OPTICALLY ACTIVE NITROGEN LIGANDS

III *. ENANTIOFACE-DISCRIMINATING TRANSFER HYDROGENATION OF ACETOPHENONE CATALYZED BY RHODIUM(I) COMPLEXES WITH CHIRAL 2-(2'-PYRIDYL)PYRIDINES

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Summary

The reduction of acetophenone by hydrogen transfer from isopropanol is catalyzed by rhodium(I) complexes containing optically active 2-(2'-pyridyl)pyridines. Optical yields up to 15% have been obtained.

Introduction

In recent years optically active chelating nitrogen ligands have found widespread application in asymmetric homogeneous catalysis by transition metal complexes [1]. In particular, it has been shown that in certain asymmetric processes such as hydrosilylation [2,3] and transfer hydrogenation [4,5] they often give higher optical yields than those obtained with phosphine ligands. Most of these nitrogen ligands have imine structures and are derived from the condensation reaction of 2-pyridine-carbaldehyde or 2-acetylpyridine with optically active primary amines (1).
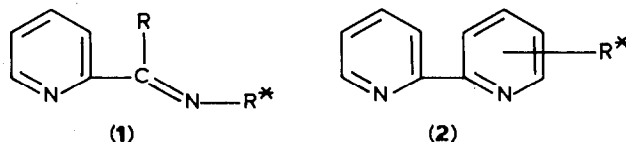

(R = H or methyl group ; R* = chiral alkyl , cycloalkyl or aralkyl group)

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* For part II see ref. 8.

In spite of the well documented catalytic activity of rhodium(I) and iridium(I) 2-(2'-pyridyl)pyridine complexes in transfer hydrogenation of prochiral ketones [4–6] no references have appeared in the literature so far on the corresponding reductions with optically active 2,2'-bipyridines (2).

We recently reported the syntheses of the four possible isomers of chiral s-butyl-2-(2'-pyridyl)pyridine with high optical purity [7,8]. In this paper we describe the preparation of other members of this class of ligands, and some results obtained in the enantioface differentiating reduction of acetophenone by hydrogen transfer using isopropanol as hydrogen supplier and rhodium(I) complexes containing the ligands of type 2 as the catalytic precursors.
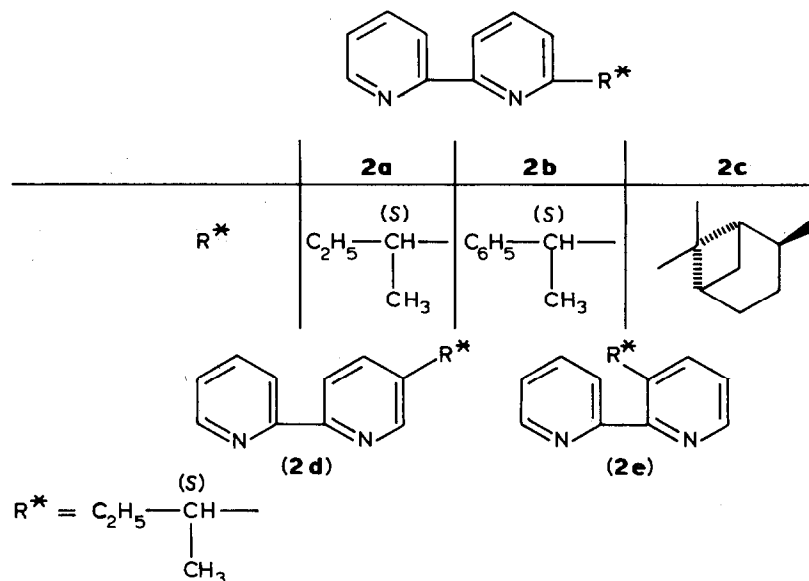

Results and discussion

Synthesis of the chiral ligands

The s-butyl-substituted ligands 2a, 2d and 2e were available in our laboratory [7,8] but the 6-(1-methylbenzyl)- and 6-(6,6-dimethylbicyclo[3.1.1]hept-2-yl)-2,2'-bipyridines 2b and 2c, respectively, were specially synthesized in a search for a higher stereodifferentiating ability in the chiral substituent.

