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Influence of β-arranged substituents in chiral seven-membered rhodium diphosphine rings on asymmetric hydrogenation of amino acid precursors

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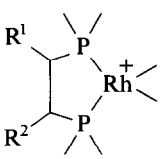
Abstract

Investigations concerning the optical induction in asymmetric hydrogenation reactions confirm the stereochemical control function of mono- and di-substituents in seven-membered chelate ring diphosphines, whereby the bulkiness of substituents in the backbone of the ligands is reflected in higher enantioselectivities.

Introduction

Chiral rhodium diphosphine five-membered ring chelates I bearing a stereogenic centre in the bridge afford extraordinarily high enantiomeric excess in the well known asymmetric hydrogenation of prochiral amino acids [1,2].



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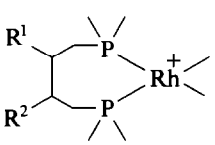


(II)

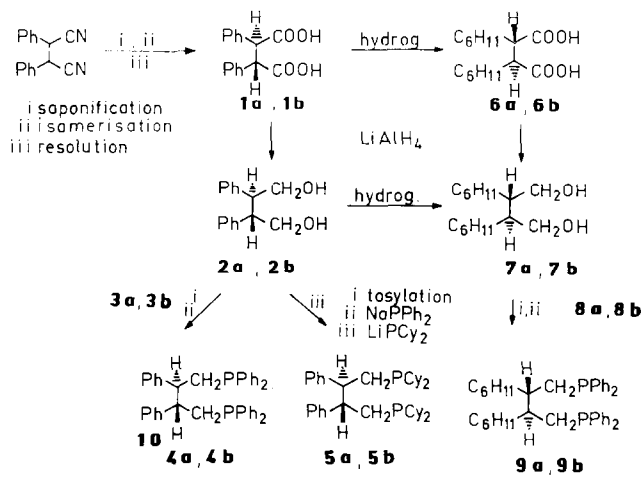
It has been pointed out, that introduction of R^1 into the rigid five-membered ring as in Prophos (R^1 = Me, R^2 = H) exerts a strong influence forcing R^1 to become equatorially arranged, and that a further substituent R^2 = Me as in Chiraphos enhances the selectivity by a few percentage points but lowers the rate considerably from that of Prophos (TN 2.5 min^{-1}) to that of Chiraphos (TN 0.6 min^{-1}) for the same substrate. Obviously one more or less bulky substituent is sufficient to fix the five-membered chelate ring. This was also verified in comparing (*S*)-Phenphos (84% ee, TN ~ 2 min^{-1}) and (*R*)-Cycphos (93% ee, TN ~ 2 min^{-1}) [3,4] the latter achieving the higher optical induction in the hydrogenation of benzamidocinnamic acid. Almost the same high enantioselectivity follows for other five-membered ring

chelates such as Norphos, Renorphos, Phellanphos, DCCP and Deguphos which all give 93–97% ee and a TN of about 1–2 min^{-1}; this means some convergence of selectivity and rate [5]. We assumed that in order to accomplish higher enantioselectivity in the analogous seven-membered chelate rings, it would be necessary to fix two bulky groups in positions 2 and 3 (II) thus increasing selectivity without reducing the high reaction rate characteristic of seven-membered chelate rings. The actions of these substituents are thought to be mainly due to steric interactions and do not reflect to any extent changes in the electron density of the donor P atoms, as has been shown recently in some other ligands [6–8].

Results and discussion

This role of the substituent was checked by the synthesis of type II compounds $R^1 = R^2$ = phenyl and enlarging the substituent to $R^1 = R^2$ = cyclohexyl. Further, the influence of steric interactions in the backbone should be clearly indicated by comparison with type II chelates with only one group (R^1 = phenyl, R^2 = H, R^1 = cyclohexyl, R^2 = H) in the bridge. The synthesis of the ligands was performed according to Schemes 1 and 2.

