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# *(R,R)*-*N*-phenyl-3,4-bis(diphenylphosphino)pyrrolidine: an *N*-aryl pyrrolidine ligand for enantioselective transfer hydrogenation

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**Abstract**

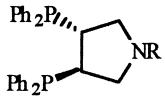
The *N*-aryl pyrrolidine diphosphine (*R,R*)-*N*-phenyl-3,4-bis*(*diphenylphosphino)pyrrolidine was obtained from natural tartaric acid. Contrary to our preliminary expectations, this new chiral ligand proved to be less selective than the corresponding *N*-benzyl pyrrolidine diphosphine. An attempted explanation of the observed behaviour based on the stereochemistry of the ligand as shown by X-ray crystallography is presented. 

*Keywords:* Transfer hydrogenation; Pyrrolidine diphosphine; Asymmetric catalysis; Five-membered chelate; Rhodium

## 1. Introduction

The use of chiral diphosphines in the enantioselective reduction of carbon–carbon double bonds constitutes one of the most frequently used processes for obtaining compounds of high optical purity [1–5]. The preferential formation of one of the two possible enantiomers of a reaction product strongly depends on the characteristics of the catalyst namely, the tridimensional structure of the chiral ligand and its electronic properties. High efficiency has been observed with diphosphine ligands which simultaneously have rigid backbone structures and form five-membered chelate rings with the metal centre [6,7].

In previous studies [8] on the enantioselective transfer hydrogenation of acrylic acid derivatives we found the rhodium(I) complex of (*R,R*)-*N*-benzyl-3,4-bis*(*diphenylphosphino)pyrrolidine **1** to be highly selective (up to 91% ee) in the reduction of acrylic acid derivatives when formic acid/sodium formate was used as the hydrogen source. The formation of a five-membered chelate between the ligand and the metal centre, the existence of a rigid cyclic backbone structure and also chiral centres close to the co-ordination sites [6,7] correspond to general characteristics of these chirality inducing ligands which proved to be highly favourable in this particular case.




**1** R = $CH_2Ph$
**2** R = Ph

The high enantiomeric excesses observed with **1** motivated us to attempt to exploit the new structural analogue, (*R,R*)-*N*-phenyl-3,4-bis*(*diphenylphosphino) pyrrolidine, NPPP (**2**). This was an unknown com-

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pound and we had to set up the conditions to overcome the difficulties encountered in its synthesis from natural tartaric acid and aniline. After overcoming the synthetic challenge, the rhodium(I) complex of the chiral diphosphine NPPP (**2)** was studied as catalyst in the transfer hydrogenation of functionalized alkenes.

## 2. Experimental

### 2.1. General

All solvents were dried prior to use following standard procedures. $[Rh(COD)Cl]_2$ was prepared according to the described procedure [9]. Reactions were carried out in an inert atmosphere using standard Schlenk-type techniques.

Melting points were determined using a Leitz–Wetzler 799 microscope with a heated plate, values are uncorrected. Optical rotations were measured using an Optical Activity AA-5 polarimeter. NMR spectra were recorded on a Bruker AMX 300 (300, 75.5 and 121.6 MHz, for $^1H$, $^{13}C$ and $^{31}P$, respectively). TMS was used as the internal standard for $^1H$ and $^{13}C$ and for $^{31}P$, 85% $H_3PO_4$ as external standard. Chemical shifts are referred in $\delta$ and coupling constants ($J$) in Hz. Infrared spectra were recorded on a Phillips PU 9800 FTIR spectrometer. Elemental analyses were carried out on a Fisons Instruments EA 1108 CHNS-O elemental analyser. Mass spectra were recorded under electron impact on a VG 7070C (70 eV). GC analyses were recorded on a HP 5890A instrument coupled to an HP 3396A integrator using a capillary column (ultra2-crosslinked 5% phenylmethylsilicone). X-ray crystallography was carried out on an Enraf–Nonius CAD-4 diffractometer.