The preparation of the bipyridine 2b was accomplished by the route previously devised for the s-butyl analogue (Scheme 1) [7]. (+)-(S)-2-(1-Methylbenzyl)pyridine (3), readily available from (−)-(S)-2-phenylpropanenitrile [9], was oxidized with 3-chloroperbenzoic acid to the corresponding N-oxide 4 which was treated with dimethyl sulphate, followed by aqueous potassium cyanide to give the nitrile 5 (isolated in 58% overall yield by chromatography) [10]. The co-cyclotrimerization of this compound with acetylene proceeded smoothly at 12 atm and 100°C in toluene solution in the presence of (π-cyclopentadienyl)cobalt-1,5-cyclooctadiene [7,11] and the expected bipyridine 2b was obtained in pure form in 80% yield.

The enantiometric purity of this ligand was determined by the lanthanide shift reagent method. From the ^{1}H NMR spectrum recorded in the presence of tris{3-
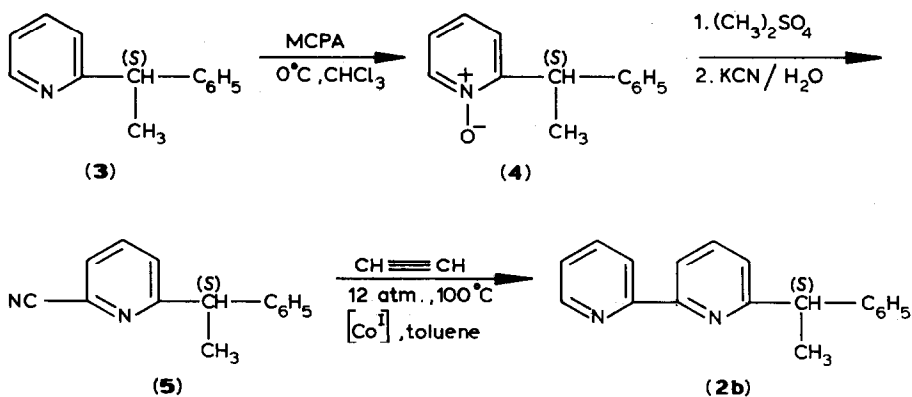
SCHEME 1. $[Co^I] = (\pi\text{-cyclopentadienyl})cobalt-1,5-cyclooctadiene.$

[(heptafluoropropyl)hydroxymethylene]-d-camphorato}europium (III), a 41.2% enantiomeric excess was assigned to a sample of **2b** showing $[\alpha]_D^{20} + 61.9$ (c 2.07; cyclohexane) (see Experimental). On this basis the maximum optical rotation for ($+$)-(S)-6-(1-methylbenzyl)-2,2'-bipyridine (**2b**) could be calculated ($[\alpha]_{D\ max}^{20} + 150.2°$).
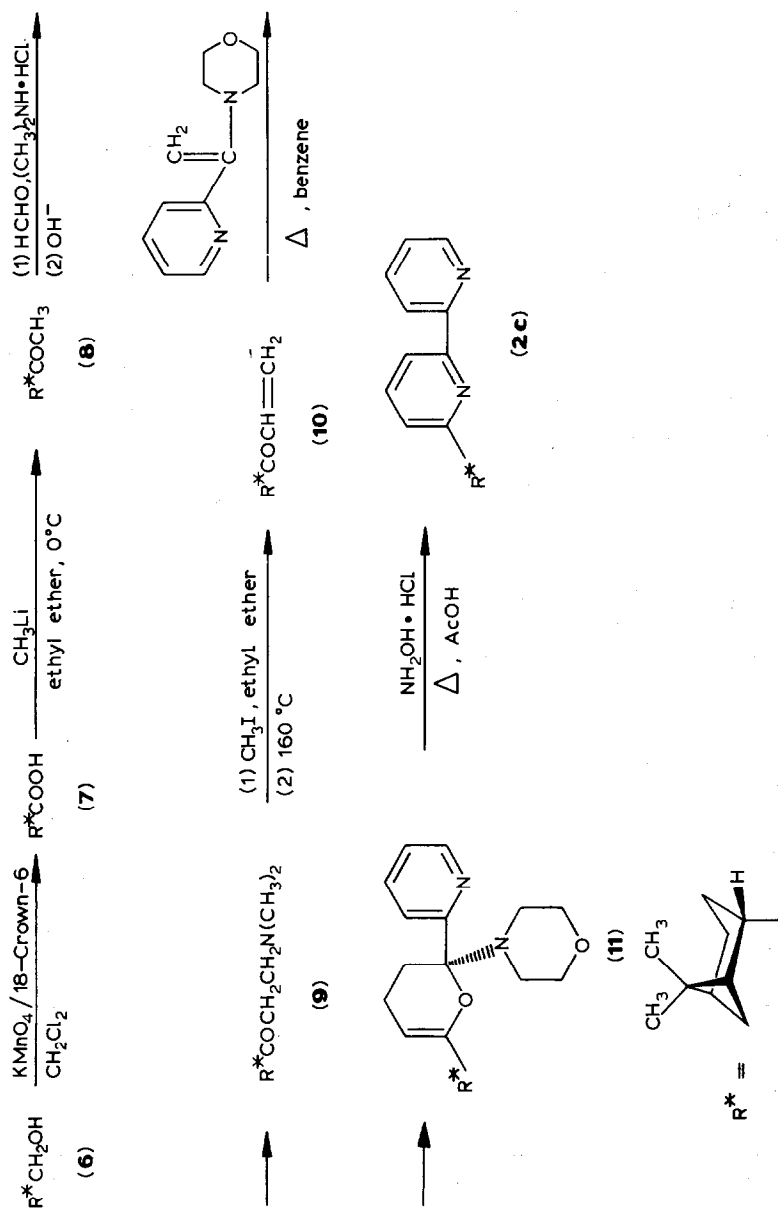
The chiral ligand 6-{(1S,2S)-6,6-dimethylbicyclo[3.1.1]hept-2-yl}-2,2'-bipyridine (**2c**) was prepared from commercially available ($-$)-$trans$-myrtanol (**6**) by the sequence shown in Scheme 2.

