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Additional Data on the Synthesis and Properties of Chiral 1,2-Bis(phosphetano)benzenes

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Abstract—The synthesis of chiral, C_2-symmetric 1,2-bis(phosphetano)benzenes **2** has been extended to the benzyl-substituted derivative **2c** (R=CH_2Ph). Stable ruthenium and palladium complexes containing ligands **2** have been isolated. X-Ray diffraction studies have been performed on the monoborane adduct of **2a** (R=*i*-Pr) and on a palladium(II) complex of **2b** (R=Me). © 1999 Elsevier Science Ltd. All rights reserved.

Introduction

Phosphorus heterocycles are increasingly and successfully used as chiral building blocks for optically active ligands.[1] In such a context the four-membered phosphetane ring has recently been considered as a chiral synthon,[2] which led to the preparation of, amongst others, 1,2-bis(phosphetano)-benzenes **2**.[3] Diphosphines **2** represent a new, easily accessible class of chiral ligands. Their catalytic efficiency has been demonstrated for the ruthenium-catalyzed hydrogenation of functionalized carbonyls and studies on further catalytic applications are in progress. Here we afford additional information on the synthesis, coordinating behavior, and structural characterizations for these new diphosphines.

Results and Discussion

The bis-phosphetanes **2** have been prepared from 1,2-bis(phosphino)benzene and cyclic sulfates of optically pure 1,3-diols according to Eq. (1) (Scheme 1).[3] Borane complexation[4] has been used to protect the phosphorus atom toward oxidation in order to facilitate the purification step.

So far compounds **2** have been prepared for R=methyl, ethyl, isopropyl and cyclohexyl. Catalytic tests on the ruthenium-catalyzed hydrogenation of functionalized ketones showed that chiral induction increases significantly with the steric hindrance of the R substituent. At least for the reactions examined to date, very bulky isopropyl or cyclohexyl groups are needed to attain high enantiomeric excesses, while the methyl substituted derivative gives moderate to low enantioselectivities. We can reasonably assume that geometrical constraints related to the four-membered ring are responsible for the observed trends. Particularly, the small intracyclic bond angles of the phosphetane moiety should entail large exocyclic bond angles at the phosphorus atom and at the α-carbons. This should increase the distance between the C_2-symmetry axis and the R substituent in **2**, with respect, for instance, to the analogous phospholane-based DuPHOS ligands.[1a] An X-ray diffraction study of the borane complex (*S*,*S*)-**3a** (R=*i*-Pr) has been performed (ORTEP drawing is given in Fig. 1. Selected bond angles and distances are reported in Table 1).

Indeed, the solid state structure shows a C5–P1–C2 angle of 108.0(1)° and a P1–C2–C18 angle of 119.3(2)° for the trivalent phosphetane moiety. Both angles are significantly larger than the corresponding bond angles in the reported (COD)Rh(MeDuPHOS)$^+PF_6^-$ complex,[5] where they are of 102.5(4) [or 104.2(4)] and 115.3(6) [or 115.6(6)] degrees, respectively. Thus, compared to the DuPHOS series, more bulky substituents are required to similarly hinder the phosphorus environment in **2**, or the metal environment in their complexes, and consequently afford significant chiral discrimination.

From the data in Table 1, the effect of borane complexation on structural parameters can also be noticed: it appears that BH_3 complexation reduces bond distances and increases bond angles at the phosphorus atom. This should result from merely electronic effects; that is, an increased s-character for the P–C bonds in the borane complex with respect to the trivalent phosphetane.

Keywords: chiral ligands; 1,2-bis(phosphetano)benzenes; hydrogenation.
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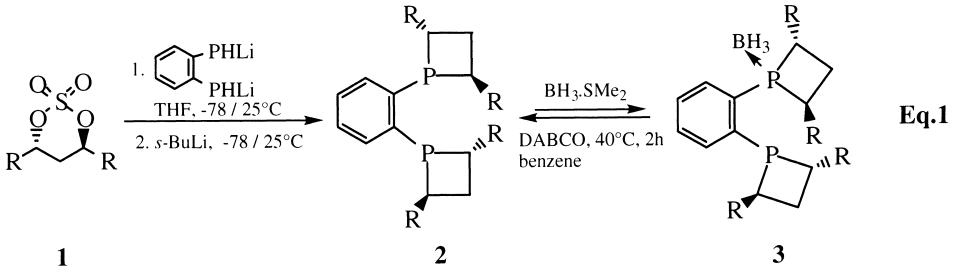


Scheme 1.