Transfer hydrogenation products were identified by comparison with pure samples prepared by catalytic hydrogenation with molecular hydrogen and characterised by NMR, mass spectrometry and elemental analysis. All catalytic experiments were repeated three to four times in order to confirm results. Enantiomeric excesses were calculated by using the reported values [11] for the following optically pure compounds: (*S*)-*N*-acetylphenylalanine $[\alpha]_D^{22}$ +46.8 (*c* 1.06, EtOH) and *(R)*-2-methylsuccinic acid $[\alpha]_D^{22}$ +15.5 (*c* 2.82, EtOH).

### 2.2. (R,R)-N-phenyl-3,4-dihydroxy-2,5-dioxopyrrolidine (4)

A suspension of tartaric acid (45 g, 0.3 mol) and aniline (27.3 ml, 0.3 mol) in 200 ml of xylene was refluxed with stirring in a round bottomed flask equipped with a Dean–Stark apparatus. The reaction was stopped when the appropriate amount of water was collected (10.8 ml, 0.6 mol). After cooling the reaction mixture, the solid was filtered and washed with xylene and cold acetone and dried. A pale yellow solid was obtained (58 g, 0.28 mol, 93%), mp 249–250°C (255°C) [12]. $[\alpha]_D^{22}$ +127 (*c* 1.5, MeOH) (+130) [12]. $^1H$ NMR ($CDCl_3$/[$D_6$]DMSO): 4.60 (d, 2H, –CH–, *J* 4,3); 6.42 (d, 2H, –OH–, *J* 5.6); 7.29–7.32 (m, 2H, aromatic); 7.37–7.49 (m, 3H, aromatic). $^{13}C$ NMR ($CDCl_3$/[$D_6$]DMSO): 74.6, 126.3, 128.2, 128.7, 131.6, 173.8. IR ($cm^{-1}$): 3356, 3061, 1728, 1709, 1503, 1402, 1190, 1107, 1005. *m/z*: 207 [$M^+$, 42.2%], 179 (10.4), 151(24.1), 120 (24.5), 119 (41.8), 93 (27.6), 91 (36.1), 77 (48.6), 60 (100). $C_{10}H_9NO_4$: calc.: C, 57.97; H, 4.38; N, 6.76; found: C, 57.83; H, 4.47; N, 6.74.

### 2.3. (S,S)-N-phenyl-3,4-dihydroxypyrrolidine (5)

Lithium aluminium hydride (0.23 mol, 8.7 g) and ethyl ether (400 ml) were placed in a round bottomed flask equipped with a Soxhlet containing (*R,R*)-*N*-phenyl-3,4-dihydroxy-2,5-dioxopyrrolidine (0.1 mol, 20.7 g). The system was refluxed until all the reagent had been consumed. At 0°C, ethyl acetate was slowly added, followed sequentially by water (8.7 ml), NaOH, 15% (8.7 ml) and water (26.1 ml). The resulting mixture was stirred for 1 h, filtered and dried with anhydrous $MgSO_4$. Crystallisation of the resulting oil in ethyl acetate/light petroleum originated a yellow brown solid (7.2 g, 0.04 mol, 40%), mp 152.5–153.5°C. By further stirring the residue in ethyl acetate for 2–3 h, an additional batch of product may be obtained. $[\alpha]_D^{22}$ +44 (*c* 0.2, $CHCl_3$). $^1H$ NMR ($C_5D_5N$): 3.61 (d, 2H, –$CH_2$–, *J* 10); 3.95 (dd, 2H, –$CH_2$–, *J* 3.9, 10); 4.83 (bs, 2H, –C<u>H</u>–); 5.57 (bs, 2H, –OH–); 6.67 (d, 2H, aromatic, *J* 8.04); 6.77 (t, $^1H$, aromatic, *J* 7.2); 7.3 (m, 2H, aromatic). $^{13}C$ NMR ($C_5D_5N$): 54.4, 76.3, 111.9, 115.6, 129.5, 148.7. IR ($cm^{-1}$): 3520, 3437, 3167, 1599, 1508, 1458, 1396, 1383. *m/z*: 179 [$M^+$, 50.4%], 119 (37.8), 106 (33.9),

104 (17.6), 91 (100), 77 (31.1). $C_{10}H_{13}NO_2$: calc.: C, 66.02; H, 7.31; N, 7.82; found: C, 65.80; H, 7.26; N, 7.42.