Saponification of the dinitrile followed by rearrangement of the *meso*-acid [9] and resolution with (1*S*,2*S*)-1-(4-nitrophenyl)-2-amino-3-hydroxypropane-1-ol (L-base) [10] provides larger amounts of the enantiomerically pure acids **1a**, **1b**, which can be hydrogenated (0.5–1.0 MPa H_2) catalytically to the acid **6a**, **6b** or reduced by $LiAlH_4$ to the alcohols **2a**, **2b** or **7a**, **7b**. The latter compounds, however, are more efficiently prepared by catalytic hydrogenation of **2a**, **2b**. Following known methods the diphosphines **4a**, **4b** and **9a**, **9b**, as well as **5a**, **5b** are achieved in moderate yields. A similar route (Scheme 2) starting from commercially available phenylsuccinic acid provides **13a**, **13b** and **16a**, **16b**. In the same manner the methyl-substituted diphosphine **20a** was obtained from methylsuccinic acid **17a**, **17b** (see Experimental section).



Scheme 1. a ≡ (*S*)-, b ≡ (*R*)-configuration.

Table 1

Catalytic asymmetric hydrogenation of (*Z*)-α-acetamidocinnamic acid (AH) and the methyl ester (AMe) by neutral rhodium complexes of **4**, **5** and **9** formed *in situ*, $[Rh(COD)Cl]_2$, 0.01 mmol

Entry	Ligand	Substrate	Half life (min)	ee [a] (%)	Configuration
1	**4b**	AH	4.0	52.4 ± 1.3 [b]	*S*
2	**4a**	AMe	4.1	21.5 ± 0.3	*S*
3	**9a**	AH	4.0	69.3 ± 0.1	*R*
4	**9a**	AMe	3.8	27.2 ± 0.1	*R*
5	**5a**	AH	12.0	33.0 ± 0.2	*R*
6	**5a**	AMe	12.5	10.0 ± 0.3	*R*

Substrate/rhodium = 100, 25 °C, 0.1 MPa H_2 pressure, 15 ml MeOH. [a] Determined by GLC. [b] Ref. 11 gives 54% ee for **4a**, configuration *R*.

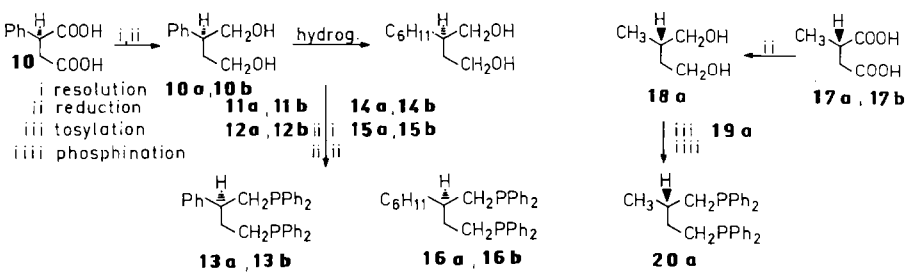
Table 2

Catalytic asymmetric hydrogenation of (*Z*)-α-acetamidocinnamic acid (AH) and the methyl ester (AMe) by cationic rhodium complexes of **4**, **5** and **9** formed *in situ*, $[Rh(COD)_2]BF_4$, 0.01 mmol

Entry	Ligand	Substrate	Half life (min)	ee [a] (%)	Configuration
1	**4a**	AH	3.7	48.2 ± 0.5	*R*
2	**4a**	AMe	3.7	21.0 ± 0.5	*S*
3	**9a**	AH	7.0	68.6 ± 0.6	*R*
4	**9a**	AMe	11.1	26.9 ± 0.5	*R*
5	**5a**	AH	10.9	32.4 ± 0.4	*R*
6	**5a**	AMe	3.0	10.6 ± 0.3	*R*

For conditions see Table 1. [a] Determined by GLC.

The diphosphines **4**, **5** and **9** form neutral and cationic rhodium complexes which were used in the asymmetric hydrogenation of acylamidocinnamic acid derivatives. The results are given in Tables 1 and 2 and show that (entries 1 and 3 or 2 and **4**, respectively) the higher optical induction exerted by **9** (bearing the two bulkier cyclohexyl groups) is clearly outlined regardless of the applied neutral or cationic complexes and of the substrates, compared with the ligand **4a**. Since rate and induction are nearly equal for neutral and cationic complexes this indicates that the same catalytically active species are formed. The necessity of two groups in the 2 and 3 positions of the seven-membered ring becomes obvious considering the values



Scheme 2.

