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ASYMMETRIC HYDROGENATION CATALYZED BY AMINOPHOSPHINE-PHOSPHINITERHODIUM COMPLEXES DERIVED FROM NATURAL AMINOALCOHOLS AND X-RAY CRYSTAL STRUCTURE OF (1,5-CYCLOOCTADIENE)-(*S*)-*N*-(DIPHENYLPHOSPHINO)-2-DIPHENYLPHOSPHINOXYMETHYLPYRROLIDINERHODIUM(I) PERCHLORATE

E. CESAROTTI*, A. CHIESA,

Istituto di Chimica Generale e Inorganica, Centro CNR, Via Venezian 21, 20133 Milano (Italy)

G. CIANI and A. SIRONI *

Centro di Studio per la Sintesi e la Struttura dei Metalli di Transizione nei bassi Stati di Ossidazione, Reparto Strutture, Via Venezian 21, 20133 Milano (Italy)

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Summary

From the cheap and readily available amino alcohols (*S*)-pyrrolidinemethanol ((*S*)-prolinol), and (*S*)-α-*N*-ethyl-aminobutanol, we have obtained two new aminophosphine-phosphinite ligands: (*S*)-*N*-(diphenylphosphino)-2-diphenylphosphinooxymethylpyrrolidine ((*S*)-Prolophos) and (*S*)-1-diphenylphosphinoxy-2-*N*-ethyl-*N*-diphenylphosphinoaminobutane ((*S*)-Butaphos). The rhodium(I) complexes of these phosphines act as efficient homogeneous hydrogenation catalysts at ambient temperature and pressures for dehydro *N*-acetyl amino acids, dehydro *N*-benzoyl amino acids and itaconic acid.

An X-ray diffraction study of the complex [Rh(COD)((*S*)-Prolophos)][ClO_4]·THF has been shown that the crystals belong to the monoclinic space group $P2_1$ with *a* 10.680(2), *b* 10.448(2), *c* 18.207(3) Å and β 104.97(1)°. Refinements based on 2105 significant counter reflections led to a final *R* value of 0.060. The cation is in a distorted square planar geometry, the rhodium atom being bound to the two phosphorus atoms and to the two double bonds of the diene molecule.

Introduction

Since the discovery of highly active homogeneous rhodium catalysts by Wilkinson in 1966 a large number of chiral diphosphines have been shown to be effective in asymmetric reductions [1,2]. Up to now more than hundred chiral phosphines have been prepared and tested as ligands in asymmetric catalytic homogeneous hydrogenation of hundreds of substrates [3]. Despite the success so far obtained in

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asymmetric catalysis it is still desirable to find new types of ligands which are more easily made and more versatile. Many of the ligands used, at least the most successfull ones, are difficult to prepare either because the synthesis involves many steps, some of them under strictly anaerobic conditions, or because they are difficult to obtain pure enough for use in asymmetric hydrogenations. Of the various chiral phosphine ligands so far reported, aminophosphines and phosphinites have attracted much interest because 1,2-diamines and 1,2-diols are chiral sources easy available in a variety of forms [4–6]. We have used aminoalcohols (*S*)-prolinol and the related (*S*)-α-*N*-ethyl-aminobutanol as sources of chiral starting materials because of their ready availability and low price *. In this paper we describe the synthesis of two new chiral aminophosphine-phosphinite ligands, (*S*)-*N*-(diphenylphosphino)-2-diphenylphosphinoxymethylpyrrolidine ((*S*)-Prolophos) and (*S*)-1-diphenylphosphinoxy-2-*N*-ethyl-*N*-diphenylphosphinoaminobutane ((*S*)-Butaphos). From these ligands we have prepared the corresponding cationic rhodium complexes, and have used them in asymmetric homogeneous catalytic reduction of a number of prochiral substrates. The results of an X-ray investigation of the complex [Rh(COD)((*S*)-Prolophos)][ClO_4] · THF are also reported and discussed.

Experimental section

(*S*)-Prolinol, (*S*)-α-aminobutanol, and diphenylchlorophosphine were purchased from Aldrich and used as received. Solvents were purified by standard methods and degassed with a vigorous stream of argon before use.

Infrared spectra were recorded on a Nicolet NX-1 spectrometer; The ^1H and ^{31}P NMR spectra were recorded on a Bruker WP80 spectrometer. Microanalyses were performed by the microanalysis service of the Istituto di Chimica Organica (Milano). MS spectra were recorded on a MAT 112 mass spectrometer; optical rotations were measured on a Perkin–Elmer polarimeter with a precision of approximately 0.01°.