TABLE 1

REDUCTION OF ACETOPHENONE BY HYDROGEN TRANSFER FROM ISOPROPANOL CATALYZED BY $[Rh(COD)Cl]_2$ AND THE CHIRAL BIPYRIDINES **2a–2e**. (Reaction conditions: 2.5×10^{-5} mol of $[Rh(COD)Cl]_2$ in 45 ml of isopropanol; Rh/Substrate $= 1/200$; T 83°C)

Run	Ligand	Rh/Ligand	Rh/KOH	T.N. [b]	Optical yield [c] (%)	(Conf.)
1 [a]	**2a**	1/2	1/10	28.0	2.7	(R)
2	**2a**	1/5	1/10	67.2	7.2	(R)
3 [a]	**2a**	1/5	1/5	12.6	3.5	(R)
4 [a]	**2a**	1/5	1/20	57.0	4.5	(R)
5	**2a**	1/15	1/10	172.0	4.5	(R)
6 [a]	**2b**	1/2	1/10	43.0	1.8	(R)
7	**2b**	1/5	1/10	39.6	4.3	(R)
8	**2b**	1/10	1/10	82.0	2.5	(R)
9	**2c**	1/5	1/10	85.0	14.8	(R)
10	**2c**	1/10	1/10	52.6	1.3	(R)
11	**2d**	1/2	1/10	48.0	2.5	(R)
12	**2d**	1/5	1/10	29.0	1.6	(R)
13	**2d**	1/10	1/10	33.6	1.7	(R)
14	**2e**	1/5	-1/10	154.0	1.1	(R)

[a] Separation of a black precipitate was observed during the reaction. [b] T.N. = turnover number = mols of substrate converted per hour and g-atom of rhodium. [c] Extrapolated to 100% optical purity of the ligand.

R^*CH_2OH

(6)

$\xrightarrow[CH_2Cl_2]{KMnO_4/18\text{-}Crown\text{-}6}$

R^*COOH

(7)

$\xrightarrow[\text{ethyl ether, 0°C}]{CH_3Li}$

R^*COCH_3

(8)

$\xrightarrow[\text{(2) OH}^-]{\text{(1) HCHO,(CH}_3\text{)}_2\text{NH•HCl}}$

$R^*COCH_2CH_2N(CH_3)_2$

(9)

$\uparrow$

$\xrightarrow[\text{(2) 160 °C}]{\text{(1) CH}_3\text{I, ethyl ether}}$

$R^*COCH{=}CH_2$

(10)

$\xleftarrow[\Delta\text{ , benzene}]{}$

(structure 8 side group drawn)

(11)

$\xrightarrow[\Delta\text{ , AcOH}]{NH_2OH•HCl}$

(2c)

$R^* =$

SCHEME 2

The acid **7** [12], easily prepared by permanganate oxidation of **6** [13], reacted with methyllithium to give the methyl ketone **8** in 50% overall yield. This compound converted (60% yield) into the vinyl derivative **10** by pyrolysis of the methiodide of the corresponding Mannich base **9**. Condensation of **10** with 2-acetylpyridine-morpholino-enamine [8], followed by reaction of the crude product **11** with a three-fold excess of hydroxylamine hydrochloride in acetic acid, gave the expected bipyridine **2c** in 25% yield.