### 2.4. (S,S)-N-phenyl-3,4-ditrifliloxypyrrolidine (**6**)

To a solution of 952.3 mg (5.32 mmol) of *N*-phenyl-3,4-di-hydroxypyrrolidine in dichloromethane (40 ml) under argon, dry pyridine (1.12 ml, 14 mmol) was added. After stirring for 10 min, the reaction temperature was lowered to −20°C and 2 ml (12.2 mmol) of triflic anhydride were added under with argon bubbling directly into the solution. The reaction was followed by TLC, being complete after about 1 h. After purification by column chromatography using silica gel and ethyl acetate/hexane (1:5), an orange-red solid (0.7 g, 1.58 mmol, 22%) resulted, which was used directly in the following step.

### 2.5. (R,R)-N-phenyl-3,4-bis(diphenylphosphino)-pyrrolidine (**2**)

In a Schlenk flask a 1 M THF solution of potassium diphenylphosphide (6.97 ml of, 3.375 mmol) was placed and the solvent evaporated without heating. To the residue DMF (4 ml), was added and to this solution at −40°C was added, all at once, 0.700 g (1.58 mmol) of *N*-phenyl-3,4-ditrifliloxypyrrolidine in DMF (4 ml). The reaction mixture was kept for 18 h at −13°C with magnetic stirring. After evaporation of the DMF at a temperature no higher than 40°C, and using Schlenk techniques, water (25 ml) was added and the mixture extracted with ethyl ether. By evaporating the solvent, a spongy solid was obtained which recrystallized in dichloromethane/*iso*-propanol to give a yellow crystalline product (0.177 g, 0.343 mmol, 22%), mp 173–175°C. $[\alpha]_D^{22}$ +149.7 (*c* 1.002, dichloromethane). $^1$H NMR ($CDCl_3$): 3.02 (2H, approximately t, $–CH_2–$, *J* 6); 3.27 (2H, dd, $–CH_2–$, *J* 10.4, 13.2); 3.88 (2H, ddd, –CH–, *J* 6.2, 10.1, $J_{CP}$ 21.2); 6.43 (2H, dd, –NPh, *J* 0.7, 8.6); 6.63 ($^1$H, t, –NPh, *J* 7.2); 7.12–7.23 (10H, m, –PPh); 7.27–7.40 (12H, m, –PPh). $^{13}$C NMR ($CDCl_3$): 38.4 (t, *J* 17.4); 50.1 (t, *J* 9.8); 111.8; 115.7; 128.5 (*q*, *J* 3); 128.9; 129.1; 133.4–133.6 (m); 133.7–133.8 (m); 136.3–136.5 (m); 136.7–136.9 (m); 147.3. $^{31}$P NMR ($CDCl_3$): −10.64. IR($cm^{-1}$): 1597, 1507, 1474, 1433, 1370, 748, 741, 694. *m/z*: 515 [$M^+$, 0.6%], 343 (1.3), 327 (1.9), 183 (19.5), 144 (100.0). $C_{34}H_{31}NP_2{\cdot}H_2O$: calc.: C, 76.53; H, 6.23; N, 2.62; found: C, 76.83; H, 5.89; N, 2.57. Crystal data for $C_{34}H_{31}NP_2$. $M = 515.54$, orthorhombic, $a = 970.2(2)$, $b = 1451.8(3)$, $c = 2005.9(3)$ pm, space group $P2_12_12_1$ (# 19), $Z = 4$, $D_c = 1.212\,g\,cm^{-3}$, $F_{000} = 1088$, $m = 0.177\,cm^{-1}$, $T = 296(3)$ K. Enraf–Nonius CAD-4 diffractometer, Mo Kα radiation, graphite monochromator, crystal size 0.20 mm × 0.18 mm × 0.15 mm. Intensity measured using $\omega - 2\theta$ scans, $3.24 \leq q \leq 22.48°$, $0 \leq h$ 10, $0 \leq k \leq 15$; $-21 \leq l \leq 19.3168$ reflections measured, 1880 with $I > 2\sigma$. No absorption correction applied to the data and no significant intensity decay observed during data collection. Structure solved by direct methods using SHELXS97 [13]. Full matrix refinement on $F^2$ using SHELXL97 [14] with all non-H atoms anisotropic. H atoms positioned at calculated positions and refined as riding using an isotropic displacement parameter equal to $1.2 \times U_{eq}$ of the parent atom. $N_{par}/N_{data} = 9.49$, final $R = 0.0312$, $R_w = 0.0763$, $S = 1.017$. Absolute configuration determined by refinement of Flack [15] parameter: $\alpha = -0.24(12)$. $R_w(S,S)/R_w(R,R) = 1.024$; applying Hamilton's test [16], the probability of error in rejecting the (*S*,*S*) configuration is lower than 0.5%. Data reduction and analysis: PLATON [17].