Preparation of (S)-Prolophos

To a vigorously stirred solution of 10.0 mmol (*S*)-Prolinol, $[\alpha] = +3.4$ ($c = 2$; MetOH) and triethylamine, 50.0 mmol, in toluene (20 ml) under nitrogen, 20.5 mmol of diphenylchlorophosphine are added dropwise at 0°C during 30 min; precipitation of triethylammoniumchloride occurs almost immediately. The mixture is stirred overnight at room temperature, filtered, and evaporated to dryness. The oily residue is kept under vacuum (10^{-2} mmHg) for two days at 40°C. The (*S*)-Prolophos is left as a viscous transparent oil in almost quantitative yield. The IR spectrum shows no ν(OH) or ν(NH) stretching bond. $[\alpha]_D^{25} = -15$ ($c = 1$, $CHCl_3$). Anal. Found: C, 72.92; H, 5.83; N, 2.78. $C_{29}H_{29}NOP_2$ calcd.: C, 74.2; H, 6.11; N, 2.99%. M^+,469.

^1H NMR ($CDCl_3$, TMS): δ (ppm) 1.6–2.0 (m, 4p), 2.5–3.0 (m, 2p), 3.6–4.1 (m, 3p), 7.4 (d, 20p).

^{31}P NMR ($CDCl_3$, H_3PO_4 ex. stand.): δ (ppm): P(O) 113.8; P(N) 46.1.

The (*S*)-Prolophos obtained as described is almost pure enough to be used in asymmetric hydrogenation but the ^{31}P NMR spectrum shows the presence of small amounts of phosphorus containing impurities. The (*S*)-Prolophos is obtained com-

* (*S*)-Prolinol and (*S*)-α-aminobutanol are commercially available in high optical purity at approximate prices of $2.0 and $0.2 per g, respectively.

pletely pure by column chromatography on silica gel with ethylacetate/diethylamine (98/2) as eluant. The rotatory power increases to $[\alpha]_D^{25} = -18$ ($c = 1$, $CHCl_3$) but there is no appreciable differences in asymmetric catalysis between the purified (*S*)-Prolophos and that obtained by prolonged exposure of the crude product to high vacuum.

(S)-α-N-ethyl-aminobutanol

A solution of (*S*)-α-aminobutanol (20 ml) in 50 ml acetic anhydride is refluxed for two hours. The mixture is allowed to cool and added to 500 ml of ice-water, neutralized with NH_3 (25%), and extracted with CH_2Cl_2. The organic layer is dried over sodium sulphate and evaporated to dryness to give (*S*)-α-*N*-acetyl-aminobutane-1-acetate as a white solid. This is reduced with $LiAlH_4$ in THF without further purification.

A solution of 28 g of (*S*)-α-*N*-acetyl-aminobutane-1-acetate in 50 ml THF is added dropwise to a suspension of $LiAlH_4$ (25 g) in 400 ml THF. The solution is refluxed overnight and the mixture then treated successively with 25 ml water, 25 ml of 15% aqueous NaOH, and 75 ml of water. The THF solution is filtered, dried over sodium sulphate, and evaporated. The oily residue is distilled in vacuum to give 16.2 g (86% yield) of (*S*)-α-*N*-ethyl-aminobutanol; $[\alpha]_D^{25} = -36.5$ ($c = 1$, $CHCl_3$), b.p. 85°C/15 mmHg.

Preparation of (S)-Butaphos

(*S*)-Butaphos is prepared in tha same way as (*S*)-Prolophos but starting from α-*N*-ethyl-aminobutanol (10.0 mmol) $[\alpha]_D^{25} = -36.5$ ($c = 1.3$, $CHCl_3$). After evaporation to dryness the IR spectrum shows no ν(OH) or ν(NH) stretching band. The ^{31}P NMR spectrum shows that the desired compound is produced in about 50% yield. It is purified by column chromatography on silica gel with ethylacetate/diethylamine (98/2) as eluant.

$[\alpha]_D^{25} = +3$ ($c = 1$, $CHCl_3$). Anal. Found: C, 72.14; H, 6.54; N, 2.72. $C_{30}H_{33}NOP_2$ calcd.: C, 74.23; H, 6.80; N, 2.89%. M^+, 485.

^1H NMR ($CDCl_3$, TMS): δ (ppm) 0.6–1.0 (m, 8p), 1.7 (q, 2p) 3.0 (d, 2p) 3.9 (m, 1p), 7.4 (d, 20p).

^{31}P NMR ($CDCl_3$, H_3PO_4 ext. stand.): δ (ppm): P(O), 113.2, P(N) 43.9.