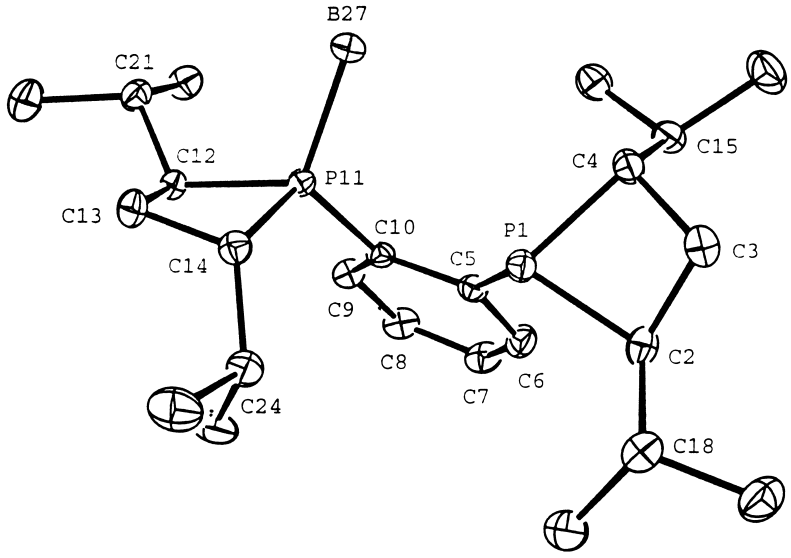


Figure 1. Crystal structure of the 1,2-bis[(*S*,*S*)-2,4-diisopropylphosphetano]benzene borane complex **3a**. The (*S*,*S*)-enantiomorph refined to lower *R* values, which is consistent with the expected (*S*,*S*)-configuration of the phosphetane moiety.

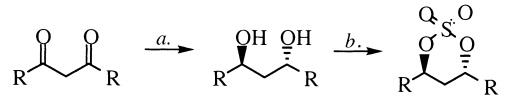
The nature of the α-substituent being a crucial structural feature of ligands **2**, we briefly examined the availability of other derivatives within the same series bearing new, bulky R groups, that is R=*t*-Bu, CH_2*t*-Bu and CH_2Ph. These syntheses require, firstly, preparation of the optically pure 1,3-diols, of the corresponding cyclic sulfates, and then reaction with 1,2-bis(phosphino)benzene. According to the reported method,[6,7] the required chiral diols should be available through ruthenium–Binap catalyzed hydrogenation of the corresponding 1,3-diketones.

Catalytic hydrogenations of 1,5-diphenyl-2,4-pentanedione **4c**[8] and 2,2,6,6-tetramethylheptanedione **4d** afforded the expected *anti* diols in high diastereomeric and enantiomeric excesses. The optically pure diols (*S*,*S*)-**5c** and (*R*,*R*)-**5d** were obtained after crystallization of the crude hydrogenation mixtures. On the other hand, the 2,2,8,8-tetramethyl-4,6-nonanedione **4e** could not be hydrogenated with adequate selectivity by the ruthenium–Binap catalyst: the *anti* diol was obtained in only moderate e.e. (about 70%) as a mixture with the *syn* isomer (d.e. of about 50%). Thus, diol **5e** could not suitably be applied to the phosphetane synthesis.

The cyclic sulfates **1c** (R=CH_2Ph) and **1d** (R=CMe_3) have been prepared according to the Sharpless procedure[9] (Eq. (2)) (Scheme 2) and then reacted with the dilithium 1,2-bis(phosphino)benzene as shown in Eq. (1). The cyclic sulfate **1d** failed to react with the lithiated diphosphine under the usual reaction conditions, although

Table 1. Selected bond angles (degrees) and distances (Å) for compound **3a**. For comparison, the corresponding values for the (COD)Rh(MeDuPHOS)$^+PF_6^-$ complex are given from Ref. 1a

Bond distances						
Compound **3a**	P1–C5	1.840(2)	P(1)–C(2)	1.863(3)	P(1)–C(4)	1.887(3)
	P11–C10	1.817(2)	P(11)–C(12)	1.851(2)	P(11)–C(14)	1.849(3)
DuPHOS–Rh		1.816(7)		1.843(8)		1.842(8)
Bond angles						
Compound **3a**	C5–P1–C2	108.0(1)	C5–P1–C4	111.7(4)	C2–P1–C4	76.9(1)
	C10–P11–C12	111.9(1)	C10–P11–C14	116.9(1)	C12–P11–C14	80.1(1)
DuPHOS–Rh		104.2(4)		109.0(4)		94.4(4)



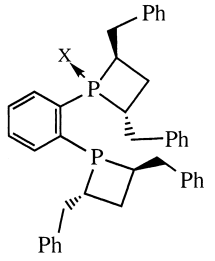
4c R = CH_2Ph
4d R = *t*-Bu
4e R = CH_2*t*-Bu

5c-e **1c, d** **Eq.2**

a. (COD)Ru(2-Me-allyl)$_2$ / (*R*)-Binap / HBr (0.2-0.5%)[7], H_2, MeOH.
b. 1. $SOCl_2$, 2. $RuCl_3$, $NaIO_4$.

Scheme 2.

1-phenyl-2,4-bis(*tert*-butyl)phosphetane could be obtained from **1d** and dilithiophenylphosphine.[10] The cyclic sulfate **1c** afforded the expected 1,2-bis(phosphetano)benzene **2c** which was isolated as its monoborane complex **3c** in 45% yield. The trivalent phosphetane **2c** has been removed from its borane adduct in quantitative yield by phosphine–amine exchange with 1,4-diazabicyclo[2.2.2]-octane, and fully characterized.



