[\alpha]_D$ = +12 (*c* = 1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.17 (d, ^3J = 5.3 Hz, 3 H, Me), 1.23 (d, ^3J = 6.1 Hz, 3 H, Me), 2.00 (ddd, *J* = 15.0, *J* = 13.1, *J* = 4.8 Hz, 1 H, PCH_2), 2.3–2.4 (m, 3 H, PCH_2), 3.20 (m, 2 H), 3.35 (m, 1 H), 3.4–3.8 (m, 14 H), 4.0 (m, 1 H), 7.4 (3 H, Ph), 7.7 (2 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2 (Me), 21.3 (Me), 38.3 (d, $^1J_{C,P}$ = 51.0 Hz, PCH_2), 39.3 (d, $^1J_{C,P}$ = 51.5 Hz, PCH_2), 42.6 (CH_2Cl), 67.5 (CHO), 67.6 (CHO), 70.3, 70.6, 70.9, 71.2, 71.3 (OCH_2), 128.3, 128.5, 130.2, 130.4, 131.2 (CH_{Ph}), 133.8 (d, $^1J_{C,P}$ = 94.4 Hz, C_{ipso}) ppm. ^{31}P NMR ($CDCl_3$): δ = 35 ppm. CI-MS (NH_3) {^{35}Cl}: *m*/*z* (%) = 455 $[M + 1]^+$. HRMS {^{35}Cl}: calcd. for $C_{20}H_{33}Cl_2O_5P{\cdot}Na$ 477.1340; found 477.1321.

(*S*,*S*)-Bis{2-[2-(2-chloroethoxy)ethoxy]-2-phenylethyl}(phenyl)phosphane Oxide (5b): The synthesis of **5b** from **1b** (1.5 g, 4 mmol) fol-

lowed the same procedure as for **5a**. After 36 h of stirring at room temperature, the reaction mixture was hydrolysed and **5b** was purified by column chromatography on silica gel with CH_2Cl_2/MeOH (97:3) as the eluent. Yield 2.1 g (90%) of a colourless oil. **5b**: $[\alpha]_D$ = +45 (*c* = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.18 (td, *J* = 14.8, *J* = 2.9 Hz, 1 H, PCH_2), 2.64 (td, $^2J_{H,P} = {}^2J_{H,H}$ = 16.0, ^3J = 2.7 Hz, 1 H, PCH_2), 2.7–2.9 (m, 2 H, PCH_2), 3.15 (m, 2 H), 3.25 (m, 1 H), 3.3–3.6 (m, 14 H), 3.75 (m, 1 H), 4.53 (ddd, *J* = 10.9, *J* = 8.6, *J* = 2.6 Hz,1 H, C*H*OH), 4.93 (ddd, *J* = 10.6, *J* = 8.0, *J* = 3.0 Hz, 1 H, C*H*OH), 7.3 (10 H, Ph), 7.4 (3 H, Ph), 7.8 (2 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.2 (d, $^1J_{C,P}$ = 48.8 Hz, PCH_2), 41.5 (d, $^1J_{C,P}$ = 49.3 Hz, PCH_2), 42.5 (CH_2Cl), 42.7 (CH_2Cl), 68.0, 70.2, 70.4, 71.0, 71.1 (OCH_2), 76.8 (d, $^2J_{C,P}$ = 3.1 Hz, CHO), 77.0 (d, $^2J_{C,P}$ = 3.0 Hz, CHO), 126.4, 126.5, 127.9, 128.0, 128.3, 128.4, 128.6, 128.7, 130.3, 130.7, 131.2, 134.2 (d, $^1J_{C,P}$ = 72.2 Hz, C_{ipso}), 141.9 (d, *J* = 6.0 Hz, C_{Ph}), 142.0 (d, *J* = 4.8 Hz, C_{Ph}) ppm. ^{31}P NMR ($CDCl_3$): δ = 37 ppm. HRMS {^{35}Cl}: calcd. for $C_{30}H_{37}O_5PCl_2$·Na 601.1653; found 601.1683.

