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Synthesis of the chiral diphosphine ligand 2,3-bis(diphenylphosphino)butane (CHIRAPHOS)

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Abstract: A new synthesis of CHIRAPHOS starting from readily available 2,3-bis(diphenylphosphinyl)-1,3-butadiene has been devised. The key step of the synthesis is the hydrogenation of the diene to *rac*-2,3-bis(diphenylphosphinyl)butane. This reduction can be conveniently performed by treating 2,3-bis(diphenylphosphinyl)-1,3-butadiene with $NaBH_4$ in THF/CH_2Cl_2 mixtures. The racemic diphosphine oxides are subsequently resolved using (2*S*,3*S*)-(+)- and (2*R*,3*R*)-(−)-2,3-*O*-dibenzoyltartaric acid [(+)- and (−)-DBTA]. Reduction of the resolved phosphine oxides is carried out using trichlorosilane.

Introduction

The chiral diphosphine ligands (2*R*,3*R*)-(+)- or (2*S*,3*S*)-(−)-2,3-bis(diphenylphosphino)butane [(*R*,*R*)- or (*S*,*S*)-CHIRAPHOS] allow high asymmetric inductions to be achieved in a variety of transition metal catalysed reactions.[1–3] For instance, in the presence of catalysts of the type {Rh(diene)[(*S*,*S*)-CHIRAPHOS]}$^+$ α-acetamidocinnamic acid is hydrogenated to *N*-acetil-3-phenylalanine with enantioselectivities up to 99%.[2]

Even though two elegant and different methods for the synthesis of Chiraphos are reported in the literature,[2,4] we wish to report here a new synthesis which, starting from non optically active and inexpensive reagents, gives, *via* resolution of the racemic mixture of the corresponding phosphine oxides, both enantiomers of CHIRAPHOS in good yields.

Results and discussion

The devised synthesis involves the four steps reported in Scheme 1.

The starting 2,3-bis(diphenylphosphinyl)-1,3-butadiene **1** is readily synthesised according to a literature method.[5] Minor modifications to the reported synthesis allowed us to obtain **1** in ≈90% yield (see the Experimental). The key step of our synthetic scheme is the diastereoselective reduction of **1** to *rac*-2,3-bis(diphenylphosphinyl)butane **2**; moreover, partial reduction of **1** can also afford the by-products depicted in Figure 1.

It is noteworthy that depending on the stereochemistry of addition of the hydrogen atoms, 2,3-bis(diphenylphosphinyl)butane can be obtained as racemic or *meso*-form. As suggested by Schmidbaur[5] the diene **1** should be in a transoid conformation; in this case: i) if the addition of the hydrogen atoms occurs from the same side of the diene then the racemate is formed; ii) if the addition of the hydrogen atoms takes place from opposite sides of the diene then the *meso* diastereomer is formed. This latter cannot be transformed in any way into the *rac*-form so when present among the reaction products it must be separated and discarded.

To carry out the overall synthesis of CHIRAPHOS in high yields it is thus important to resort to an hydrogenating system able to give diastereoselectively *rac*-**2**. Among the several reducing systems we

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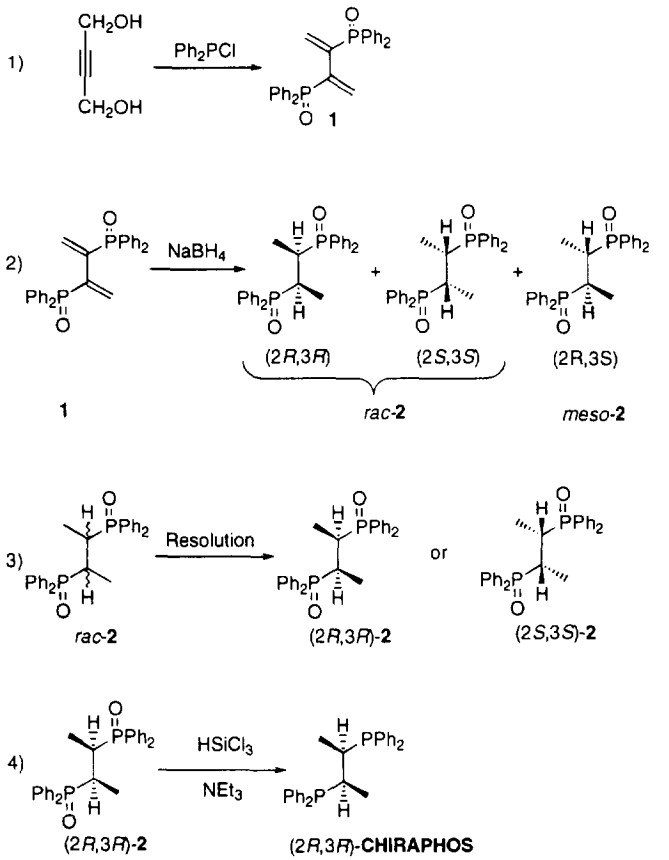