Rhodium complexes

The rhodium complexes were prepared either by the method of Schrock and Osborn [7] or by displacing one of the COD ligands in $[Rh(COD)_2] \cdot ClO_4$ by the appropriate phosphine.

[Rh(COD)((S)-Prolophos)][ClO₄] · CH₂Cl₂

The complex $[Rh(COD)_2][ClO_4]$ (0.418 g, 1.0 mmol) is dissolved in 5 ml CH_2Cl_2 under argon, and a solution of (*S*)-Prolophos (0.516 g,1.1 mmol) in 5 ml CH_2Cl_2 is added dropwise during 5 min. The deep red solution is reduced to 2 ml, then a layer of 2 ml THF is introduced above the solution and 30 ml ether are carefully added. On standing overnight yellow orange microcrystals separate. The crystals are filtered off, washed with ether, and vacuum dried (yield 85%). The complex is solvated with one molecule of CH_2Cl_2 as indicated by the ^1H NMR spectrum (δ 5.30 ppm).

[Rh(COD)((*S*)-Prolophos)][ClO_4] · CH_2Cl_2 : Anal. Found: C, 53.13; H, 4.90; N, 1.79. $C_{37}H_{41}NOP_2RhClO_4 \cdot CH_2Cl_2$ calcd.: C, 52.75; H, 4.97; N, 1.62%.

[Rh(COD)((S)-Butaphos)][ClO_4] · CH_2Cl_2

The complex is prepared in the same way as the (*S*)-Prolophos complex. Anal. Found: C, 53.21; H, 5.50; N, 1.74. $C_{38}H_{45}NOP_2RhClO_4 \cdot CH_2Cl_2$ calcd.: C, 53.15; H, 5.34; N, 1.60%.

[Rh(COD)((S)-Prolophos)][ClO_4] · THF

The [Rh(COD)((*S*)-Prolophos)][ClO_4] · THF complex chosen for the X-ray crystal structure study was made by the method of Schrock and Osborne [7]. To a solution of $[Rh(COD)Cl]_2$, (0.468 g, 9.95 mmol) and $NaClO_4$ (0.4 g) in acetone (5 ml) a solution of (*S*)-Prolophos (1 g, 2.13 mmol) in 5 ml CH_2Cl_2 is slowly added under nitrogen. A further 15 ml of CH_2Cl_2 is added, the suspension is filtered, and the precipitate washed with CH_2Cl_2. The filtrate is concentrated to 5 ml, then 5 ml THF are added and 30 ml ether then introduced as a layer above the 10 ml of the orange THF/CH_2Cl_2 solution. On standing at room temperature overnight a crop of yellow orange microcrystals separates, giving a few well-formed crystals on the walls which were suitable for X-ray diffraction studies.

The bulk of the material obtained is solvated with 0.5 molecule CH_2Cl_2 as shown by ^1H NMR spectroscopy (δ 5.30 ppm). Anal. Found: C, 53.97; H, 5.31; N, 1.79%. $C_{37}H_{41}NOP_2RhClO_4 \cdot 0.5CH_2Cl_2$ calcd.: C, 54.74; H, 5.31; N, 1.70%.

X-Ray analysis of [Rh(COD)((S)-Prolophos)][ClO_4] · THF

Crystal data. $C_{41}H_{49}ClNO_6P_2Rh$, $M = 852.2$, Monoclinic, a 10.680(2), b 10.448(2), c 18.207(3) Å, β 104.97(1)°, U 1962.7 Å^3, D_c 1.44 g cm^{-3} for $Z = 2$, $F(000) = 884$, Mo-K_α radiation λ 0.71073 Å, μ(Mo-K_α) 6.2 cm^{-1}, space group $P2_1$ (No. 4).

Intensity data. A single prismatic crystal of dimensions 0.07 × 0.08 × 0.31 mm was mounted on a NONIUS CAD-4 diffractometer and the setting angles of 25 random intense reflections,in the range $20° < 2\theta < 26°$, were used to determine accurate cell parameters by the least-squares method. 3244 reflections, corresponding to the $\pm h, k, l$ quarter of the sphere, in the range $3° < \theta < 24°$ were collected by the ω-scan method, at a constant rate of 2.5°/min, the scan width being $(1.00 + 0.35 \tan\theta)°$ with a 25% extension at each end for background determination. The intensities of three standard reflections were measured every two hours during the exposure to X-rays and no decay was observed.