(S,S)-**2c** X = lone pair
(S,S)-**3c** X = BH_3

As a preliminary evaluation of the catalytic properties, the new ligand has been tested as a chiral auxiliary in the ruthenium catalyzed hydrogenations of β-ketoesters and compared to the previously reported phosphetanes **2**. Results are given in Table 2. The catalyst amount and conditions for these model reactions are nonoptimized. On the whole, the catalytic activity as well as the enantioselectivity levels obtained with **2c** are comparable to those obtained with the isopropyl- and cyclohexyl-substituted phosphetanes **2a** and **2f** in analogous conditions.

For all the hydrogenation tests performed with ligands **2**, the ruthenium catalyst was prepared in situ from (COD)Ru(2-methylallyl)$_2$ and the chiral diphosphine by addition of two equivalents of methanolic HBr. In such conditions '(diphosphine)$RuBr_2$' complexes are supposed to be formed and act as catalyst precursors.[7] When the reaction was performed with ligand **2b** (R=Me), ^{31}P-NMR analysis of the reaction mixture showed the presence of a major compound (δ=92 ppm) and small amounts of other ruthenium complexes (δ=129 ppm; 118.2 (t, J=17.4 Hz) and 93.9(t) ppm). When isolated in the pure state, the major compound does not afford an active catalyst, while the crude mixture displays acceptable catalytic activity. A similar behavior has been reported for the ruthenium–Binap catalyst generated from (Binap)Ru(OCOMe)$_2$ and two equivalents of HCl.[11]

Table 2. Ruthenium–**2c** catalyzed hydrogenations of β-ketoesters. For comparison, results obtained with other phosphetanes **2** are reported (1% catalyst, MeOH, 80 bars, 80°C, 20 h)

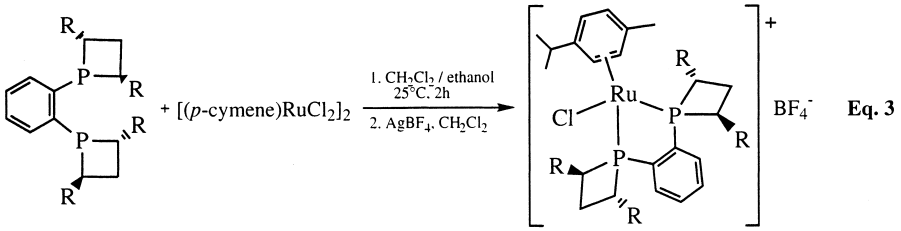
Substrate	Ligand (*S,S*)-**2c**		Ligand	e.e.%	[conv.]
	e.e.%	[conv.]			
$MeCOCH_2CO_2Me$	85(*S*)	100	**2a** R=*i*Pr	86(*R*)	100
			2f R=Cy	84(*R*)	100
$PhCOCH_2CO_2Et$	86(*R*)	100	**2a** R=*i*Pr	86(*S*)	100
i$PrCOCH_2CO_2Et$	87(*R*)	50	**2a** R=*i*Pr	90(*S*)	75

More detailed studies are required to establish the precise nature of the catalytically active species, all the more because the coordinating properties and behavior of phosphetanes **2** toward transition metals are totally unknown to date. Thus, to get insight into this field, we started studies on the synthesis and characterization of metal complexes of phosphetanes **2** by using **2a** (R=*i*-Pr) and **2b** (R=Me) as model substrates. The first examples of ruthenium and palladium complexes containing **2** are described hereafter.

Ruthenium complexes of the bis(phosphetano)benzenes have been prepared by reacting **2a** (R=*i*-Pr) or **2b** (R=Me) with the (*p*-cymene)ruthenium dichloride dimer in a dichloromethane–ethanol mixture[12] (Eq. (3)) (Scheme 3). Complexation of **2** takes place in mild conditions. Subsequent addition of $AgBF_4$ and crystallization afforded complexes **6a** or **6b**, respectively, in about 40% yield, as orange-yellow, air stable solids. ^{31}P-NMR spectra show the AB patterns characteristic for the ruthenium–*p*-cymene–diphosphine complexes: δ 85.1 and 96.2 (AB, J_{P-P}=29.9 Hz) for **6a** and δ 101.8 and 115.2 (AB, J_{P-P}=29.9 Hz) for **6b**. Other NMR and analytical data fully support the proposed structures.

Palladium complexes of **2a** and **2b** have also been prepared by ligand exchange reactions starting from $(PhCN)_2PdCl_2$ according to Eq. (4) (Scheme 4). The final products were purified by crystallization and fully characterized.

Typical patterns are observed in the ^{13}C-NMR spectra of **7**, due to the virtual coupling of the two phosphorus atoms (see

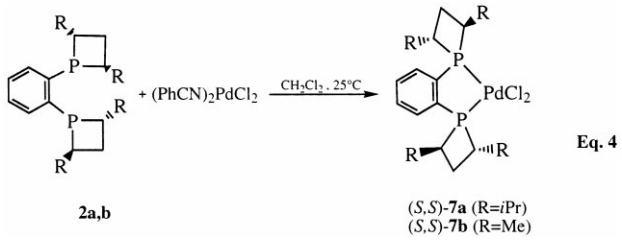


2a,b

(*S,S*)-**6a** (R=*i*Pr)
(*S,S*)-**6b** (R=Me)

Eq. 3

Scheme 3.