Scheme 1.

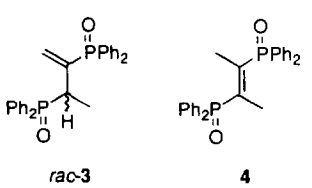
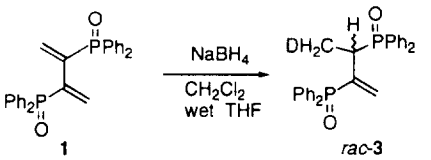


Figure 1. Partially reduced products from diene **1**.

have tested,[6] the best results have been achieved using $NaBH_4$. Indeed, pure *rac*-**2** can be obtained in 68% yield by reacting **1** with a fourfold excess of $NaBH_4$ in wet THF/CH_2Cl_2 mixtures at r.t. (see the Experimental). The reaction can be easily monitored by ^{31}P-NMR spectroscopy: this technique reveals that the reduction occurs in two steps *via* the formation of 2,3-bis(diphenylphosphinyl)-1-butene *rac*-**3**, which can be trapped by quenching the reaction with water (see the Experimental).

It is worth noting that usually simple olefinic double bonds are not reduced by $NaBH_4$ unless they carry electronwithdrawing substituents. Therefore, it appears that the P=O group is an EWG strong enough to activate the carbon–carbon double bonds towards the addition of $NaBH_4$. The exact role played by the presence of a few percent of water in THF[7] is uncertain but undoubtedly it contributes to enhance the reaction rate probably by favouring the hydrolysis of the B–C bond formed as an intermediate during the reaction: as a matter of fact experiments carried out using $NaBD_4$ revealed that

the D atom adds to the more electrophilic carbon atom of the substrate as schematised in Scheme 2, while an H atom adds to the P substituted carbon atom.



Scheme 2.

During the reduction of the second double bond a white precipitate is formed. The ^{1}H- and ^{31}P-NMR spectra of the liquid phase indicate that it contains only *rac*-**2**, which can be thus recovered in ca. 70% yield by removal of the solvents. On the other hand, treatment of the solid phase with an aqueous acid and extraction with dichloromethane affords spectroscopically pure (^{1}H- and ^{31}P-NMR) *meso*-**2** in ca. 30% yield. Therefore it appears that $NaBH_4$ plays two important roles: i) it reduces with moderate diastereoselectivity the diene **1** to afford a mixture (70/30) of *rac*-**2** and *meso*-**2**; ii) it selectively forms an insoluble adduct with *meso*-**2**, thus allowing a straightforward purification of the desired racemic mixture. Since the intermediate monoene *rac*-**3** is formed as a racemic mixture, the diastereoselective choice takes place during the reduction of the second double bond. Hence the stereogenic centre formed from the reduction of the first C–C double bond must be able to stereochemically direct the subsequent attack of the reducing agent on the second prochiral centre present on the substrate. Vicinal stereocontrol in reductions is well-documented in literature[8] and it is accounted for by invoking steric factors. In our case, the arrangement of the substituents at the stereogenic sp^3 carbon atom is such that in the *R*-**3** enantiomer the attack of the BH_4^- on the less hindered face is favoured giving the (2*R*,3*R*)-**2** enantiomer (Figure 2) and vice versa for the *S*-**3** enantiomer.

The structure of the adduct formed by *meso*-**2** with $NaBH_4$ is still under investigation, but it can be tentatively formulated as *meso*-**2**.NaOH.$NaBH_4$ on the basis of elemental analysis, of the determination of the number of hydrides, and of its IR spectrum which shows a broad and strong band at 3460 cm^{-1} which can be attributed to an OH group (see the Experimental).