Data reduction, structure solution and refinements. The structure was solved by the heavy-atom method, on the basis of 2105 significant reflections, with $I > 3\sigma(I)$, corrected for Lorentz, polarization, and absorption effects (the maximum, minimum and average relative transmission factors were 1.00, 0.92 and 0.96, respectively, from an empirical correction based on ψ-scan). The space group was assigned on the basis of systematic absences and successful refinements. The non-phenyl atoms of the cation and the chlorine atom of the anion were refined with anisotropic thermal parameters. The hydrogen atoms were located in their idealized positions (C–H 0.95 Å) after each full-matrix least-squares cycle, with an isotropic factor of 5.0 Å^2, but not refined. At this stage a difference-Fourier map showed the presence of a clathrate THF molecule (confirmed also by GLC analysis of few crystals dissolved in CH_2Cl_2). Refinements of the five peaks attributable to THF, in spite of convergence, gave an unreliable geometry for the solvent molecule because of some disorder difficult to rationalize, but lowered the conventional agreement indices. The

(Continued on p. 86)

TABLE 1

FINAL POSITIONAL AND THERMAL PARAMETERS WITHIN [Rh(COD)((*S*)-Prolophos)][ClO_4]·THF [a,b]

Anisotropic atoms

Atom	*x*	*y*	*z*	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Rh	−0.3003(1)	0.0000	−0.17422(6)	0.00671(8)	0.00641(9)	0.00216(2)	0.0007(4)	0.00223(7)	0.0003(2)
Cl	0.4471(4)	−0.4272(5)	−0.1730(3)	0.0135(5)	0.0124(6)	0.0065(2)	−0.0048(9)	0.0072(5)	0.0031(6)
P(1)	−0.4141(3)	0.0220(4)	−0.2983(2)	0.0074(3)	0.0065(5)	0.0020(1)	0.0026(8)	0.0018(3)	−0.0001(4)
P(2)	−0.1240(4)	−0.0814(4)	−0.2058(2)	0.0069(4)	0.0066(4)	0.0027(1)	−0.0003(8)	0.0019(4)	0.0007(5)
O	−0.1211(8)	−0.091(1)	−0.2936(5)	0.0076(9)	0.008(1)	0.0029(3)	0.000(2)	0.0028(9)	0.000(1)
N	−0.396(1)	−0.082(1)	−0.3620(6)	0.006(1)	0.008(1)	0.0027(4)	0.005(2)	0.000(1)	0.000(1)
C(1)	−0.460(1)	0.106(2)	−0.1356(7)	0.009(2)	0.014(2)	0.0021(5)	0.006(3)	0.004(1)	0.000(2)
C(2)	−0.468(1)	−0.030(1)	−0.1220(7)	0.011(1)	0.009(2)	0.0032(5)	−0.002(3)	0.005(1)	−0.003(2)
C(3)	−0.418(2)	−0.092(2)	−0.0469(9)	0.015(2)	0.019(3)	0.0045(7)	−0.008(4)	0.008(2)	0.004(2)
C(4)	−0.286(2)	−0.056(2)	−0.0011(8)	0.015(2)	0.020(3)	0.0022(5)	0.010(4)	0.003(2)	0.005(2)
C(5)	−0.198(1)	−0.008(2)	−0.0491(7)	0.013(2)	0.012(2)	0.0030(5)	−0.007(5)	0.002(1)	−0.004(3)
C(6)	−0.182(2)	0.103(2)	−0.0733(8)	0.013(2)	0.011(2)	0.0031(5)	−0.003(3)	0.004(2)	−0.007(2)
C(7)	−0.261(2)	0.220(2)	−0.0600(11)	0.016(2)	0.011(2)	0.0065(8)	−0.013(4)	0.006(2)	−0.007(2)
C(8)	−0.404(2)	0.200(2)	−0.0755(9)	0.023(3)	0.011(2)	0.0043(7)	0.010(4)	0.007(2)	−0.002(2)
C(9)	−0.189(1)	−0.191(1)	−0.3422(8)	0.014(2)	0.006(2)	0.0042(7)	0.002(3)	0.006(2)	−0.003(2)
C(10)	−0.331(1)	−0.201(1)	−0.3461(8)	0.009(2)	0.008(2)	0.0023(5)	0.002(3)	0.001(1)	−0.002(2)
C(11)	−0.397(2)	−0.292(2)	−0.4124(10)	0.012(2)	0.010(2)	0.0053(8)	0.003(4)	0.000(2)	−0.006(2)
C(12)	−0.448(2)	−0.205(2)	−0.4766(11)	0.022(3)	0.018(3)	0.0050(9)	0.007(6)	−0.003(3)	−0.001(3)
C(13)	−0.479(2)	−0.082(2)	−0.4411(8)	0.014(2)	0.011(2)	0.0027(5)	0.004(4)	0.002(2)	−0.004(2)