Table 3

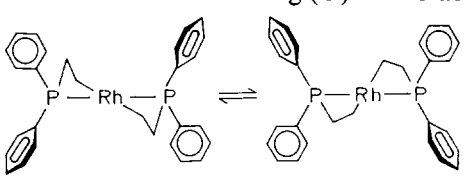
Catalytic asymmetric hydrogenation of (*Z*)-α-acetamidocinnamic acid (AH) and the methyl ester (AMe) by neutral rhodium complexes of **13**, **16** and **20** formed *in situ*, $[Rh(COD)Cl]_2$, 0.01 mmol

Entry	Ligand	Substrate	Half life (min)	ee [a] (%)	Configuration
1	**13b**	AH	1.8	13.2±0.2	*S*
2	**16a**	AH	2.8	43.4±0.3	*R*
3	**20a**	AH	1.2	25.3±0.1	*S*
4	**13b**	AMe	2.5	10.1±0.1	*R*
5	**16a**	AMe	2.9	23.2±0.1	*R*
6	**20a**	AMe	1.2	13.7±0.1	*S*

For conditions see Table 1. [a] Determined by GLC.

of Tables 3 and 4, where the results for ligands which bear only one substituent on the stereogenic centre (phenyl **13**, cyclohexyl **16** or methyl **20**) are compiled.

In step with the change from AH to AMe, the enantiomeric excess is generally lowered and the half-life increased. Once more the bulkier the group in the backbone, the higher the ee%, being lower for the AMe series compared with the AH series. The most striking effect, however, is due to the observed configuration of the amino acids. Following general rules [12] one would anticipate for the seven-membered chelates of C_2-symmetry using the (*S*,*S*)-configurated catalysts, the chair λ-conformation indicating (*S*)-amino acids.



Configurations in Tables 1–4 display the inverse relationship observed previously [11] with two exceptions (see below). This may be attributed to the steric hindrance of the equatorially arranged substituents giving rise to a twisted boat-conformation and hence to (*R*)-amino acids, an assumption to be established by X-ray structure analysis. Hydrogenation of substrate acids and esters results in a 2.4- to 2.6-fold

Table 4

Catalytic asymmetric hydrogenation of (*Z*)-α-acetamido-cinnamic acid (AH) and the methyl ester (AMe) by cationic rhodium complexes of **13**, **16** and **20** formed *in situ*, $[Rh(COD)_2]BF_4$, 0.01 mmol

Entry	Ligand	Substrate	Half life (min)	ee [a] (%)	Configuration
1	**13b**	AH	1.4	13.1±0.1	*S*
2	**16a**	AH	1.3	43.1±0.2	*R*
3	**20a**	AH	1.4	26.2±0.4	*S*
4	**13b**	AMe	1.2	10.2±0.2	*R*
5	**16a**	AMe	1.8	23.5±0.2	*R*
6	**20a**	AMe	1.8	13.6±0.2	*S*

For conditions see Table 1. [a] Determined by GLC.

Table 5

Catalytic asymmetric hydrogenation of α-acetamidoacrylic acid (AH) and ester (aMe), benzoylamidocinnamic acid (BH) and ester (BMe) catalysed by neutral rhodium complexes, 0.01 mmol

Ligand	Substrate	Half life (min)	ee [a] (%)	Configuration
4b	aH	2.6	58.3	*S*
4a	aMe	2.9	13.0	*S*
4a	BH	3.0	6.9	*R*
4a	BMe	2.9	60.0	*S*

For conditions see Table 1. [a] Determined by GLC.

higher enantioselectivity for the acids regardless of the catalyst used (Tables 1 and 2). This indicates a different type of substrate bonding which must also account for ligand **4** (Tables 1 and 2 entry 2 *) where configuration changes only with the ester (AMe). To confirm this finding further substrates were included under the same conditions yielding the same results (Table 5). Even in the series of mono-substituted ligands **13a**, **13b** the exceptional behaviour of the esters becomes evident (see Tables 3 and 4, entries 1 and 4).