The following step of the synthesis is the resolution of *rac*-**2** which was performed by diastereomer adduct formation with two different resolving agents: (1*S*)-(+) and (1*R*)-(−)-10-camphorsulfonic acid [(+)- and (−)-CSA] or (2*S*,3*S*)-(+)- and (2*R*,3*R*)-(−)-2,3-*O*-dibenzoyltartaric acid [(+)- and (−)-DBTA].[9,10] Although the adducts have been proved to form in both cases, the best results are obtained with (+)- and (−)-DBTA. An equimolecular mixture of *rac*-**2** and (+)-DBTA was prepared by addition of a hot ethyl acetate solution of (+)-DBTA to *rac*-**2** dissolved in boiling $CHCl_3$. Double crystallization from ethyl acetate/toluene provided (2*R*,3*R*)-**2**-(+)-DBTA 1:1 complex in 92% yield and 99.6% o.p.(see

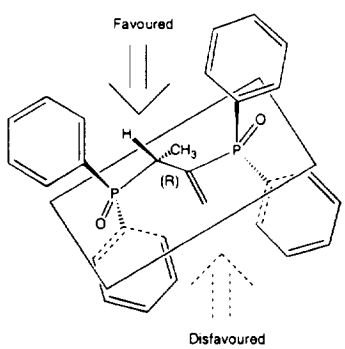


Figure 2. Diastereoface differentiating reduction leading to the formation of (2*R*,3*R*)-**2**.

the Experimental). (2*R*,3*R*)-**2** was finally obtained in 87% yield based on *rac*-**2** by treating the tartrate adduct with aqueous base followed by standard work-up.

Enantiomerically enriched (2*S*,3*S*)-**2** was recovered from the mother liquor by treatment with aqueous base. Complexation with (−)-DBTA, recrystallization from ethyl acetate/toluene and subsequent work-up afforded (2*S*,3*S*)-**2** in 90% yield and 99.1% o.p..

The final reduction of the phosphine oxide enantiomers to the corresponding optically active CHIRAPHOS was accomplished in almost quantitative yield and no racemization by a standard procedure.[11]

Experimental

All manipulations were carried out under inert atmosphere in Schlenk-type glassware. Analytical grade solvents (C. Erba) were purified following standard methods described in literature.[12] Chlorodiphenylphosphine, 2-butin-1,4-diol, (2*S*,3*S*)-(+)-2,3-*O*-dibenzoyltartaric acid [(+)-DBTA], monohydrated (2*R*,3*R*)-(−)-2,3-*O*-dibenzoyltartaric acid [(−)-DBTA.H_2O], (1*S*)-(+) and (1*R*)-(−)-10-camphorsulfonic acid [(+)- and (−)-CSA], $NaBH_4$, $NaBD_4$ and authentic samples of (2*R*,3*R*)-(+)- and (2*S*,3*S*)-(−)-bis(diphenylphosphino)butane [(+)- and (−)-CHIRAPHOS] were purchased by Aldrich. Wet THF was prepared by adding 2% (v/v) of water to the anhydrous solvent.

^{1}H- and ^{31}P-NMR were obtained on a Bruker AC 200 spectrometer operating at 200.13 and 81.01 MHz, respectively. The ^{31}P-NMR chemical shifts are reported with positive values downfield from 85% H_3PO_4. IR spectra were registered on a Nicolet 750 FT-IR interferometer. Atomic absorption data were obtained on a Perkin Elmer 3100 spectrophotometer.

Elemental analyses were carried out by the Department of Organic Chemistry of the University of Florence. Optical rotations were measured on a Perkin Elmer 241 polarimeter. Melting points are uncorrected and were obtained with a conventional melting point apparatus (Aldrich).

2,3-Bis(diphenylphosphinyl)-1,3-butadiene **1**

A solution of chlorodiphenylphosphine (10.5 ml, 11.6 g, 52.6 mmol) in 30 ml of THF was added dropwise to a cold (0°C) solution of 2-butin-1,4-diol (2.27 g, 26.3 mmol) and pyridine (5 ml, 62 mmol) in 30 ml THF. After the addition was complete, the reaction mixture was allowed to reach r.t.. The resulting suspension was hydrolized with 40 ml H_2O and extracted with CH_2Cl_2 (3 x 200 ml); the organic layer was washed with 5% solution of HCl, then with a 10% solution of $NaHCO_3$, and finally twice with water. The organic phase was dried over Na_2SO_4 and rotoevaporated. Recrystallization from THF/diethyl ether gave **1** as white crystals (10.87 g, 91% yield).