(continued)

Table 1 (continued)

Isotropic atoms

Atom	x	y	z	B(Å^2)	Atom	x	y	z	B(Å^2)
O(1)	0.375(2)	−0.538(2)	−0.1902(9)	12.0(5)	C(214)	−0.036(1)	−0.499(3)	−0.1299(8)	5.3(3)
O(2)	0.352(2)	−0.332(2)	−0.1624(10)	12.6(6)	C(215)	−0.145(2)	−0.438(2)	−0.1192(9)	5.1(4)
O(3)	−0.458(1)	−0.433(1)	−0.1007(8)	9.1(4)	C(216)	−0.170(1)	−0.310(1)	−0.1419(8)	3.4(3)
O(4)	−0.501(2)	−0.374(2)	−0.2267(9)	11.0(5)	C(221)	0.021(1)	0.011(2)	−0.1727(7)	3.7(3)
					C(222)	0.119(1)	−0.018(2)	−0.1110(8)	4.9(4)
C(111)	−0.592(1)	0.041(1)	−0.3227(7)	3.3(3)	C(223)	0.228(2)	0.058(2)	−0.0854(10)	6.4(5)
C(112)	−0.654(2)	0.149(2)	−0.3564(9)	5.3(4)	C(224)	0.233(2)	0.165(2)	−0.1226(10)	6.4(5)
C(113)	−0.793(2)	0.150(2)	−0.3772(11)	7.2(5)	C(225)	0.142(2)	0.205(2)	−0.1862(10)	5.8(4)
C(114)	−0.854(2)	0.043(2)	−0.3628(12)	8.8(6)	C(226)	0.031(2)	0.123(2)	−0.2075(10)	5.7(4)
C(115)	−0.800(2)	−0.058(2)	−0.3295(11)	7.0(5)	C(S1)[c]	0.214(3)	0.564(3)	0.6355(16)	13.2(10)
C(116)	−0.660(1)	−0.067(2)	−0.3068(9)	5.1(4)	C(S2)	0.278(2)	0.509(3)	0.5774(11)	9.6(6)
C(121)	−0.351(1)	0.170(2)	−0.3244(8)	4.0(3)	C(S3)	0.195(3)	0.549(3)	0.5417(16)	14.7(11)
C(122)	−0.370(2)	0.286(2)	−0.2900(9)	5.0(4)	C(S4)	0.072(2)	0.525(4)	0.6313(14)	13.2(9)
C(123)	−0.305(2)	0.399(2)	−0.3048(11)	7.7(6)	C(S5)	0.047(3)	0.589(3)	0.5764(15)	11.6(8)
C(124)	−0.227(2)	0.394(2)	−0.3497(10)	6.3(5)					
C(125)	−0.208(2)	0.283(2)	−0.3853(11)	6.6(5)					
C(126)	−0.272(2)	0.169(2)	−0.3718(9)	5.1(4)					
C(211)	−0.085(1)	−0.243(1)	−0.1720(8)	3.2(3)					
C(212)	0.030(1)	−0.303(2)	−0.1791(8)	3.5(3)					
C(213)	0.049(2)	−0.430(2)	−0.1593(10)	5.7(4)					

Hydrogen atoms

Atom	x	y	z	Atom	x	y	z
H(1)	−0.4931	0.1364	−0.1861	H(23)	−0.8400	0.2231	−0.4000
H(2)	−0.5078	−0.0826	−0.1639	H(24)	−0.9456	0.0428	−0.3793
H(3)	−0.4176	−0.1813	−0.0554	H(25)	−0.8519	−0.1272	−0.3197
H(4)	−0.4766	−0.0720	−0.0173	H(26)	−0.6160	−0.1415	−0.2828
H(5)	−0.2474	−0.1297	0.0263	H(27)	−0.4251	0.2888	−0.2567
H(6)	−0.2944	0.0091	0.0337	H(28)	−0.3190	0.4782	−0.2820
H(7)	−0.1456	−0.0720	−0.0633	H(29)	−0.1832	0.4697	−0.3579
H(8)	−0.1179	0.1149	−0.1007	H(30)	−0.1529	0.2818	−0.4185
H(9)	−0.2466	0.2869	−0.0919	H(31)	−0.2591	0.0922	−0.3964
H(10)	−0.2299	0.2444	−0.0082	H(32)	0.0927	−0.2563	−0.1970
H(11)	−0.4450	0.2802	−0.0902	H(33)	0.1237	−0.4714	−0.1665
H(12)	−0.4224	0.1721	−0.0298	H(34)	−0.0196	−0.5862	−0.1170
H(13)	−0.1492	−0.2703	−0.3241	H(35)	−0.2030	−0.4829	−0.0966
H(14)	−0.1808	−0.1760	−0.3922	H(36)	−0.2468	−0.2691	−0.1363
H(15)	−0.3360	−0.2319	−0.2978	H(37)	0.1120	−0.0943	−0.0840
H(16)	−0.4660	−0.3380	−0.4002	H(38)	0.2958	0.0340	−0.0428
H(17)	−0.3366	−0.3498	−0.4235	H(39)	0.3058	0.2189	−0.1039
H(18)	−0.5235	−0.2396	−0.5100	H(40)	0.1515	0.2808	−0.2134
H(19)	−0.3842	−0.1900	−0.5037	H(41)	−0.0390	0.1494	−0.2485
H(20)	−0.4599	−0.0103	−0.4681				
H(21)	−0.5682	−0.0805	−0.4413				
H(22)	−0.6058	0.2210	−0.3658				