Scheme 4.

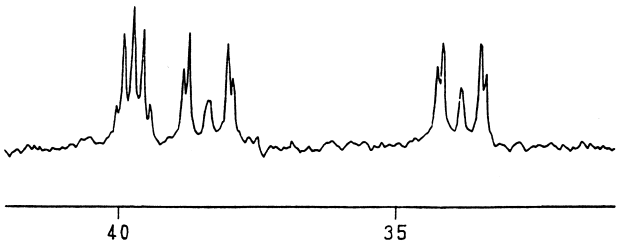


Figure 2. ^{13}C-NMR spectrum of **7b**: $CDCl_3$, phosphetane ring signals.

Fig. 2). The solid state structure of **7b** has also been determined. The ORTEP drawing, selected bond angles and distances are given in Fig. 3. Fig. 3 clearly shows the two untouched phosphetane rings as well as chelation of the bidentate ligand to palladium. Bond angles and distances at the phosphorus atom in **7b** are very similar to those observed in the borane complexed moiety of **3a** (see above).

Thus, the experiments of Eqs. (3) and (4) confirm that the 1,2-bis(phosphetano)benzenes **2** behave as chelating ligands and, especially, that Ru(II) and Pd(II) derivatives do not affect the four-membered phosphetane ring, as required for catalytic reactions. Further studies on the coordination chemistry and catalytic properties of ligands **2** are in progress. Results will be reported later.

Experimental

All reactions were carried out under argon in dry solvents. NMR spectra were recorded on a Bruker AM 200 spectrometer (200.13 MHz for ^{1}H, 50.32 MHz for ^{13}C, 81.01 MHz for ^{31}P) or on a Bruker 400 spectrometer at 400.13 MHz for ^{1}H, 100.61 MHz for ^{13}C and 161.97 MHz for ^{31}P. Chromatographic separations were performed on neutral alumina columns.

Ruthenium catalyzed hydrogenations of the β-diketones 4c–e (Eq. (2))

Diketone **4c** was prepared in 36% yield according to Ref. 8. Diketone **4e** was prepared in 66% yield by Claisen condensation of phenyl 3,3-dimethylbutyrate with methyl neopentyl ketone in the presence of LDA and purified via the copper chelate complex.[13]

The catalytic hydrogenation of **4c** to **5c** is given hereafter as a representative example.

(*R*,*R*)-1,5-Diphenyl-2,4-pentanediol (5c). (*R*)-BINAP (32 mg, 0.05 mmol) and (COD)Ru(2-methylallyl)$_2$ (12.7 mg, 0.04 mmol) were placed in a 50 mL flask and 2 mL of anhydrous acetone (distilled over K_2CO_3) were added. To the resulting suspension was added a methanolic HBr solution (0.52 mL, 0.17 M) and the reaction mixture was stirred at room temperature for 30 min. The solvent was removed under vacuum. Methanol (10 mL) and 1,5-diphenyl-2,4-pentanedione (1.0 g, 4 mmol) were added to the reaction vessel which was then placed in a 250 mL stainless steel autoclave, under argon. The argon atmosphere was replaced by hydrogen and the autoclave pressurized to an initial pressure of 70 bars H_2. The reaction was allowed to proceed at 50°C for 70 h. Complete conversion to the *anti* diol **5c** was confirmed by ^{1}H NMR analysis: δ ($CDCl_3$) 1.73 (t, $^3J_{H-H}$=5.8 Hz, 2H, CH_2), 2.79 (d, $^3J_{H-H}$=6.6 Hz, 4H, CH_2), 4.22 (m, 2H, CHOH), 7.2–7.3 (m, Ph) ppm. The product was determined to be >95% enantiomerically pure (^{1}H NMR of the Mosher ester prepared from (*S*)-MTPA-Cl in pyridine at 60 °C for 4 h. ^{1}H NMR of the (*R*,*R*)-**5c**-(*R*)-MPTA diester: δ 1.76 (dd, $^3J_{H-H}$=7.4 and 5.4 Hz, 2H, CH_2), 2.56 (dd, *A*B, $^2J_{A-B}$=13.7 Hz, $^3J_{H-H}$=7.5 Hz, 2H, CH_2), 2.91 (dd, A*B*, $^3J_{H-H}$=5.9 Hz, CH_2), 3.30 (6H, OMe), 5.24 (m, 2H, CH–O) ppm). The crude reaction mixture was recrystallized from ether–pentane to afford the enantiomerically pure diol **5c** (1.0 g, 90% yield). The absolute configuration was assigned from