Transfer hydrogenation experiments

The procatalysts were prepared in situ by addition of the chiral ligand to [Rh(COD)Cl]$_2$ in isopropanol. Potassium hydroxide was then added, and the solution was refluxed for 1 h to promote the formation of the actual catalyst. The substrate was then introduced and the reductions were carried out at 83°C under nitrogen, the progress of the reaction being monitored by GLC.

Table 1 shows the experimental conditions and the results obtained in the transfer hydrogenation of acetophenone, used as a model substrate for prochiral ketones, with isopropanol as the hydrogen supplier and potassium hydroxide as the base.

The dependence of the reaction parameters on the concentration of the inorganic base was briefly investigated. In the presence of ligand **2a** both the rate and the stereoselectivity showed the same behaviour, reaching their maxima at a KOH/Rh ratio of 10 (runs 2, 3 and 4). This ratio was then used in all the other experiments under these reaction conditions.

The values of the turnover numbers spread over more than one order of magnitude, and, although in most cases they increase with increasing ligand/metal ratio, there are some exceptions and so no generalization could be made.

Usually a considerable ligand excess was required for a satisfactory reaction rate. At lower ratios separation of a black precipitate, probably metallic rhodium, was sometimes observed, and this causes a sharp decrease in the catalytic activity. This may indicate that the formation constants of the complexes which display the highest catalytic activity are rather small, probably as a consequence of the steric hindrance from the alkyl substituent when it is close to one of the nitrogen atoms. The extent of this effect is particularly clear in the case of the 6-substituted ligands, which require a 5–10 fold excess of the bipyridine in order to force the more hindered nitrogen atom to remain in the coordination sphere of the metal.

The position and the structure of the chiral alkyl substituent also has a strong influence on the stereoselectivity. For ligands bearing the same substituent the highest stereodifferentiation is observed when the chiral group is closest to nitrogen (i.e. **2a** is better than **2d** and **2e**), while among the 6-alkylbipyridines the bulkiest substituent is also the most effective (i.e. **2c** is better than **2a** and **2b**).

The optical purities of 1-phenylethanol obtained in these experiments are rather low, reaching about 15% in the best case (run 9). The fact that in every case the product showed the predominant (*R*) configuration irrespective of the ligand used suggests that the chiral information transferred from the alkyl group to the vacant active site is always of the same type. In fact the ligands **2a**, **2b** and **2c** have the same configuration at the asymmetric carbon linked to the heteroaromatic ring.

These results can be rationalized by assuming that the arrangement of the chelating bipyridine around rhodium in the catalytically active species is very close

to that proposed recently by Brunner [1] for the pyridine imine derivatives 1. According to this model the closer the optically active moiety is to the vacant active site of the intermediate catalytic complex (which happens for ligands 2a–2c) the stronger is the chiral information felt by the prochiral substrate approaching the rhodium. Moreover, larger steric hindrance in the chiral group of the ligand, which improves the conformational homogeneity of the true catalyst, generally leads to higher asymmetric induction.

It must be noted that, although the optical yields obtained in the course of this work are unsatisfactory and usually lower than those obtained in the same process using chiral imine ligands [14], bipyridines show some advantages compared with the latter. Firstly, they can be easily recovered at the end of the reaction in high yield and without any optical loss by simply washing with dilute acid. Secondly, the recovered ligand can be re-used several times in the asymmetric process with no effect on the stereoselectivity of the reaction. Finally, the introduction into the bipyridine rings of one or more chiral substituents different from those reported here can result in remarkable enhancements of the stereoselectivity and we are at present working along that line.