IR (KBr): 3050 (m), 3005 (w), 2970 (w), 1595 (m), 1560 (m), 1430 (s), 1190 cm^{-1} (vs). ^{1}H-NMR ($CDCl_3$): 5.53 (d, 1H, C=C*H*, *J*(H–P)=20 Hz), 6.63 (d, 1H, C=C*H*H, *J*(H–P)=42 Hz), 7.40–7.80 ppm (m, 20H, arom.). ^{31}P-NMR ($CDCl_3$): 33.24 ppm (s). m.p.: 179–181°C. Elem. Anal. calc. for $C_{28}H_{24}O_2P_2$ (454.44): C 74.00, H 5.32%; found: C 73.94, H 5.35%.

rac-*2,3-Bis(diphenylphosphinyl)butane* rac-**2**

To a solution of 2,3-bis(diphenylphosphinyl)-1,3-butadiene (100 mg, 0.22 mmol) in CH_2Cl_2 (5 ml) were added 5 ml of wet THF. Then 33 mg (0.88 mmol) of $NaBH_4$ were added and the reaction mixture was stirred at 20°C for 42 h. The resulting slurry was filtered and the liquid phase rotoevaporated to give a white solid. Recrystallization from benzene/n-hexane afforded *rac*-**2** as white crystals (68 mg, 68% yield).

IR (KBr): 3060 (w), 2980 (w), 2880 (w), 1435 (m), 1185 cm^{-1} (vs). ^{1}H-NMR ($CDCl_3$): 1.31 (m, 6H, C*H*$_3$), 2.86 (m, 2H, C*H*), 7.20–7.80 ppm (m, 20H, arom.). ^{31}P-NMR ($CDCl_3$): 37.32 ppm (s). m.p.: 183–184°C. Elem. Anal. calc. for $C_{28}H_{28}O_2P_2$ (458.48): C 73.35, H 6.16; found: C 73.20, H 6.20.

meso-*2,3-Bis(diphenylphosphinyl)butane* meso-*2*

To a solution of 2,3-bis(diphenylphosphinyl)-1,3-butadiene (100 mg, 0.22 mmol) in CH_2Cl_2 (5 ml) were added 5 ml of wet THF. Then 33 mg (0.88 mmol) of $NaBH_4$ were added and the reaction mixture was stirred at 20°C for 42 h. The solid phase of the resulting slurry was recovered by filtration, washed with a few ml of dichloromethane and treated with 10 ml of 2 M aqueous acetic acid and 20 ml CH_2Cl_2. The organic layer was separated, washed with a 10% solution of $NaHCO_3$, dried over Na_2SO_4 and then in vacuo to afford *meso*-**2** as a white solid (30 mg, 30% yield).

IR (KBr): 3057 (m), 2980 (m), 2900 (w), 1440 (s), 1165 cm^{-1} (vs). ^{1}H-NMR ($CDCl_3$): 0.97 (m, 6H, C*H*$_3$), 3.08 (m, 2H, C*H*), 7.40–7.90 ppm (m, 20H, arom.). ^{31}P-NMR ($CDCl_3$): 36.85 ppm (s). m.p.: 238–240°C. Elem. Anal. calc. for $C_{28}H_{28}O_2P_2$ (458.48): C 73.35, H 6.16; found: C 73.16, H 6.18.

Characterization of the adduct meso-*2,3-bis(diphenylphosphinyl)butane.NaOH.NaBH*$_4$

The solid phase formed as described in the preceding paragraph was collected by filtration and oven-dried at 70°C for 24 h to give 34 mg of a white solid used for characterization.

IR (KBr): 3460 (br, s), 3055 (m), 2990 (w), 2905 (w), 2290 (s), 2225 (s), 1440 (s), 1197 cm^{-1} (vs).

Elemental analysis: C 62.57, H 6.05, Na 8.0% (The percentage of Na in the adduct was determined by atomic absorption).