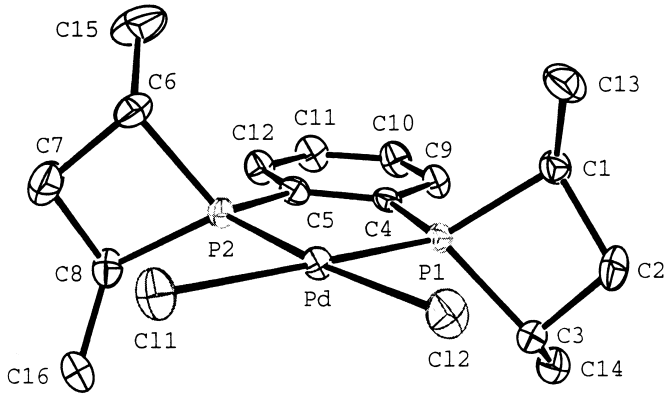


Figure 3. Solid state structure of (*S*,*S*)-**7b**. Selected bond distances: P(1)–C(4) 1.813(3), P(1)–C(1) 1.841(3), P(1)–C(3) 1.859(4), P(1)–Pd 2.2223(8), Pd–Cl(2) 2.3707(8). Bond angles: C(4)–P(1)–C(1) 111.1(1), C(4)–P(1)–C(3) 116.1(2), P(1)–C(1)–C(13) 120.0(3), C(1)–P(1)–C(3) 79.5(2), P(1)–Pd–Cl(2) 90.88(3).

the optical rotation value, by comparison with literature data[14] ($[\alpha]_D$=+6 (*c*=1, $CHCl_3$)).

(*S,S*)-2,2,6,6-Tetramethyl-3,5-heptanediol (5d). Hydrogenation of **4d** (5 g, 27 mmol) was performed with 0.25% of the ruthenium–(*R*)-BINAP catalyst at 100 bars of hydrogen pressure, at 80°C for 6 days. ^{1}H NMR ($CDCl_3$) δ 0.93 (18H, Me), 1.45 (dd, $^3J_{H-H}$=5.2 and 7.5 Hz, 2H, CH_2), 3.54 (m, 2H, CHOH) ppm. $[\alpha]_D$=−78 (*c*=1, MeOH).

2,2,8,8-Tetramethyl-4,6-nonanediol (5e). Hydrogenation of **4e** was performed on a 2 g scale with 0.5% of Ru–BINAP catalyst at 50 bar. The reaction mixture was heated at 50°C for 8 days. A 2:1 mixture of the *anti* and *syn* diols was obtained. A small amount of the pure *anti* diol was recovered from the crude product after crystallization from dichloromethane–ether. *Anti*-**5e**: ^{1}H NMR ($CDCl_3$) 0.97 (18H, Me), 1.34 (dd, AB, $^2J_{H-H}$=14.5 Hz, $^3J_{H-H}$=2.9 Hz, 2H, CH_2), 1.51 (dd, AB, $^3J_{H-H}$=8.1 Hz, 2H, CH_2), 1.58 (dd, $^3J_{H-H}$=6.2 and 5.3 Hz, 2H, CH_2), 2.18 (OH), 4.1 (m, 2H, CHOH) ppm.

Preparation of the cyclic sulfates 1c,d

(*R,R*)-1,5-Diphenyl-2,4-pentanediol cyclic sulfate (1c). To a solution of (*R,R*)-1,5-diphenyl-2,4-pentanediol (0.84 g, 3.3 mmol) in 6 mL CCl_4 were added 0.26 mL (3.6 mmol) of thionyl chloride. The resulting solution was heated at reflux for 1 h. The solvent was removed on a rotary evaporator and the residue was dissolved in a mixture of CCl_4 (2 mL), MeCN (2 mL) and water (3 mL), and cooled to 0°C. $RuCl_3$ (about 10 mg, 5×10^{-2} mmol) and $NaIO_4$ (1.0 g, 4.9 mmol) were added. The mixture was allowed to warm up to room temperature and stirred for about 1 h. Ether (30 mL) was added, the organic phase was separated, washed with water and dried over $MgSO_4$. The ether solution was filtered through a pad of silica gel. Evaporation of the solvent afforded pure **1c** which was recrystallized from a hexane–ether mixture (yield 0.88 g, 85%), colorless solid. ^{1}H NMR ($CDCl_3$) δ 2.04 (t, $^3J_{H-H}$=5.6 Hz, 2H, CH_2), 3.06 (dd, AB, $^2J_{AB}$=14.0 Hz, $^3J_{H-H}$=7.6 Hz, 2H, CH_2), 3.38 (dd, AB, $^3J_{H-H}$=6.7 Hz, CH_2), 5.12 (m, CH–O), 7.15–7.36 (Ph); ^{13}C NMR ($CDCl_3$) δ 30.5 (CH_2), 39.7 (CH_2), 83.7 (CH–O), 127.3, 128.8, 129.2, 134.9 (Ph) ppm. $[\alpha]_D$=+33 (*c*=1, $CHCl_3$).

(*S,S*)-2,2,6,6-Tetramethyl-3,5-heptanediol cyclic sulfate (1d). The same procedure as for **1c** afforded **1d** as a colorless solid in 67% yield. ^{1}H NMR ($CDCl_3$) δ 1.04 (s, 18H, Me), 2.02 (t, $^3J_{H-H}$=8.1 Hz, 2H, CH_2), 4.33 (t, $^3J_{H-H}$=8.1 Hz, 2H, OCH) ppm. $[\alpha]_D$=+48 (*c*=1, $CHCl_3$).