3,20-Dimethyl-1-phenyl-11,12-benzo-4,7,10,13,13,19-hexaoxa-1-phosphacyclohenicosane 1-Oxide (6): A mixture of catechol (145 mg, 1.3 mmol) and K_2CO_3 (182 mg, 1.3 mmol) in butanol (8 mL) was heated to reflux for 20 min. A solution of the phosphane oxide **5a** (200 mg, 0.43 mmol) in butanol (4 mL) was then added dropwise while heating. After the mixture had been heated at reflux in butanol for 14 h, the solvent was removed and the residue was taken up in a CH_2Cl_2/water mixture. After the usual workup, the final product was purified by chromatography with CH_2Cl_2/MeOH (98:2). Yield 15% (32 mg). **6**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.21 (d, ^3J = 5.1 Hz, 3 H, Me), 1.23 (d, ^3J = 4.6 Hz, 3 H, Me), 2.06 (td, *J* = 14.9, *J* = 4.9 Hz, 1 H, PCH_2), 2.3 (m, 1 H, PCH_2), 2.5 (m, 2 H, PCH_2), 3.3 (m, 1 H), 3.4 (m, 1 H), 3.5 (m, 1 H), 3.6–3.8 (m, 8 H), 3.8–3.9 (m, 3 H), 4.0–4.2 (m, 5 H), 6.90 (br. s, 4 H), 7.4 (3 H, Ph), 7.8 (m, 2 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.0 (d, $^1J_{C,P}$ = 8.1 Hz, Me), 21.2 (d, $^1J_{C,P}$ = 9.3 Hz, Me), 38.2 (d, $^1J_{C,P}$ = 65.9 Hz, PCH_2), 38.9 (d, $^1J_{C,P}$ = 68.2 Hz, PCH_2), 67.1, 67.8, 69.4, 69.9, 70.0, 70.7, 70.9, 71.0, 115.2 ($CH_{o\text{-catechol}}$), 115.6 ($CH_{o\text{-catechol}}$), 121.7 ($CH_{m\text{-catechol}}$), 121.8 ($CH_{m\text{-catechol}}$), 128.4, 128.5, 130.4, 130.5, 131.4, 133.4 (d, $^1J_{C,P}$ = 93.5 Hz, C_{ipso}), 149.3 ($C_{ipso\text{-catechol}}$) ppm. ^{31}P NMR ($CDCl_3$): δ = 36 ppm. CI/MS (NH_3): *m*/*z* = 493 $[M + H]^+$. HRMS (E.S.I.): calcd. for $C_{26}H_{37}O_7P$·Na 515.2175; found 515.2139.

(*S*,*S*)-3,17-Dimethyl-1-phenyl-10-tosyl-4,7,13,16-tetraoxa-10-aza-1-phosphacyclooctadecane 1-Oxide (7a): Tosylamine (170 mg, 1 mmol), K_2CO_3 (550 mg, 4 mmol) and the phosphane oxide **5a** (450 mg, 1 mmol) were heated at reflux in anhydrous DMF (20 mL) for 10 h. After evaporation of the solvent under vacuum, a saturated aqueous solution of $NaHCO_3$ was added. Extraction with CH_2Cl_2 and drying with $MgSO_4$ afforded a crude mixture, which was separated by chromatography with an Et_2O/MeOH gradient (from 95:5 to 90:10). Yield 66% (360 mg of a colourless oil). **7a**: $[\alpha]_D$ = +11 (*c* = 1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.20 (d, ^3J = 6.0 Hz, 3 H, Me), 1.23 (d, ^3J = 6.0 Hz, 3 H, Me), 2.06 (td, $^2J = {}^2J_{H,P}$ = 15.0, *J* = 6.0 Hz, 1 H, PCH_2), 2.25 (ddd, $^2J_{H,P}$ = 17.5, ^2J = 15.5, ^3J = 6.5 Hz, 1 H, PCH_2), 2.39 (s, 3 H, Me), 2.47 (ddd, ^2J = 15.5, $J_{H,P}$ = 10.5, ^3J = 7.0 Hz, 1 H, PCH_2), 2.59 (m, 1 H, PCH_2), 3.2–3.7 (17 H), 4.05 (m, 1 H, MeC*H*O), 7.29 (d, *J* = 8.0 Hz, 2 H, Ar), 7.4–7.5 (3 H, Ph), 7.69 (d, *J* = 8.0 Hz, 2 H, Ar), 7.80 (2 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.6 (d, $^1J_{C,P}$ = 8.2 Hz, Me), 21.0 (d, $^1J_{C,P}$ = 8.3 Hz, Me), 21.4 (Me), 37.8 (d, $^1J_{C,P}$ = 65.7 Hz, PCH_2), 38.7 (d, $^1J_{C,P}$ = 67.9 Hz, PCH_2), 48.6 (NCH_2), 48.7 (NCH_2), 67.1, 67.5, 70.3, 70.4, 70.6 (CH), 70.8 (CH), 127.0, 128.3, 128.5, 129.6, 130.4, 130.5, 131.4, 133.0 (d, $^1J_{C,P}$ = 93.3 Hz, C_{ipso}), 136.6 (C_{Ar}), 143.2 (C_{Ar}) ppm. ^{31}P NMR ($CDCl_3$): δ = 37 ppm. EI/MS: *m*/*z* (%) = 398 $[M - Ts]^+$ (46). CI/MS (NH_3): *m*/*z* = 554 $[M + 1]^+$. HRMS (E.S.I.): calcd. for $C_{27}H_{40}NO_7PS$·Na 576.2161; found 576.2151.