The number of hydrides present in the adduct was determined by measuring with a gas burette the volume of hydrogen evolved upon mineralization of the solid with an acid. In a typical experiment 9.9 mg of the adduct were suspended in 10 ml of 1,2-dichloroethane and mineralised with 1 ml of acetic acid to give 1.9 ml of hydrogen at 25°C and 1 atm. Assuming for the adduct a F.W. of ca. 500–550 the amount of hydrogen evolved indicates the presence of four hydrides.

These findings together with the observation that upon mineralization 33 mg of the adduct release 30 mg of *meso*-**2** (preceding paragraph) are in keeping with a crude formula: $C_{28}H_{33}O_3P_2Na_2B$ (536.18) which calc. elem. anal. is C 62.67, H 6.20, Na 8.58%.

To account for this formulation it is necessary to resort to an adduct between *meso*-**2**, one molecule of $NaBH_4$ and one molecule of NaOH. As a matter of fact, the presence of OH in the IR spectrum stems from a broad strong absorption at 3460 cm^{-1}.

rac-*2,3-Bis(diphenylphosphinyl)-1-butene* rac-*3*

To a solution of 2,3-bis(diphenylphosphinyl)-1,3-butadiene (100 mg, 0.22 mmol) in CH_2Cl_2 (5 ml) were added 5 ml of wet THF. Then 33 mg (0.88 mmol) of $NaBH_4$ were added and the reaction mixture was stirred at 20°C for 2 h. At that time 10 ml of water were added. The organic phase was separated and dried over Na_2SO_4. Removal of the solvent gave *rac*-**3** as a white solid (90 mg, 90% yield).

IR (KBr): 3040 (m), 2960 (w), 2920 (w), 1580 (w), 1430 (s), 1185 cm^{-1} (vs). ^{1}H-NMR ($CDCl_3$): 1.30 (dd, 3H, C*H*$_3$, *J*(H–H)=7.0 Hz, *J*(H–P)=15 Hz), 4.03 (m, 1H, CH_3–C*H*), 5.46 (dd, 1H, C=C*H*H, *J*(H–H)=2.7 Hz, *J*(H–P)=18 Hz), 6.91 (dd, 1H, C=CH*H*, *J*(H–P)=42 Hz), 7.20–7.80 ppm (m, 20H, arom.). ^{31}P-NMR ($CDCl_3$): 32.32 (d, 1P, *J*(P–P)=22 Hz), 34.57 ppm (d, 1P). m.p.: 148–150°C. Elem. Anal. calc. for $C_{28}H_{26}O_2P_2$ (456.46): C 73.68, H 5.74; found: C 73.85, H 5.80. Polarimetric analysis showed that the sample has no optical activity.

2,3-Bis(diphenylphosphinyl)-1-butene-4-d$_1$

This compound was prepared as described for *rac*-**3** using $NaBD_4$ as reducing agent.

^{1}H-NMR ($CDCl_3$): 1.30 (br, dd, 2H, CD*H*$_2$, *J*(H–H)=7.0 Hz *J*(H–P)=15 Hz), 4.03 (m, 1H, CDH_2–C*H*), 5.46 (dd, 1H, C=C*H*H, *J*(H–H)=2.7 Hz, *J*(H–P)=22 Hz), 6.91 (dd, 1H, C=CH*H*, *J*(H–P)=42 Hz), 7.20–7.80 ppm (m, 20H, arom.).

Resolution of rac-*2,3-bis(diphenylphosphinyl)butane by formation of (2R,3R)-(+)-2,3-bis(diphenylphosphinyl)butane-[(+)-DBTA]*

2.0 g (4.36 mmol) of *rac*-2,3-bis(diphenylphosphinyl)butane were dissolved in 15 ml $CHCl_3$. The solution was heated at reflux and a hot solution of 1.56 g (4.36 mmol) of (+)-DBTA in 20 ml

Table 1. $[\alpha]^{22}_{D,max}$ determined as reference values for this work

(2*S*,3*S*)-(-)-CHIRAPHOS [a]	$[\alpha]^{22}_D$ = - 191 (c 1.5 in $CHCl_3$)
(2*R*,3*R*)-(+)-CHIRAPHOS [a]	$[\alpha]^{22}_D$ = + 195 (c 1.5 in $CHCl_3$)
(2*S*,3*S*)-(-)-CHIRAPHOS oxide	$[\alpha]^{22}_D$ = - 38.5 (c 2.0 in CH_2Cl_2)
(2*R*,3*R*)-(+)-CHIRAPHOS oxide	$[\alpha]^{22}_D$ = + 39.4 (c 2.0 in CH_2Cl_2)
(2*R*,3*R*)-(+)-CHIRAPHOS oxide-[(+)-DBTA]	$[\alpha]^{22}_D$ = + 53.0 (c 2.0 in CH_2Cl_2)