Experimental

Materials

Isopropanol and acetophenone (Fluka AG) were distilled before use under nitrogen. $(-)$-trans-Myrtanol, $[\alpha]_D^{20}$ $-29.2°$ (neat) was used as received (Fluka AG). Chloro(1,5-cyclooctadiene)rhodium(I) dimer was prepared from rhodium trichloride hydrate as reported in the literature [15]. 2-Acetylpyridinemorpholino-enamine was prepared as previously described [8]. $(+)$-(S)-2-Methylbenzylpyridine, $[\alpha]_D^{20}$ $+29.36°$, was prepared from $(-)$-(S)-2-phenylpropanenitrile as described in ref. 9.

The ligands $(-)$-(S)-3-s-butyl (2e), $[\alpha]_D^{25}$ -39.90 (c 2.04; cyclohexane), $(+)$-(S)-5-s-butyl (2d), $[\alpha]_D^{25}$ $+26.45°$ (c 2.02; cyclohexane), and $(+)$-(S)-6-s-butyl-2-(2'-pyridyl)pyridine (2a), $[\alpha]_D^{20}$ $+29.51°$ (c 2.057, cyclohexane) were prepared by published procedures [7,8]. The optical purities of these ligands were 95, 95, and 63%, respectively [7,8].

General procedures

Melting points were determined on a Büchi melting point apparatus and are uncorrected. GLC analyses were performed on a Perkin–Elmer 3920B instrument using 6 ft packed columns of 5% SE-30 and 15% Carbowax 20M on Chromosorb W 80–100 mesh. ^{1}H NMR spectra were recorded with a Varian T-60 spectrometer using tetramethylsilane as internal standard ($\delta = 0$). Optical rotations were measured with a Perkin–Elmer 241 polarimeter. IR spectra were recorded with a Perkin–Elmer 683 spectrophotometer. Elemental analyses were performed with a Perkin–Elmer Elemental Analyzer 240 B.

(S)-2-(1-Methylbenzyl)pyridine N-oxide (4)

A solution of 3-chloroperbenzoic acid (4.8 g, 28.1 mmol) in $CHCl_3$ (80 ml) was slowly added to a cold solution of $(+)$-(S)-2-(1-methylbenzyl)pyridine (3) (3.4 g, 18.7 mmol) in $CHCl_3$ (10 ml). The mixture was then stirred at room temperature for 24 h, and subsequently treated with 10% K_2CO_3 (50 ml). The organic layer was

separated and the aqueous phase extracted with $CHCl_3$ (3 × 25 ml). The combined organic extracts were dried over Na_2SO_4 and the solvent was evaporated. The solid residue was repeatedly washed with anhydrous ether to give the N-oxide as white crystals (2.85 g, 77% yield), m.p. 105°C.

(S)-2-Cyano-6-(1-methylbenzyl)pyridine (5)

A mixture of compound 4 (2.85 g, 14.4 mmol) and dimethyl sulfate (1.83 g, 14.4 mmol) was stirred at 80–85°C for 3 h. After cooling, the crude N-methoxy-pyridinium methyl sulfate was taken up in water (10 ml) and this solution was slowly added with stirring to aqueous potassium cyanide (2.2 g, in 10 ml) at 0°C. The mixture was stirred overnight at room temperature, extracted with ether, and dried over sodium sulfate. Removal of the solvent gave 5 (3.0 g), 80% pure by GLC. Column chromatography over silica gel (50 g/1 g product) using benzene as eluant gave pure 5 (2.25 g; 75% yield): b.p. 130°C at 0.02 mmHg.

^{1}H NMR ($CDCl_3$) δ: 7.76–7.04 (m, 3H); 7.17 (s, 5H); 4.27 (q, 1H); 1.69 (d, 3H) ppm. IR (neat): ν(C≡N) 2239 cm^{-1}. (Found: C, 80.57; H, 6.09; N, 13.14. $C_{14}H_{12}N_2$ calcd.: C, 80.74; H, 5.80; N, 13.45%).

(+)-(S)-6-(1-Methylbenzyl)-2-(2'-pyridyl)pyridine (2b)

A solution of 5 (2.2 g, 10.6 mmol) and (π-cyclopentadienyl)cobalt-1,5-cyclooctadiene (0.15 g) in degassed toluene (12 ml) was introduced by suction into a 200 ml autoclave from which the air had been evacuated (to 0.1 mmHg). The reaction vessel was pressurized to 12 atm with acetylene and then heated at 100°C. The theoretical amount of acetylene was adsorbed within 24 h. After cooling and releasing of the residual gas, the suspension was filtered, and the filtrate extracted with 10% HCl. Treatment of the acidic extracts with saturated aqueous Na_2CO_3, extraction with ether and distillation in vacuo gave pure 2b as a pale yellow oil (2.2 g, 80% yield): b.p. 147°C at 0.2 mmHg; $[\alpha]_D^{20}$ +61.87° (c 2.07, cyclohexane).