[a] The form of the anisotropic thermal parameter is: $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$. [b] Estimated standard deviations in the last significant digits are shown in parentheses. [c] Atoms of the solvent molecule.

final values of R and R_w were 0.0604 and 0.0599, respectively. The final difference-Fourier map showed some residual peaks of no more than 0.8 $e/Å^3$, near to the disordered solvent molecule.

Because of the previous knowledge of the absolute configuration of the proline moiety [8], we chose the correct enantiomer at the initial stage of the refinement. After the conclusive refinement, we also refined the other enantiomer, which gave slightly higher R and R_w values of 0.0607 and 0.0602, respectively.

All computations were made on a PDP 11/34 computer using the ENRAF-NONIUS structure determination package (SDP) and the physical constants listed therein. Final positional and thermal parameters are given in Table 1. A list of computed and observed structure factors can be obtained from the authors.

Asymmetric hydrogenations

All asymmetric hydrogenations are carried out in EtOH at 20°C with one atm partial pressure of hydrogen and with a molar ratio substrate/catalyst 200. The approximate amount of substrate (2 mmol) is introduced into a thermostated reactor provided with a serum cap and connected to a gas burette. The reactor is evacuated and filled several times with purified hydrogen; 18 ml EtOH are added with a syringe through the serum cap and the solution is equilibrated for 30 min. 10^{-2} mmol of catalyst are dissolved in 2 ml EtOH, rehydrogenated, bubbling H_2 for 15 min, transferred into the substrate solution and hydrogen uptake is monitored. When reaction is complete, 1 g of Dowex 50W-X2 resin is added and the mixture stirred for 30 min, as described by Bosnich [9], in order to remove most of the catalyst. Subsequently different procedures are followed for the various substrates as follows.

(a) N-Acetyl-alanine. The reaction mixture is filtered and the resin washed with warm ethanol. The solvent is pumped off and the oily residue is shaken with hexane. The white precipitate is filtered off and air dried, and its identity and the degree of the conversion determined by ^1H NMR spectroscopy.

(b) N-Acetyl-phenylalanine, N-acetyl-leucine and methylsuccinic acid. The solution is filtered into a volumetric flask and the resin is washed with warm ethanol. The solution is allowed to cool and the rotatory power is measured. To confirm the rotatory power values the solution is pumped off, the oily residue is dissolved in NaOH 0.5 N (10 ml), then the solution is extracted twice with chloroform, neutralized with HCl 0.5 N, and extracted with ether. The ethereal layer is dried over sodium sulphate, filtered, and evaporated to dryness. The identity and the conver-