[a] Aldrich products

ethyl acetate was added under stirring. The mixture was heated at reflux for further two minutes and then allowed to cool. The solvent was removed under reduced pressure to give a white solid. The crude product was recrystallized twice from ethyl acetate/toluene to afford (2*R*,3*R*)-(+)-2,3-bis(diphenylphosphinyl)butane-[(+)-DBTA] (1.63 g, 2.00 mmol, 92% yield).

IR (KBr): 3400 (br, w), 3060 (w), 2980 (w), 2960 (w), 2850 (w), 1720 (br, vs), 1250 (br, s), 1190 cm^{-1} (br, s). ^{1}H-NMR ($CDCl_3$): 1.05 (m, 6H, C*H*$_3$), 2.90 (m, 2H, CH_3CH), 6.08 (s, 2H, C*H*COO), 6.80 (broad, 2H, COO*H*), 7.20–8.20 ppm (m, 30H, arom.). ^{31}P-NMR ($CDCl_3$): 40.71 ppm (s). m.p.: 115–116°C. $[\alpha]^{22}_D$=+52.8 (c 2.0 in CH_2Cl_2). The o.p. is 99.6%, as compared with the specific rotation value determined on an enantiomerically pure sample of (+)-**2**-[(+)-DBTA] prepared for this purpose from a commercially available sample (see Table 1).

Mother liquors were evaporated under vacuum and the crude was treated with NaOH to recover the CHIRAPHOS oxides mixture which was then treated with [(−)-DBTA.H_2O] to obtain (2*S*,3*S*)-(−)-2,3-bis(diphenylphosphinyl)butane.

(2R,3R)-(+)-2,3-Bis(diphenylphosphinyl)butane (+)-2

1.63 g (2.00 mmol) of (2*R*,3*R*)-(+)-2,3-bis(diphenylphosphinyl)butane-[(+)-DBTA] were dissolved in $CHCl_3$. The organic layer was treated with portions of NaOH 0.1 N (3x10 ml), twice with water, dried over Na_2SO_4 and taken to dryness under reduced pressure. Recrystallization from a 1/1 mixture benzene/n-hexane provided 0.87 g (1.89 mmol) of (2*R*,3*R*)-(+)-2,3-bis(diphenylphosphinyl)butane (87% overall yield from *rac*-**2**). m.p.: 106–107°C. $[\alpha]^{22}_D$=+39.0 (c 2.0 in CH_2Cl_2). The o.p. is 99.1% by comparison with the maximum optical rotation value determined on a sample of (+)-**2** obtained by oxidizing with H_2O_2 an enantiomerically pure commercial sample of (+)-CHIRAPHOS (see Table 1).

*(2R,3R)-(+)-2,3-Bis(diphenylphosphino)butane (+)-**CHIRAPHOS***

440 mg of (+)-CHIRAPHOS oxide (+)-**2** (0.96 mmol) were dissolved in 20 ml xylene. The resulting mixture was cooled to 0°C with an ice bath and through a septum 2.0 ml of $HSiCl_3$ (2.6 g, 19.2 mmol) were added under stirring. The temperature was allowed to rise gradually to r.t., then the reaction mixture was heated at 100°C for 1h, 120°C for another hour and finally at reflux temperature for further 3 h. To the cool mixture (r.t.) 20 ml of 30% $NaOH_{aq}$. were added and the mixture was again heated to 60°C until both the organic and the aqueous layers became clear. The aqueous layer was removed and the organic phase washed with water (2x20 ml) and dried over Na_2SO_4. After filtration of the Na_2SO_4 the solvent was removed under vacuum and the white powder obtained recrystallised from CH_3OH. (2*R*,3*R*)-(+)-2,3-bis(diphenylphosphino)butane was obtained in 95% yield (390 mg). $[\alpha]^{22}_D$=+193.0 (c 1.5 in $CHCl_3$). o.p. 99.0%.

Acknowledgements

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