^{1}H NMR ($CDCl_3$) δ: 8.65–8.90 (m, 12H, aromatic); 4.29 (q, 1H); 1.75 (d, 3H) ppm. (Found: C, 82.95; H, 6.37; N, 10.54. $C_{18}H_{16}N_2$ calcd.: C, 83.04; H, 6.19; N, 10.76%).

Determination of the enantiomeric purity of 2b

The ^{1}H NMR spectra of 2b were recorded on a Varian XL-100 spectrometer using $CDCl_3$ as the solvent and TMS as internal standard. The chiral shift reagent employed was tris{3-[(heptaflouropropyl)hydroxymethylene]-d-camphorato}europium(III), supplied by Sigma Chemical Corp.

The most satisfactory spectrum for enantiomeric purity determination was obtained using a sample containing 5 mg of 2b, $[\alpha]_D^{20}$ +61.87° (c 2.07, cyclohexane) and 30 mg of the chiral shift reagent in 0.5 ml of the solvent. Under these conditions a comparison with the spectrum of the racemic compound revealed two distinctly resolved signals for the (S) and (R) enantiomer at 9.13 and 9.55 ppm, respectively, in a 2.4/1 ratio.

(−)-(1S,2S)-6,6-Dimethylbicyclo[3.1.1]heptane-2-carboxylic acid (7)

A mixture of (−)-trans-myrtanol (6) (10.4 g, 67 mmol), $KMnO_4$ (14.3 g, 90 mmol) and dicyclohexyl-18-crown-6 (1 g) in CH_2Cl_2 (100 ml) was stirred vigorously at room temperature for 60 h. Manganese dioxide was filtered off and washed with

CH_2Cl_2 (2 × 20 ml). The combined filtrate and washings were extracted with 10% NaOH, and the aqueous phase was separated, acidified with 10% HCl, and extracted with ether (2 × 30 ml). Drying over Na_2SO_4, evaporation of the solvent, and distillation of the oily residue gave pure 7 (7.9 g, 70% yield): b.p. 105°C at 0.5 mmHg; $[\alpha]_D^{25}$ −6.29° (c 2.2 cyclohexane). ^1H NMR (CCl_4) δ: 2.83 (t, 1H); 1.23 (s, 3H); 0.87 (s, 3H) ppm.

(+)-1-{(1S,2S)-6,6'-Dimethybicyclo[3.1.1]hept-2-yl}ethanone (8)

To a cooled solution (0°C) of 7 (13.5 g, 80 mmol) in anhydrous ether (50 ml) a 1.6 M solution of methyllithium in ether (100 ml) was added during 80 min. After 1 h stirring at room temperature the mixture was treated with ice. The organic layer was separated and dried (Na_2SO_4), and the solvent was removed in vacuo to give 8 (13.4 g), 75% pure by GLC.

Purification of 8 was accomplished by column chromatography (silica gel; 70 g/1 g product; benzene as the eluant) affording the pure product (9.4 g, 71% yield): b.p. 95°C at 3 mmHg; $[\alpha]_D^{25}$ +59.95° (c 2.20, cyclohexane). ^1H NMR (CCl_4) δ: 2.83 (t, 1H); 2.00 (s, 3H); 1.24 (s, 3H); 0.90 (s, 3H) ppm. (Found: C, 79.30; H, 11.25. $C_{11}H_{18}O$ calcd.: C, 79.46; H, 10.91%).

1-{(1S,2S)-6,6-Dimethylbicyclo[3.1.1]hept-2-yl}-3-dimethylamino-1-propanone (9)

A mixture of 8 (8.25 g, 50 mmol), dimethylamine hydrochloride (4.1 g, 51 mmols), and paraformalehyde (1.7 g) in ethanol (6 ml) containing a few drops of concentrated HCl was refluxed for 17 h. After cooling, the mixture was diluted with water, and the resulting solution was extracted three times with ether. The combined extracts were washed twice with 10% HCl, and the aqueous phase and the acidic extracts were combined, made alkaline with 10% NaOH and extracted with ether. Drying over Na_2SO_4, evaporation of the solvent, and distillation gave 9 (9.45 g, 85% yield): b.p. 105° at 0.05 mmHg.