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data centre as supplementary publication no. CCDC-138258. Copies of the data can be obtained free of charge on application to CCDC, 12, Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233/336-033; e-mail: deposit@ccdc.cam.uc.uk).

### 2.6. General procedure for transfer reductions using formic acid/sodium formate

To 10 ml of 80% aqueous formic acid 20.3 μmol of $[Rh(COD)Cl]_2$, 48.8 μmol of diphosphine, 2 mmol of substrate and 200 mg of sodium formate were added. The reaction was heated at 90°C for the required time. Reactions were monitored by taking aliquots at regular intervals, treating with diazomethane and analyzing by gas chromatography. Upon completion of the reaction, the formic acid was evaporated, 10% NaOH was added to the residue and the precipitated catalyst was filtered.

The reaction mixture was acidified with 10% HCl, extracted with ether and the combined organic extracts were dried over $MgSO_4$. The solid product was obtained by evaporation from ethyl acetate/hexane.

## 3. Results and discussion

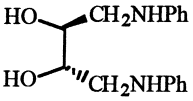
### 3.1. Ligand synthesis

Contrary to the previous experience in the synthesis of pyrrolidine diphosphines with non-aromatic amines [18], the synthesis of (*R*,*R*)-*N*-phenyl-3,4-bis*(*diphenylphosphino)pyrrolidine (**2**) using an aromatic amine posed quite a few problems, requiring the use of specific reduction conditions, use of the trifliloxy leaving group instead of the mesyloxy and use of the more reactive potassium diphenylphosphide instead of the in situ prepared sodium diphenylphosphide. The newly established synthetic sequence is outlined in Scheme 1.

The dioxopyrrolidine (**4**) was easily obtained from natural tartaric acid and aniline by reaction in xylene with the elimination of water through a Dean–Stark apparatus. However, the reduction to the pyrrolidinediol (**5**) with lithium aluminium hydride in diethyl ether presented the first problems. Only using a Soxhlet and normal addition of the reducing agent (addition of the substrate to the hydride) were we successful in performing this step.

Although these reaction conditions gave a slow reduction, requiring several days for completion, it was the only way in which the desired product was obtained exclusively.

The attempted use of THF as solvent or an inverse addition of the hydride (addition of the hydride to the substrate) favoured shorter reaction times, albeit in this case with the formation of another product, in equal or greater quantity than the required **5**. Spectroscopic studies allowed the identification of this product as the diamine (**7**) [10]. This results from an alternative reaction pathway favoured by the reaction conditions used [19,20].

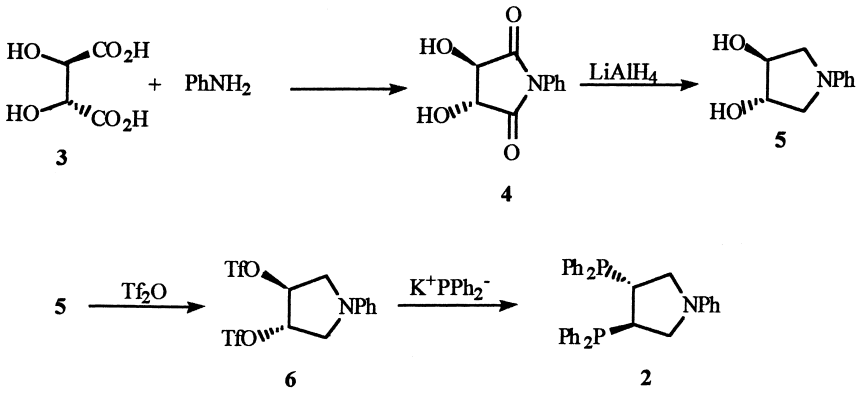



**7**

In our first attempt to obtain the diphosphine (**2**) we converted **5** into the corresponding dimesyl derivative, but this resulted in a very impure product formed only in trace amounts. Contrarily, the use of triflic anhydride allowed the preparation of the more reactive derivative **6**, with acceptable purity and yield after column chromatography. In order to successfully transform **6** to the diphosphine NPPP (**2**) we had to use the more reactive potassium diphenylphosphide instead of the in situ prepared sodium analogue.