(*S*,*S*)-1,3,17-Triphenyl-10-tosyl-4,7,13,16-tetraoxa-10-aza-1-phosphacyclooctadecane 1-Oxide (7b): Compound **7b** was prepared according to the same procedure as for **7a**, from **5b** (2.3 g, 4 mmol). Compound **7b** was obtained in 44% yield (1.2 g) as a colourless solid, m.p. 68 °C. $[\alpha]_D$ = +38 (*c* = 1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.40–2.45 (m, 2 H), 2.43 (s, Me), 2.94 (m, 1 H), 3.07 (m, 1 H), 3.15 (m, 1 H), 3.28 (m, 1 H), 3.38 (m, 1 H), 3.4–3.8 (13 H), 4.36 (m, 1 H), 4.87 (m, 1 H), 7.2–7.8 (Ar), 8.03 (1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, selected data): δ = 21.4 (Me), 40.2 (d, $^1J_{C,P}$ = 67.9 Hz, PCH_2), 49.0 (NCH_2), 67.6, 68.0, 70.1, 70.2, 70.3, 70.5 (CH_2), 76.9, 77.0 (CH) ppm. ^{31}P NMR ($CDCl_3$): δ = 35 ppm. HRMS (E.S.I.): calcd. for $C_{37}H_{44}NO_7PS$·Na 700.2474; found 700.2447. Crystals of **7b** suitable for X-ray diffraction studies were grown from a dichloromethane/ethanol mixture.

X-ray Crystallography: Details of data collection and solution refinement are given in Table 2. X-ray data were collected with a Nonius Kappa CCD diffractometer with use of graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). A combination of 1.7° (exposure of 60 s/°) φ and ω (with κ offsets) scans was used to collect sufficient data to 2θ = 19.8°. The data frames were integrated and scaled by use of the Denzo-SMN package.[32] The structure was solved by direct methods (SHELX-S) and all non-hydrogen atoms were refined with anisotropic displacement parameters by use of SHELX-L by full-matrix least squares on F^2 values. Some hydrogen atoms were located in difference Fourier syntheses (the rest of them were placed in calculated positions) but all were included in the final cycles of refinement in a riding model, with

Table 2. Crystallographic data for compound **7b**.