1,2-bis[(*S,S*)-2,4-Dibenzylphosphetano]benzene borane complex (3c). A solution of 1,2-bis(phosphino)benzene (0.20 g, 1.4 mmol) in THF (10 mL) was cooled to −78°C and *n*-BuLi (2.5 M solution in hexane, 1.2 mL, 2.2 eq.) was added. After warming to room temperature, the resulting orange-red solution of dilithium bis(phosphino)benzene was then added to a solution of the cyclic sulfate **1c** (0.92 g, 2.9 mmol) in THF (150 mL) at −78°C. The reaction mixture was allowed to warm to room temperature and stirred for about 1 h. After cooling to −78°C, 2.2 eq. of *s*-BuLi (1.3 M solution, 2.4 mL, 3.1 mmol) were added. The reaction was allowed to proceed for about 30 min at −78°C, then warmed up to r.t. and stirred for 2 h. Then, 0.3 mL of the $BH_3{\cdot}SMe_2$ complex were added. After hydrolysis, the crude mixture was concentrated under vacuum. Addition of a degassed hexane–ether 1:1 mixture led to a gelatinous precipitate which was filtered under inert atmosphere. The colorless solution was evaporated and the residue chromatographed on alumina with a hexane–ether gradient as eluent. The borane complex **3c** was eluted with a hexane–ether 90:10 mixture. The colorless solid (0.39 g, 45% yield) was recrystallized from ether–pentane. ^{31}P NMR (C_6D_6) δ 10.0 (d, $^3J_{P-P}$=34.3 Hz), 50.8 (broad); ^{13}C NMR (C_6D_6) (100.6 MHz, selected data) δ 29.4 (d, $^2J_{C-P}$=11.1 Hz, CH_2), 31.8 (d, $^1J_{C-P}$=6.5 Hz, CH), 32.7 (CH_2), 32.9 (d, $^1J_{C-P}$=4.9 Hz, CH), 36.2 (m, $2CH_2$), 36.5 (dd, J_{C-P}=40.4 and 8.7 Hz, CH), 38.1 (CH_2), 38.5 (d, $^1J_{C-P}$=37.9 Hz, PCH), 41.2 (d, $^2J_{C-P}$=20.9 Hz, CH_2) ppm. Mass spectrum (DCI/NH_3) *m/e* 597 (M+1, 38%), 583 (100%). $[\alpha]_D$=+302 (*c*=0.5, CH_2Cl_2). Anal. Calcd. for $C_{40}H_{43}BP_2$: C, 80.54; H, 7.26. Found, C, 78.49; H, 7.14.

1,2-bis[(*S,S*)-2,4-Dibenzylphosphetano]benzene (2c). The phosphine–borane complex **3c** (150 mg, 0.25 mmol) was reacted with DABCO (30 mg, 0.27 mmol) in benzene (3 mL) at 50°C for 2 h. The reaction mixture was directly chromatographed under argon on a short alumina column with hexane–ether 95:5 as eluent. The final product, **2c**, was obtained in quantitative yield as a colorless oil. ^{31}P NMR (C_6D_6) δ 11.7; ^{1}H NMR (C_6D_6) δ 2.0–2.15 (m, 6H), 2.7–2.9 (m, 10H), 6.8–7.0 (m, Ph); ^{13}C NMR (100.6 MHz, selected data), (C_6D_6) δ 29.1 (CH), 30.8 (CH_2), 33.3 (t, J_{C-P}=6.7 Hz, CH), 36.8 (CH_2), 40.1 (t, J_{C-P}=9.2 Hz, CH_2) ppm.

Ruthenium–2c catalyzed hydrogenations of carbonyl derivatives. The ruthenium catalyst was prepared as in Ref. 7 from (COD)Ru(2-methylallyl)$_2$ (3.2 mg, 1×10^{-2} mmol) and ligand **2c** (7.0 mg, 1.2×10^{-2} mmol) in acetone. After addition of 2.2 eq. of methanolic HBr and stirring for 30 min, the solvent was evaporated under vacuum. A solution of the appropriate substrate (1 mmol) in 1 mL of degassed methanol (or ethanol) was added to the catalyst. The glass vessel was placed under argon in a stainless steel autoclave which was then pressurized with H_2 at 80 bars. The reaction was allowed to proceed at 80°C for 20 h. Conversion rates were determined by ^{1}H NMR. Enantiomeric excesses and absolute configurations of the final alcohols were assigned by GC (Lipodex A column).

Synthesis of the ruthenium complexes 6. [(*p*-cymene)-$RuCl_2$]$_2$ (65 mg, 0.11 mmol) was reacted with **2b** (0.24 mmol) in a dichloromethane (0.5 mL)–ethanol (1.5 mL) mixture. After 2 h at room temperature, the solvent was removed under vacuum. The residue was taken up in dichloromethane (1 mL) and $AgBF_4$ (42 mg, 0.2 mmol) was added. After a few minutes a pale yellow solid formed which was separated from the reaction mixture. Recrystallization from dichloromethane–ether afforded pure **6b** in 43% yield. The same procedure was applied to the synthesis of **6a**.