TABLE 2

OPTICAL YIELDS (%) AND ABSOLUTE CONFIGURATIONS

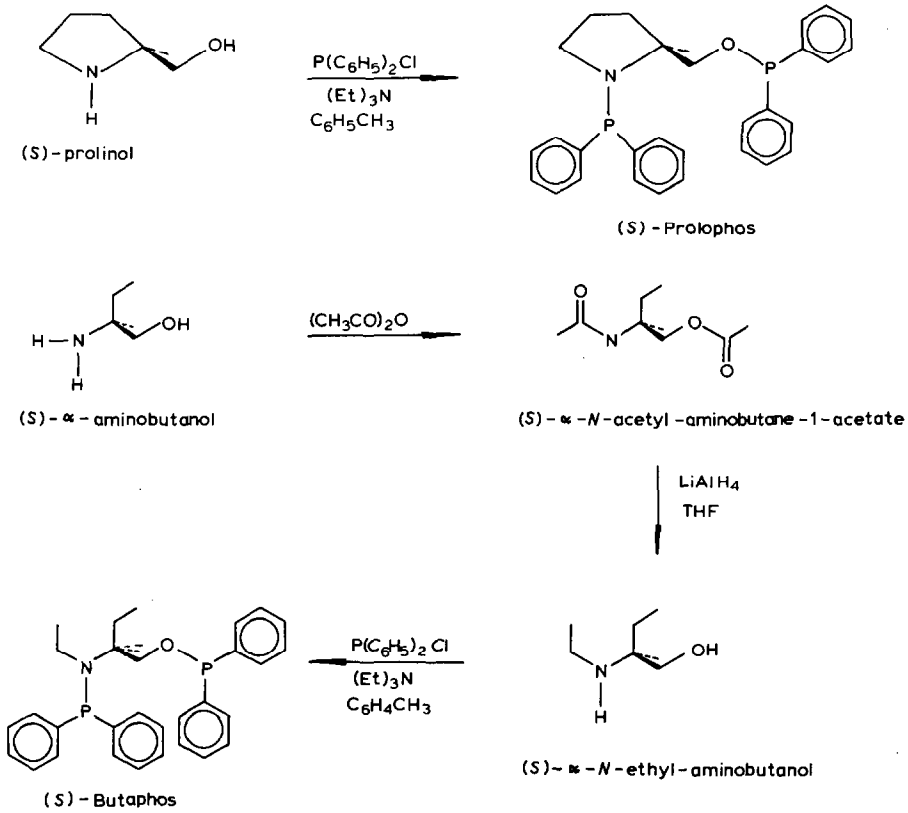
Substrate	[Rh(COD)((*S*)-Prolophos)]-[ClO_4]	[Rh(COD)((*S*)-Butaphos)]-[ClO_4]
CH_2=C(COOH)CH_2COOH	20 - (*R*)	10 - (*R*)
CH_2=C(NHCOCH_3)COOH	80 - (*S*)	55 - (*S*)
C_6H_5CH=C(NHCOCH_3)COOH	78 - (*S*)	23 - (*S*)
C_6H_5CH=C(NHCOC_6H_5)COOH	62 - (*S*)	49 - (*S*)
$(CH_3)_2$CHCH=C(NHCOCH_3)COOH	96 - (*S*)	64 - (*S*)
$(CH_3)_2$CHCH=C(NHCOC_6H_5)COOH	45 - (*S*)	57 - (*S*)

sion are determined by ^1H NMR spectroscopy. An approriate amount of the product is weighed into a volumetric flask and the rotatory power is measured again. The values are usually lower (3%) for *N*-acetyl-phenylalanine and *N*-acetyl-leucine but higher (3–5%) for methylsuccinic acid.

(c) N-Benzoyl-phenylalanine, N-benzoyl-leucine. The isolation of the products was by the usual method [10].

Results and discussion

The routes to (*S*)-Prolophos and (*S*)-Butaphos are indicated in Scheme 1;



SCHEME 1

Both ligands are obtained by a one-step process in high yield, which is almost quantitative in the case of (*S*)-Prolophos.

In Table 2 are shown the results of asymmetric hydrogenation of a series of prochiral substrates.

Both complexes [Rh(COD)((*S*)-Prolophos)][ClO_4] and [Rh(COD)((*S*)-Butaphos][ClO_4] are efficient homogeneous asymmetric catalysts. The (*S*)-Prolophos ligand gives better results than (*S*)-Butaphos. Both catalysts give 100% conversion in 10–60 min and the products of hydrogenation have the (*S*)-configuration of the natural amino acids.

The higher optical yields obtained with the (*S*)-Prolophos ligand are probably

TABLE 3

BOND DISTANCES AND ANGLES WITHIN THE CATION [Rh(COD)((*S*)-Prolophos)]$^+$

Distances (Å)

Rh–P(1)	2.283(3)	C(3)–C(4)	1.48(2)	P(2)–C(221)	1.791(13)
Rh–P(2)	2.271(3)	C(4)–C(5)	1.53(2)	P(2)–O	1.609(8)
Rh–C(1)	2.292(13)	C(5)–C(6)	1.27(2)	N–C(10)	1.420(15)
Rh–C(2)	2.255(14)	C(6)–C(7)	1.54(2)	N–C(13)	1.482(15)
Rh–C(5)	2.260(14)	C(7)–C(8)	1.49(2)	C(10)–C(11)	1.55(2)
Rh–C(6)	2.224(13)	P(1)–C(111)	1.851(12)	C(11)–C(12)	1.47(2)
C(1)–C(2)	1.44(2)	P(1)–C(121)	1.794(16)	C(12)–C(13)	1.51(2)
C(1)–C(8)	1.48(2)	P(1)–N	1.638(10)	C(10)–C(9)	1.50(2)
C(2)–C(3)	1.48(2)	P(2)–C(211)	1.810(12)	C(9)–O	1.442(15)

Angles (deg.)