### 3.2. X-ray crystallography

The absolute structure of **2** (Fig. 1) was determined taking advantage of the significant anomalous dispersion of phosphorous at the Mo Kα wavelength. Both




Scheme 1. Synthetic sequence for NPPP.

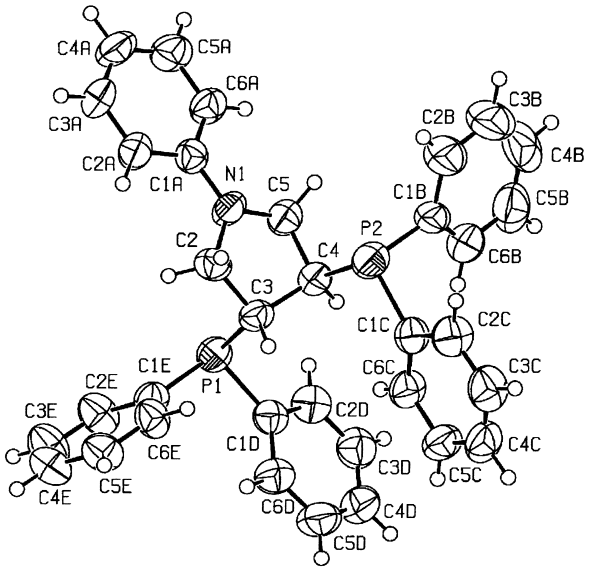



Fig. 1. ORTEPII [22] plot of the molecule of NPPP. Displacement ellipsoids are drawn at the 50% level.

a Flack analysis of the diffraction data and the results of separate refinements of the two enantiomers unambiguously assigned the (*R*) absolute configuration to the two chiral centres C3 and C4. The pyrrolidine ring is somewhat puckered, the average endocyclic torsion angle is 24.4(2)°. The puckering amplitude and phase angle according to Cremer and Pople [21] are $q_2 = 34.6(4)$ pm and $\phi_2 = 92.7(7)°$, corresponding to a twist of the molecule around a pseudo-rotation axis passing through N1 and the middle of the C3 and C4 bond. The phase angle $\phi_2$ of a pure $^3T_4$ conformation is 90°. The $C_2$[C3–C4] asymmetry parameter is 2.9(4)°. The deviations of the atoms from the least-squares plane of the pyrrolidine ring are: N1, 1.1(2); C2, 12.1(2); C3, 20.5(2); C4, 21.0(2); C5, 13.7(2) pm.

Bond lengths and angles display no unusual features (Table 1). The average $C_{aryl}$–P and $C_{sp^3}$–P bond lengths are 183.4(4) and 186.4(15) pm, respectively, which are in good agreement with reported average values [23]. The *N*-phenyl and pyrrolidine rings are practically in the same plane, the dihedral angle between the least-squares planes of the two rings being 7.2(3)°. The dihedral angles between the two phenyl rings bonded to the phosphorous atoms are 87.44(16)° (rings B and C) and 75.12(11)° (rings D and E).