16a and **16b**, because of the bulky cyclohexyl group, behave like **9** concerning the configuration of the amino acid formed. This does not hold for the methyl-derivative **20a** which affords an (*S*)-configuration pointing to an assumed chair-λ-conformation.

Alterations of the amino acid configuration can also be achieved in different polar solvents as given for the cationic complex of **4a** in Table 6.

Finally ligand **5** displays a marked decrease in selectivity and rate as outlined in Tables 1 and 2 (entries 5, 6). The same effect was observed in the aminophosphine-phosphinite ligands [14] and reveals a tendency to induce the opposite enantiomer.

Table 6

Catalytic asymmetric hydrogenation of methyl-α-acetamidocinnamate (AMe) catalysed by **4a**-Rh^+

Solvent	*t*/2 (min)	ee %	Configuration
MeOH	3.6	20.5	*S*
	3.7	21.5	*S*
EtOH	9.0	14.0	*S*
	9.6	14.1	*S*
Dioxane	4.4	11.7	*R*
	5.4	11.3	*R*

For conditions see Table 1.

* To ensure the configuration, the optical rotation was measured from the isolated product to be $[\alpha]_D^{22}$ +9.9 (*c* 1.04, EtOH), i.e. 21.3% ee (*S*) [13].

Experimental

Apparatus

Optical rotations were measured by a Polamat A polarimeter (Carl Zeiss, Jena). ^{31}P NMR spectra were taken (proton decoupled) on a VARIAN CFT-20 spectrometer. For NMR spectra δ was given in ppm. The enantiomeric excess (ee%) was determined directly by GLC using a Hewlett Packard 5880 A Chromatograph fitted with a 6 m capillary column deactivated by Carbowax 20M for acetylphenylalanine-methylester (135 °C) or a 4.30 m column XE-60 for benzoylphenylalanine-methylester (175 °C) both of them coated with *N*-stearoyl-tert-butylvalineamide. FID: split 1 : 60. All preparations were carried out under argon, the solvents were purified and dried if possible over sodium/benzophenone and $LiAlH_4$, otherwise according to standard procedures. Hydrogenation was performed as described principally by Kagan [15]. The hydrogenated acids were esterified by diazomethane for GLC estimation.

$[Rh(COD)Cl]_2$ [16], $[Rh(COD)_2]BF_4$ [17] and chlorodicyclohexylphosphine [18] were obtained by known methods. Chlorodiphenylphosphine, phenyl- and methylsuccinic acid were purchased from Merck/Darmstadt.

The substrates were prepared according to the literature: (*Z*)-α-acetamidocinnamic acid [19], (*Z*)-methyl-α-acetamidocinnamate [20], (*Z*)-α-benzamidocinnamic acid [19], (*Z*)-methyl-α-benzamidocinnamate [21], 2,3-diphenylsuccinonitrile [22], *meso*-2,3-diphenylsuccinic acid [2].

Procedures

Racemic 2,3-diphenylsuccinic acid. 0.04 mol *meso* acid was added to a solution of 0.082 mol $Ba(OH)_2 \cdot 8\ H_2O$ in 750 ml water and autoclaved at 210 °C (approx. 2.2 MPa using a 1 l autoclave) for 12 h. The insoluble Ba-salt formed was filtered from the cooled mixtures, washed with water and transformed into the sodium salt by addition of 50 ml saturated Na_2SO_4 solution with stirring for 30 min. $BaSO_4$ was removed by filtration and the crude acid precipitated by diluted H_2SO_4. The product was washed with water and air dried. The yield was 70%, m.p. 175–210 °C. IR spectra (KBr, cm^{-1}): 3615s, 3560s, 1700ss, 1180s, 730s, 700s.

*(2S,3S)-2,3-diphenylsuccinic acid (**1a**).* The acid was obtained as we have described previously [10]. **1a**: yield 88%, $[\alpha]_D^{22}$ +398° (*c* 0.2, acetone), (Lit. [24] $[\alpha]_D^{14}$ +397.9° (*c* 2.3, l = 2, acetone)), m.p. 212–214 °C.