6a: Orange solid; ^{31}P NMR (CD_2Cl_2) δ 85.1 and 96.2 (AB, J_{P-P}=29.9 Hz); ^{1}H NMR (CD_2Cl_2) δ (400.1 MHz, selected

data) δ 0.04 (d, $^3J_{H-H}$=6.5 Hz, 3H, Me), 0.37 (d, $^3J_{H-H}$=6.5 Hz, 3H, Me), 0.53 (d, $^3J_{H-H}$=6.6 Hz, 3H, Me), 0.82 (d, $^3J_{H-H}$=6.4 Hz, 3H, Me), 0.92 (d, $^3J_{H-H}$=6.3 Hz, 3H, Me), 0.98 (d, $^3J_{H-H}$=6.3 Hz, 3H, Me), 1.09 (d, $^3J_{H-H}$=6.4 Hz, 3H, Me), 1.15 (d, $^3J_{H-H}$=6.8 Hz, 3H, Me), 1.27 (d, $^3J_{H-H}$=6.9 Hz, 3H, Me), 1.34 (d, $^3J_{H-H}$=7.0 Hz, 3H, Me), 2.07 (s, Me), 6.18 (d, $^3J_{H-H}$=6.3 Hz, 1H, CH),), 6.22 (d, $^3J_{H-H}$=6.0 Hz, 1H, CH), 6.55 (CH), 6.65 (CH), 7.7 (m, 2H), 8.0–8.2 (m, 2H); ^{13}C NMR (CD_2Cl_2; 100.6 MHz, selected data) δ 46.4 (d, $^1J_{C-P}$=33.1 Hz, PCH), 49.3 (d, $^1J_{C-P}$=31.4 Hz, PCH), 51.7 (d, $^1J_{C-P}$=30.4 Hz, PCH), 56.4 (d, $^1J_{C-P}$=37.5 Hz, PCH), 87.1 (d, $^2J_{C-P}$=9.1 Hz, CH-*p*-cymene), 87.5 (d, $^2J_{C-P}$=8.8 Hz, CH-*p*-cymene), 89.9 (CH-*p*-cymene), 95.7 (C-*p*-cymene), 98.2 (CH-*p*-cymene) ppm. Anal. Calcd. for $C_{34}H_{54}BClF_4P_2Ru$: C, 54.59; H, 7.27. Found, C, 53.41; H, 7.13.

6b: Yellow solid; ^{31}P NMR (CD_2Cl_2) δ 101.8 and 115.2 (AB, J_{P-P}=29.9 Hz); ^{1}H NMR (CD_2Cl_2, selected data) δ 0.86 (dd, $^3J_{H-P}$=18.2 Hz, $^3J_{H-H}$=7.2 Hz, 3H, Me), 1.14 ($^3J_{H-H}$=6.9 Hz, Me), 1.23 ($^3J_{H-H}$=6.8 Hz, Me), 1.0–1.2 (m, Me), 1.5–1.7 (2 Me), 2.11 (s, Me), 6.18 (d, $^3J_{H-H}$=6.0 Hz, CH-*p*-cymene), 6.30 (d, $^3J_{H-H}$=6.5 Hz, CH-*p*-cymene), 6.60 (d, $^3J_{H-H}$=6.2 Hz, CH-*p*-cymene), 6.70 (d, $^3J_{H-H}$=6.5 Hz, CH-*p*-cymene), 7.7 (m, 2H), 8.2 (m, 2H); ^{13}C NMR (CD_2Cl_2; 100.6 MHz, selected data) δ 33.8 (d, $^1J_{C-P}$=40.8 Hz, PCH), 35.1 (d, $^1J_{C-P}$=33.7 Hz, PCH), 39.1 (d, $^1J_{C-P}$=34.4 Hz, PCH), 39.4 (d, $^2J_{C-P}$=15.9 Hz, CH_2), 39.6 (d, $^2J_{C-P}$=11.6 Hz, CH_2), 41.6 (d, $^1J_{C-P}$=39.7 Hz, PCH), 86.8, 90.4, 93.5, 97.6 (CH-*p*-cymene), 139.1 (dd, J_{C-P}=37.2 and 27.2 Hz, PC), 140.1 (dd, J_{C-P}=33.3 and 26.7 Hz, PC) ppm. Anal. Calcd. for $C_{26}H_{38}BClF_4P_2Ru$: C, 49.1; H, 6.02. Found, C, 48.82; H, 6.09.

Synthesis of the palladium complexes 7. A solution of the bis(phosphetane) **2b** (42 mg, 0.15 mmol) in dichloromethane (1 mL) was added to a CH_2Cl_2 solution of $(PhCN)_2PdCl_2$ at room temperature. After a few minutes, the solvent was removed under vacuum and the residue recrystallized from CH_2Cl_2–ether. Crystals for X-ray studies were grown from a $CDCl_3$–ether mixture. Complex **7b** was obtained as an almost colorless solid in 64% yield (44 mg). The same procedure was applied to the synthesis of complex **7a**.