Empirical formula	$C_{37}H_{44}NO_7PS$·0.5(C_2O)[a]
Formula mass	697.77
Crystal colour, shape	colourless, thin plate
Crystal size [mm]	0.45×0.15×0.025
Crystal system	monoclinic
Space group	$P2_1$
a [Å]	10.7493(6)
b [Å]	11.2768(11)
c [Å]	16.6953(15)
β [°]	92.379(5)
V [Å^3]	2022.0(3)
Z	2
$D_{calcd.}$ [g cm^{-3}]	1.146
F(000)	740
μ [mm^{-1}]	0.165
λ (Mo-K_α) [Å]	0.71073
T [K]	293(2)
hkl range	$-10 \le h \le 10$ $-10 \le k \le 10$ $-15 \le l \le 15$
2θ range [°] (completness [%])	$2.21 < 2\theta < 19.77$ (99.7)
Number of reflections collected	7833
Number of independent reflns/R_{int}	3484 (Friedel pairs not merged)/0.03
Refined data/observed data [$I > 2\sigma(I)$]	3474/3081
Restraints/parameters	79/464
Final *R*1, *wR*2 [$I > 2\sigma(I)$]	0.0500, 0.1419
Final *R*1, *wR*2 (all data)	0.0594, 0.1512
Goodness-of-fit on F^2	1.081
$\Delta\rho_{min}$,$\Delta\rho_{max}$ [e·Å^{-3}]	–0.180, 0.309

[a] These are EtOH molecules (0.25%) which are included in the crystal. The C and O atoms have been taken into account for structure refinement.

U_{iso}(H) set to ≥ 1.2 times that of the attached C atom. The asymmetric unit consists of one molecule of the compound **7b** and disordered solvent molecules in the cavity running through the crystal along the screwed twofold crystallographic *b*-axis, and treated as ethanol with two independent orientations and respective partial occupancy factor (1/4), allowing hydrogen bonding between the hydroxy group and the oxygen atom carried by the phosphorus atom. Disorder was also found at the level of the C5–O5 bond from the "central 18-atom cycle" and subsequently treated with alternate positions for these two atoms with a refined occupancy rate of 60–40%. The absolute stereochemistry as determined by Flack's method [Flack *x* parameter = 0.12(13)] was confirmed by weak intensity differences (owing to anomalous contributions from S and P atoms) detected for Bijvoet pairs, still showing a significant agreement between ΔF_{obs} and $\Delta F_{calcd.}$ (11 matching pairs over 14 $|\Delta F_{calcd.}| > 0.4$). CCDC-264452 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Reduction Procedure: The phosphane oxides **7a** or **7b** (0.2 mmol in 1 mL THF) were treated with 3 equiv. of AlH_3 in THF[28] at 0 °C. After the mixture had warmed up to 50 °C, the progress of the reaction was checked by ^{31}P NMR spectroscopy. After about 20 h, a few drops of MeOH were added to consume the excess AlH_3. Evaporation of the solvent afforded a white powder, which was washed twice with pentane. The pentane solution was recovered, and the solvents were evaporated under vacuum to afford phosphanes **8** as air-sensitive, colourless oils.

(*S*,*S*)-3,17-Dimethyl-1-phenyl-10-tosyl-4,7,13,16-tetraoxa-10-aza-1-phosphacyclooctadecane (8a): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.14 (d, ^3J = 6.5 Hz, 3 H, Me), 1.21 (d, ^3J = 6.0 Hz, 3 H, Me), 1.76 (dd, J = 13.5, J = 6.0 Hz, 1 H, PCH_2), 2.04 (dd, J_{AB} = 14.0, J = 5.5 Hz, 1 H, PCH_2), 2.14 (dd, J_{AB} = 14.0, J = 6.0 Hz, 1 H, PCH_2), 2.33 (ddd, J = 13.5, J = 7.5, J = 2.0 Hz, 1 H, PCH_2), 2.44 (s, 3 H, Me), 3.4–3.7 (18 H), 7.31 (d, J = 8.8 Hz, 2 H, Ar), 7.4 (3 H, Ph), 7.56 (2 H, Ph), 7.73 (d, J = 8.5 Hz, 2 H, Ar) ppm. ^{31}P NMR ($CDCl_3$): δ = –34 ppm. HRMS (E.S.I.): calcd. for $C_{27}H_{40}NO_6PS{\cdot}H$ 538.2392; found 538.2410.