*(2R,3R)-2,3-diphenylsuccinic acid (**1b**).* **1b**: yield 82%, $[\alpha]_D^{22}$ −393° (*c* 0.2, acetone), (Lit. [24] $[\alpha]_D^{13}$ −368° (*c* 2.33, l = 2, EtOH)), m.p. 178–210 °C, MS: *m/e* 270 (M^+), 180 (M^+ −2 COOH), 135 ($M^+/2$).

*(2S,3S)-2,3-diphenylbutane-1,4-diol (**2a**) [25].* Prepared from 18 mmol **1a** and 55 mmol $LiAlH_4$. Yield 50%, m.p. 98–100 °C, $[\alpha]_D^{20}$ +57.8° (*c* 0.32, $CHCl_3$), MS: *m/e* 242 (M^+), 224 ($M^+ - H_2O$), 180 (dibenzyl), ^{13}C NMR * ($CDCl_3$): C_1 51.00, C_2 65.52.

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* ^{13}C NMR: $-\overset{|}{C_1}-\overset{|}{C_2}-OH$.

*(2R,3R)-2,3-diphenylbutane-1,4-diol (**2b**).* $[\alpha]_D^{20}$ −57.9° (*c* 0.34, $CHCl_3$), (Lit. [9] $[\alpha]_D^{20}$ −48.2° (*c* 0.32, $CHCl_3$)).

*(2S,3S)-2,3-dicyclohexylbutane-1,4-diol (**7a**).* 1.89 g (0.2 mmol) of **2a** or **2b** were dissolved in a mixture of 16 ml EtOH and 4 ml acetic acid. 20 mg of the PtO_2/Rh_2O_3 catalyst were added and the mixture after flushing several times with argon and hydrogen was autoclaved at 0.9 MPa hydrogen pressure. Within 4–6 hours at room temperature hydrogen uptake was complete (clear solution). The catalyst (pyrophoric) was filtered off, washed with ethanol and the solution evaporated under vacuum to an oil from which adherent acid was removed by drying over KOH. Recrystallisation from hexane affords 75% yield, m.p. 106–108°C. $[\alpha]_D^{20}$ −16.4° (*c* 0.4, EtOH), ^{13}C NMR * ($CDCl_3$): C_1 43.8, C_2 58.9.

*(2R,3R)-2,3-dicyclohexylbutane-1,4-diol (**7b**).* $[\alpha]_D^{20}$ +16.4° (*c* 0.4 EtOH), $[\alpha]_D^{20}$ −2.1° (*c* 0.4, $CHCl_3$).

*(2S,3S)-2,3-dicyclohexylsuccinic acid (**6a, 6b**).* 3.7 mmol **1a** was hydrogenated as outlined above using 100 mg of the Adams type catalyst. **6a**: yield 70%, m.p. 169–170°C, $[\alpha]_D^{20}$ +43.4° (*c* 0.23, MeOH), MS: *m/e* 264 ($M^+ - H_2O$), 182 (264 − cyclohexyl), 138 (182 − carboxyl). **6b**: $[\alpha]_D^{22}$ −41.5° (*c* 0.23, MeOH).

*(2S,3S)-2,3-diphenylbutane-1,4-diol di-p-toluenesulphonate (**3a, 3b, 8a, 8b**).* The compounds were prepared according to ref. 9.

*(2S,3S)-2,3-diphenyl-1,4-bis(diphenylphosphino)butane (**4a, 4b**).* Yield 30%, m.p. 144–146°C, ^1H NMR $(CDCl_3)_3$: 2.26 (4H, m), 3.08 (2H, m), 6.76–7.56 (30H, m). ^{31}P NMR (CH_2Cl_2): −26.8. **4a** $[\alpha]_D^{20}$ +86.8° (*c* 0.73, benzene). **4b** $[\alpha]_D^{20}$ −89.8° (*c* 0.49, benzene). (Lit. [11] α_D^{22} +81.8° (*c* 1.6, benzene)).