7a: Pale yellow solid; ^{31}P NMR ($CDCl_3$) δ 92.5; ^{1}H NMR ($CDCl_3$) δ 0.40 (d, $^3J_{H-H}$=6.5 Hz, 6H, Me), 0.89 (d, $^3J_{H-H}$=5.9 Hz, 12H, Me), 0.92 (d, $^3J_{H-H}$=6.3 Hz, 6H, Me), 1.92 (m, 2H), 2.5–3.1 (m, 8H), 3.7 (m, 2H), 7.8 (m, 2H), 8.1 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 19.7 (t, J_{C-P}=7.5 Hz, Me), 19.9 (t, J_{C-P}=8.1 Hz, Me), 20.5 (Me), 22.3 (Me), 29.8 (4×CH), 34.2 (m, CH_2), 45.9 (m, PCH), 51.0 (m, PCH), 132.3, 132.5, 132.6, 133.1, 141.2 (t, J_{C-P}=30.1 Hz, C) ppm.

7b: ^{31}P NMR ($CDCl_3$) δ 100.1; ^{1}H NMR ($CDCl_3$) δ 1.18 (dd, $^3J_{H-P}$=19.0 Hz, $^3J_{H-H}$=7.7 Hz, 6H, Me), 1.70 (dd, $^3J_{H-P}$=22.1 Hz, $^3J_{H-H}$=7.2 Hz, 6H, Me), 2.5–3.3 (m, 6H), 4.1 (m, 2H), 7.8 (m, 2H), 8.1 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 15.6 (Me), 18.1 (Me), 33.6 (m, PCH), 38.2 (m, PCH), 39.5 (m, CH_2), 140.8 (t, J_{C-P}=29.3 Hz, C) ppm. $[\alpha]_D$=+148 (c=0.3, $CHCl_3$).

References

1. For selected references see: (a) Burk, M. J.; Gross, M. F.; Harper, T. G. P.; Kalberg, C. S.; Lee, J. R.; Martinez, J. P. *Pure Appl. Chem.* **1996**, *68*, 37 and references therein. (b) Jiang, Q.; Jiang, Y.; Xiao, D.; Cao, P.; Xhang, X. *Angew. Chem.* **1998**, *110*, 1203. (c) Dierkes, P.; Ramdeehul, S.; Barloy, L.; De Cian, A.; Fischer, J.; Kamer, P. C. J.; van Leeuwen, P. W. N.; Osborn, J. A. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3116.
2. Marinetti, A.; Kruger, V.; Buzin, F.-X. *Coord. Chem. Rev.* **1998**, *178–180*, 755.
3. (a) Marinetti, A.; Kruger, V.; Buzin, F.-X. *Tetrahedron Lett.* **1997**, *38*, 2947. (b) Marinetti, A.; Genêt, J.-P.; Jus, S.; Blanc, D.; Ratovelomanana-Vidal, V. *Chem. Eur. J.* **1999**, *5*, 1160.
4. For a recent review on phosphine–borane complexes see: Ohff, M.; Holz, J.; Quirmbach, M.; Börner, A. *Synthesis* **1998**, 1391.
5. Burk, M. J.; Feaster, J. E.; Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1993**, *115*, 10125.
6. Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley: New York, 1994, pp 1–93 and references therein.
7. (a) Genêt, J. P.; Pinel, C.; Ratovelomanana-Vidal, V.; Mallart, S.; Pfister, X.; Bischoff, L.; Caño De Andrade, M. C.; Darses, S.; Galopin, C.; Laffitte, J. A. *Tetrahedron: Asymmetry* **1994**, *5*, 675. For recent reviews see: (b) Genêt, J. P. In *Advances in Asymmetric Synthesis;* Stephenson, G. R., Ed.; Chapman & Hall: London, 1996; pp 60–92. (c) Ratovelomanana-Vidal, V.; Genêt, J.-P. *J. Organomet. Chem.* **1998**, *567*, 163.
8. Bryant, D. R.; Hauser, C. R. *J. Org. Chem.* **1962**, *27*, 694.
9. Gao, Y.; Sharpless, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 7538.
10. Marinetti, A. et al., unpublished results.
11. Mashima, K.; Hino, T.; Takaya, H. *J. Chem. Soc., Dalton Trans.* **1992**, 2099.
12. Mashima, K.; Kusano, K.; Sato, N.; Matsumura, Y.; Nozaki, K.; Kumobayashi, H.; Sayo, N.; Hori, Y.; Ishizaki, T.; Akutagawa, S.; Takaya, H. *J. Org. Chem.* **1994**, *59*, 3064.
13. Nonhebel, D. C.; Smith, J. *J. Chem. Soc. (C)* **1967**, 1919.
14. Rychnovsky, S. D.; Griesgraber, G.; Zeller, S.; Skalitzky, D. J. *J. Org. Chem.* **1981**, *56*, 5161.