1-{(1S,2S)-6,6-Dimethylbicyclo[3.1.1]hept-2-yl}-2-propen-1-one (10)

A solution of methyl iodide (7.4 g, 52 mmol) in anhydrous ether (15 ml) was slowly added to an ethereal solution of 9 (9.45 g, 42.4 mmol in 30 ml ether) at 0°C. After the addition was complete, the reaction mixture was stirred overnight at 0°C. Evaporation of the solvent gave the crude tetralkylammonium salt in quantitative yield. Thermolysis of this compound was performed in a bulb-to-bulb distillation apparatus at 160°C under reduced pressure (0.1 mmHg). The decomposition products were collected and redistilled to give 10 (5.4 g, 71% yield): b.p. 120°C at 0.5 mmHg; $[\alpha]_D^{25}$ +38.64° (c 2.2, cyclohexane).

^1H NMR (CCl_4) δ: 6.30–6.07 (m, 2H); 5.63–5.42 (m, 1H); 3.10 (t, 1H); 1.23 (s, 3H); 0.90 (s, 3H) ppm. (Found: C, 80.77; H, 10.27, $C_{12}H_{18}O$ calcd.: C, 80.85; H, 10.17%).

(+)-6-{(1S,2S)-6,6-Dimethylbicyclo[3.1.1]hept-2-yl}-2-(2'-pyridyl)pyridine (2c)

A solution of 10 (3.3 g, 18.5 mmol) and 2-acetylpyridine morpholinoenamine (3.52 g, 18.5 mmol) was refluxed in anhydrous benzene (20 ml) for 60 h. After evaporation of the solvent the residue was taken up in acetic acid (20 ml), hydroxylamine hydrochloride (3.0 g, 43 mmol) was added, and the mixture was heated at 115°C for 2 h. After cooling, the solvent was removed in vacuo, 10%

aqueous NaOH (10 ml) was added, and the mixture was extracted with ether. Drying over Na_2SO_4, evaporation of the solvent, and bulb-to-bulb distillation gave 2c (1.03 g, 20% yield): b.p. 160°C at 0.05 mmHg; $[\alpha]_D^{25} +23.10°$ (c 2.09, cyclohexane).

Compound 2c showed a diastereomeric purity higher than 95%, as determined by GLC analysis at 250°C on a 50 m × 0.23 mm i.d. fused silica capillary column coated with SE-30 (retention time, 29 min.).

^{1}H NMR (CDCl$_3$) δ: 8.60–7.97 (m, 3H); 7.80–7.37 (m, 2H); 7.25–6.90 (m, 2H); 3.67–3.13 (m, 1H); 2.70–1.50 (m, 8H); 1.27 (s, 3H); 1.00 (s, 3H) ppm. (Found: C, 81.84; H, 8.28; N, 9.91. $C_{19}H_{22}N_2$ calcd.: C, 81.97; H, 7.96; N, 10.06%).

Catalytic transfer hydrogenations, general procedure

The catalyst was prepared in situ by adding the required amount of the relevant bipyridine to a solution of [Rh(COD)Cl]$_2$ (2.5×10^{-5} mol) in 2-propanol (40 ml) under nitrogen. After addition of KOH (5×10^{-4} mol) in 5 ml of 2-propanol the solution was refluxed for 1 h and then stirred overnight at room temperature before addition of the substrate (0.01 mol). The progress of the reaction was monitored by GLC (10% SP-1000 on 80/100 Supelcoport; 3 m × 3 mm, 170°C).

The product was isolated by distillation under reduced pressure after evaporation of the solvent and washing of the residue with dilute hydrochloric acid. The optical purity of the carbinol was determined in methanol solution (c 4.9) using a value of $[\alpha]_{Dmax}^{23} -45.5°$ for the (S) isomer [16].

Recovery of the chiral ligand

The reaction mixture from run 5 (Table 1), containing 160 mg of ligand 2a, $[\alpha]_D^{25}$ +29.51°, was worked up as above. Processing the aqueous acid extracts gave, after bulb-to-bulb distillation, 155.3 mg of 2a, $[\alpha]_D^{25}$ +29.24°, corresponding to a 97% recovery and less than 1% loss of optical purity.

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