*(2S,3S)-2,3-dicyclohexyl-1,4-bis(diphenylphosphino)butane (**9a**).* 2.5 mmol of the ditosylate **8a** were dissolved in 10 ml of toluene and added to $NaPPh_2$-$KPPh_2$/dioxane suspension prepared according to ref. 26. The mixture was stirred for 30 min, filtered off from excess K/Na, washed twice with 20 ml of toluene and concentrated leaving an oil which by addition of 5 ml of MeOH and standing for some weeks gave colourless crystals. The yield was 15%, m.p. 100–102°C, $[\alpha]_D^{20}$ −20.1° (*c* 0.45, benzene), MS: *m/e* 590 (M^+), 508 (M^+ − cyclohexyl), 405 ($M^+ - 2$ − cyclohexyl). ^{31}P NMR (benzene): −16.4.

*(2S)-2-phenylsuccinic acid (**10a, 10b**).* Racemic 2-phenylsuccinic acid, 10 g (0.05 mol) dissolved in hot MeOH (60 ml) was added to a solution of 21.2 g (0.1 mol) of (+)-(1*S*,2*S*)-1-(*p*-nitrophenyl)-2-aminopropane-1,3-diol (so called L-base) in MeOH (310 ml), the mixture heated to reflux and cooled to room temperature. On standing for 12 h 16.8 g of the (+) diastereomer was deposited and was filtered off. The salt was decomposed by addition of 10% NaOH filtered and acidified by 10% HCl affording 3.3 g phenylsuccinic acid $[\alpha]_D^{20}$ +55.8 (*c* 0.2, acetone). The filtrate was concentrated under reduced pressure, treated with NaOH and HCl as above to yield 3.8 g of the (*R*)-enantiomer, $[\alpha]_D^{20}$ −66.9° (*c* 0.2, acetone). Repeating the procedure yielded 2.8 g (2*S*)-(+)-phenylsuccinic acid $[\alpha]_D^{20}$ +79.3° (*c* 0.2, acetone), (sometimes higher values were found) and after a third resolution 1.9 g (38%) optically pure acid $[\alpha]_D^{20}$ +180.8° (*c* 0.2, acetone), (Lit. [27] $[\alpha]_D^{25}$ +171.4 (*c* 1, acetone)), m.p. 167–168°C, MS: *m/e* 176 ($M^+ - H_2O$), 150 ($M^+ - CO_2$). The (2*R*)-2-phenylsuccinic acid from the first resolution was treated twice with D-base giving first $[\alpha]_D^{20}$ −101.7° (*c* 0.2, acetone) and finally 1.7 g (35%), $[\alpha]_D^{20}$ −190° (*c* 0.2, acetone), m.p. 167–168°C.

*(2S)-2-phenylbutane-1,4-diol (**11a, 11b**).* **11a** $[\alpha]_D^{20}$ +42.2° (*c* 0.3, $CHCl_3$) and

11b $[\alpha]_D^{20}$ −39.0° (*c* 0.3, $CHCl_3$) were obtained as **2a**, **2b**, b.p.$_4$ 163–168°C, yield 49.3%, MS: *m/e* 148 ($M^+ - H_2O$).

(2S)-2-cyclohexylsuccinic acid. 1 g (5.15 mmol) **10a** or **10b** respectively, were hydrogenated as described for **6a**. Hydrogen uptake proceeds within one hour. Work up was performed according to **7a**. $[\alpha]_D^{20}$ +35.1° (*c* 0.48, EtOH), (Lit. [28] $[\alpha]_D^{31}$ +26.3° (*c* 1.9, EtOH)), m.p. 90–91°C, MS: *m/e* 200 (M^+).

*(2S)-2-cyclohexylbutane-1,4-diol (**14a**).* $[\alpha]_D^{20}$ −17.5° (*c* 0.49, EtOH), yield 56.1%, b.p.$_5$ 195–200°C, prepared according to **2a**.