Table 1
Selected bond lengths and angles

| | Bond length (pm) | | Bond angle (°) |
|---|---|---|---|
| N1–C2 | 144.8(4) | C2–N1–C5 | 112.7(3) |
| C2–C3 | 152.9(5) | C3–C2–N1 | 104.3(3) |
| C3–C4 | 154.2(6) | C4–C3–C2 | 103.6(3) |
| C4–C5 | 153.1(5) | C5–C4–C3 | 102.5(3) |
| C5–N1 | 144.3(5) | N1–C5–C4 | 104.7(3) |
| N1–C1A | 137.0(5) | C1A–N1–C5 | 122.5(3) |
| P1–C3 | 186.2(4) | C1A–N1–C2 | 124.2(3) |
| P1–C1D | 183.1(4) | C1E–P1–C1D | 102.1(2) |
| P1–C1E | 182.5(4) | C1D–P1–C3 | 101.45(17) |
| P2–C4 | 186.5(4) | C3–P1–C1E | 101.9(2) |
| P2–C1B | 183.9(5) | C4–P2–C1C | 103.25(18) |
| P2–C1C | 184.3(4) | C1C–P2–C1B | 99.6(2) |
| | | C1B–P2–C4 | 99.5(2) |

### 3.3. Enantioselective catalysis experiments

We tested the Rh(I)/NPPP catalyst using α-acetamidocinammic acid (**8**) and itaconic acid (**9**), substrates of choice for evaluating the efficiency of new enantioselective catalytic reduction systems for carbon–carbon double bonds. The reductions were carried out with formic acid/sodium formate as hydrogen donor at 90°C in the presence of the catalyst, prepared in situ from $[Rh(COD)Cl]_2$ and NPPP. Reactions were found to be complete after 48 h, (*S*)-*N*-acetylphenylalanine (**10**) and (*R*)-2-methylsuccinic acid (**11**) being formed in 40 and 34.5% ee, respectively.

The optical purities of these reduction products were surprisingly lower than those we had observed with the same substrates and the Rh(I) complex of **1** (91% ee for **10** and 57% ee for **11**) [8,10]. The enantiomer of **10** which was formed in excess has the expected (*S*) absolute configuration while the enantiomer of **11** has the unexpected (*R*). The results are identical using both NPPP and **1**.

Considering the apparent structural similarities of ligands **1** and **2** the present results might be considered unexpected. However, looking at the structure of **2** determined by X-ray crystallography and comparing it with the structures of analogous pyrrolidine diphosphines [18,24–27], of which **1** is an example, we observed significant explanatory differences.

The asymmetric induction in hydrogenation reactions is attributed to discriminating interactions between the substrate and ligand in the catalyst complex,

particularly the P-atom phenyl groups. The exact orientation of these groups in the catalyst is dependant on the chiral conformation of each ligand which in turn is determined by the backbone structure in each particular case [28–36]. The phenyl group directly bonded to the nitrogen in **2** confers upon this atom significant $sp^2$ character as can be confirmed by bond angles C1A–N1–C5, 122.5(3); C1A–N1–C2, 124.2(3); and C5–N1–C2, 112.5(3) as well as the N1–C1A bond length, 137.0(5) pm. Unlike other known pyrrolidine ligands [18,24–27] this new chiral ligand NPPP has a quasi coplanar arrangement of the two rings which imposes an extended rigidity upon the ligand. However, what was expected to be a favourable characteristic proved not to contribute to the efficient induction of chirality, as shown by the transfer hydrogenation results presented. The small distortion of the pyrrolidine ring originated by the partial double bond character of the N–C bond may be the main factor responsible for the distortion and consequently unfavourably disturb the conformation of the chelate formed by NPPP and the metal centre. Any eventual favourable secondary interactions by the nitrogen non-bonding electrons also become impaired.

The synthesis and study of the behaviour of new similar structures having substituted phenyls and fused ring systems is under way in order to better clarify the mechanism and in the hope of modulating a more efficient induction of chirality using the structures to whose synthesis this work has opened the way.

## 4. Conclusions

The synthetic procedure for a chiral *N*-aryl pyrrolidine ligand has been established and is described. The structure of the ligand determined by X-ray crystallography revealed the coplanarity of the pyrrolidine and *N*-phenyl rings, a unique characteristic comparatively to other structural analogues. This alters the conformations of the pyrrolidine ring as well as the ligand-metal chelate, a factor that in the case of the parent *N*-aryl pyrrolidine ligand we have prepared is apparently responsible for the low discrimination in the enantioselective transfer hydrogenation process. Ligands with the same basic pyrrolidine structure and different *N*-substituents are expected to contribute to a clearer understanding of the role each of the features plays on the induction of chirality and hopefully lead the way to better catalysts.

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