(*S*,*S*)-1,3,17-Triphenyl-10-tosyl-4,7,13,16-tetraoxa-10-aza-1-phosphacyclooctadecane (8b): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.89 (dd, J = 13.5, J = 3.9 Hz, 1 H, PCH_2), 2.3 (m, 2 H, PCH_2), 2.33 (s, 3 H, Me), 2.48 (dd, J = 13.8, J = 9.6 Hz, 1 H, PCH_2), 3.2–3.8 (m, 16 H), 4.3 (m, 2 H), 7.0–7.8 (Ph) ppm. ^{31}P NMR ($CDCl_3$): δ = –32 ppm. HRMS (E.S.I.): calcd. for $C_{37}H_{44}NO_6PS{\cdot}Na$ 684.2525; found 684.2524.

Synthesis of the Ruthenium Complex 9: The ruthenium dimer [(*p*-cymene)$RuCl_2]_2$ (34 mg, 0.055 mmol) was added to a solution of the crude phosphane **8b** in CH_2Cl_2 (2 mL), obtained by reduction of the phosphane oxide **7b** (100 mg, 0.14 mmol). After the mixture had been stirred at room temperature for 15 min, ^{31}P NMR analysis showed total conversion of **8b** into the ruthenium complex **9**. The final product was purified by flash chromatography on silica gel with hexane/ethyl acetate (30:70) as the eluent. **9:** Orange-red solid, m.p. 124 °C. $[\alpha]_D$ = +8 (*c* = 0.2, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.10 (d, ^3J = 6.5 Hz, 3 H, Me), 1.20 (d, ^3J = 7.0 Hz, 3 H, Me), 1.68 (s, Me), 2.3 (m, 2 H, C*H*Me_2 + CH_2), 2.43 (s, Me), 2.54 (dd, J = 14.0, J = 5.5 Hz, 1 H, CH_2), 2.92 (ddd, J = 16.0, J = 9.0, J = 3.5 Hz, 1 H, CH_2), 3.08–3.17 (m, 3 H), 3.3–3.65 (m, 9 H), 3.7 (m, 1 H), 3.77 (m, 1 H), 3.85–3.96 (m, 3 H), 4.3 (q, J = 7.5 Hz, 1 H, CHO), 5.03 (d, ^3J = 6.0 Hz, 1 H, $CH_{p\text{-cymene}}$), 5.19 (t, ^3J = 10.0 Hz, 1 H, CHO), 5.23 (d, ^3J = 6.0 Hz, 1 H, $CH_{p\text{-cymene}}$), 5.28 (d, ^3J = 6.0 Hz, 1 H, $CH_{p\text{-cymene}}$), 5.35 (d, ^3J = 6.0 Hz, 1 H, $CH_{p\text{-cymene}}$), 7.16–7.22 (4 H, Ar), 7.3 (Ar), 7.4–7.5 (4 H, Ar), 7.5 (3 H, Ar), 7.72 (d, J = 8.5 Hz, 2 H, Ar), 8.02–8.06 (2 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, selected data): δ = 16.7 (Me), 20.5 (Me), 21.0 (Me), 21.6 (Me), 28.9 (d, $^1J_{C,P}$ = 22.6 Hz, PCH_2), 29.24 (C*H*Me_2), 37.5 (d, $^1J_{C,P}$ = 23.3 Hz, PCH_2), 49.4 (NCH_2), 50.1 (NCH_2),65.3, 68.0, 68.8, 69.2, 69.5, 70.7 (OCH_2), 76.3 (d, $^2J_{C,P}$ = 9.8 Hz, OCH), 78.2 (d, $^2J_{C,P}$ = 9.8 Hz, OCH), 84.0, 84.8, 85.6, 86.1 ($CH_{p\text{-cymene}}$), 133.8 (d, $^1J_{C,P}$ = 40.0 Hz, PC_{Ar}), 134.8 (C_{Ar}), 141.1 (d, $^3J_{C,P}$ = 9.8 Hz, C_{Ar}), 142.2 (C_{Ar}), 142.8 (d, $^3J_{C,P}$ = 13.6 Hz, C_{Ar}) ppm. ^{31}P NMR ($CDCl_3$): δ = 13 ppm. MS (E.S.I.) {^{35}Cl, ^{102}Ru}: *m*/*z* (%) = 932 (4) [*M* – Cl]$^+$, 762 (32) [(phosphane) Ru – H]$^+$, 684 [phosphane + Na]$^+$ (100).

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