*(2S)-2-phenylbutane-1,4-diol-di-*p*-toluenesulphonate (**12a, 12b**).* The tosylates were prepared similar to ref. 9, **12a** $[\alpha]_D^{20}$ +24.8° (*c* 0.3, $CHCl_3$), m.p. 77–78°C, yield 48.3%, MS: *m/e* 302 ($M^+ - HOSO_2 - C_6H_4CH_3$). **12b** $[\alpha]_D^{20}$ −25.6° (*c* 0.3, $CHCl_3$), m.p. 87–88°C, yield 53.6%.

*(2R)-2-phenyl-1,4-bis(diphenylphosphino)butane (**13b**).* Was prepared similar to ref. 26. **13b** $[\alpha]_D^{20}$ −77.5° (*c* 0.9, toluene), m.p. 101–103°C, MS: *m/e* 502 (M^+), 425 ($M^+ - C_6H_5$), ^{31}P NMR (benzene): P_1 −20.61, P_2 −16.08.

*(2S)-2-cyclohexyl-1,4-diol-di-*p*-toluenesulphonate (**15a**).* **15a** $[\alpha]_D^{20}$ −7.3° (*c* 0.24, $CHCl_3$), m.p. 74–76°C, yield 65%, MS: *m/e* 480 (M^+), 309 ($M^+ - OSO_2 C_6H_4CH_3$).

*(2S)-2-cyclohexyl-1,4-bis(diphenylphosphino)butane (**16a**).* **16a** was prepared in an analogous manner to [26], $[\alpha]_D^{20}$ +49.8° (*c* 0.7, toluene), oil, MS: *m/e* 508 (M^+), ^{31}P NMR (benzene): P_1 −15.60, P_2 −18.98.

*(2S)-2-methylsuccinic acid (**17a**).* Racemic 2-methylsuccinic acid, 10 g (0.075 mol) dissolved in hot MeOH (60 ml) was added to a solution of (+)-(1*S*,2*S*)-1-(*p*-nitrophenyl)-2-aminopropane-1,3-diol) (L-base), 31.8 g (0.15 mol) in MeOH (450 ml). The mixture was heated to reflux and cooled to room temperature. On standing for 12 h the (+)-diastereomer (24 g) deposited and was filtered off. The filtrate was concentrated under reduced pressure, yielding 17 g (−)-diastereomer. The (+)- and (−)-salts were decomposed by addition of 10% NaOH and the L-base removed by filtration. The di-Na-salts were acidified by use of cationic ionic exchanger (Wofatit KS10). **17a** $[\alpha]_D^{20}$ −20° (*c* 0.2, acetone), (Lit. [29] $[\alpha]_D^{24}$ −15.0°, (*c* 1.89, abs. EtOH)), m.p. 107–109°C, yield 28%, MS: *m/e* 114 ($M^+ - H_2O$) **17b** $[\alpha]_D^{20}$ +19.1° (*c* 1.0, acetone), (Lit. [29] $[\alpha]_D^{24}$ +15.5° (*c* 3.0, EtOH), m.p. 103–106°C, yield 35%, MS: *m/e* 114 ($M^+ - H_2O$).

*(2S)-2-methylbutane-1,4-diol (**18a**).* **18a** $[\alpha]_D^{21}$ −12.6° (*c* 0.34, EtOH), b.p.$_3$ 85°C, (Lit. [30] for racemic diol b.p.$_2$ 98°C), yield 29%, was obtained analogously to **2a**, **2b**.

*(2S)-2-methyl-1,4-diol-di-*p*-toluenesulphonate (**19a**).* **19a** was prepared similar to ref. 9, $[\alpha]_D^{21} \approx 0$ (*c* 0.3, $CHCl_3$), oil, MS: *m/e* 412 (M^+), 241 ($M^+ - OSO_2 - C_6H_4CH_3$).

*(2S)-2-methyl-1,4-bis(diphenylphosphino)butane (**20a**).* **20a** preparation in an analogous manner to ref. 26, $[\alpha]_D^{20}$ +13.3° (*c* 0.57, toluene), m.p. 63–64°C, MS: *m/e* 440 (M^+), 363 ($M^+ - C_6H_5$), 255 ($M^+ - P(C_6H_5)_2$), ^{31}P NMR benzene): P_1 −15.6, P_2 −20.45.

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