P(1)–Rh–P(2)	93.0(1)	N–C(13)–C(12)	105.8(12)
Rh–P(1)–C(111)	120.0(4)	C(13)–C(12)–C(11)	105.0(13)
Rh–P(1)–C(121)	102.0(5)	C(12)–C(11)–C(10)	104.1(13)
Rh–P(1)–N	120.3(4)	C(11)–C(10)–N	105.7(11)
Rh–P(2)–C(211)	113.3(4)	C(11)–C(10)–C(9)	109.5(12)
Rh–P(2)–C(221)	114.3(5)	N–C(10)–C(9)	112.6(11)
Rh–P(2)–O	120.3(3)	C(10)–C(9)–O	115.0(10)
C(111)–P(1)–C(121)	106.1(6)	C(9)–O–P(2)	121.2(8)
C(111)–P(1)–N	101.5(5)	C(2)–C(1)–C(8)	124(1)
C(121)–P(1)–N	105.4(6)	C(1)–C(2)–C(3)	124(1)
C(211)–P(2)–C(221)	106.8(7)	C(2)–C(3)–C(4)	118(1)
C(211)–P(2)–O	102.7(5)	C(3)–C(4)–C(5)	113(1)
C(221)–P(2)–O	97.5(5)	C(4)–C(5)–C(6)	131(2)
P(1)–N–C(10)	125.4(9)	C(5)–C(6)–C(7)	123(2)
P(1)–N–C(13)	122.6(8)	C(6)–C(7)–C(8)	116(1)
C(10)–N–C(13)	109.7(10)	C(7)–C(8)–C(1)	115(1)

attributable to the presence of the five-membered ring fused with the seven-membered ring generated by the chelation of the aminophosphine-phosphinite ligand to the rhodium atom. This rigid backbone plays an important role in determining the conformation of the chelating ring as well as the chiral array of the phenyl groups of the phosphine, as revealed by the X-ray structure. This increases the stereodiscrimination of the catalyst in respect to the prochiral face of the incoming substrate and may account for the high and comparable optical yields obtained from (*S*)-Prolophos and DIOP. The absence of the fused ring in (*S*)-Butaphos allows a less rigid conformation or a large number of possible chelate conformers, leading to lower optical yields.

The mechanism of hydrogenation using rhodium(I) complexes with chelating phosphines has been elucidated in detail [11,12], and appears to involve four steps: substrate coordination, oxidative addition of hydrogen, formation of σ-alkyl(hydrido)rhodium complexes, and insertion of hydrogen to give the hydrogenated substrate. In contrast the origin of the stereodiscrimination is still uncertain, and the optical yield may be determined by kinetic and/or thermodynamic factors acting separately in each step of the process [13].Because of the complexity of the overall

process, additional stereoelectronic effects cannot be excluded in aminophosphine-phosphinite rhodium complexes, since one of the phosphorus atoms is bound to a nitrogen while the other is bound to an oxygen atom. Such effects could have a significant influence, at least in the formation of the σ-alkyl(hydrido)rhodium intermediate. Further studies on the correlation between electronic effects to asymmetric induction are in progress.

Crystal structure of [Rh(COD)((S)-Prolophos)][ClO_4] · THF

[Rh(COD)((*S*)-Prolophos)][ClO_4] · THF has an ionic packing, which seems to be predominantly determined by Van der Waals' interactions between the bulky rhodium cations. The cavities between the cations are occupied by the comparatively small $[ClO_4]^-$ anions and by disordered THF molecules. A view of the cation is given in Fig. 1, together with the numbering scheme adopted.

The relevant bond parameters are listed in Table 3.

The rhodium cation is a 16 valence electron, somewhat distorted square planar complex, the vertices of the square being occupied by the phosphorus atoms of the (*S*)-Prolophos and by the two η^2-bonded double bonds of the 1,5-cyclooctadiene. The dihedral angle between the plane defined by P(1)–Rh–P(2) and the plane containing Rh and the middle points of the two double bonds is 22.7°. The Rh–P

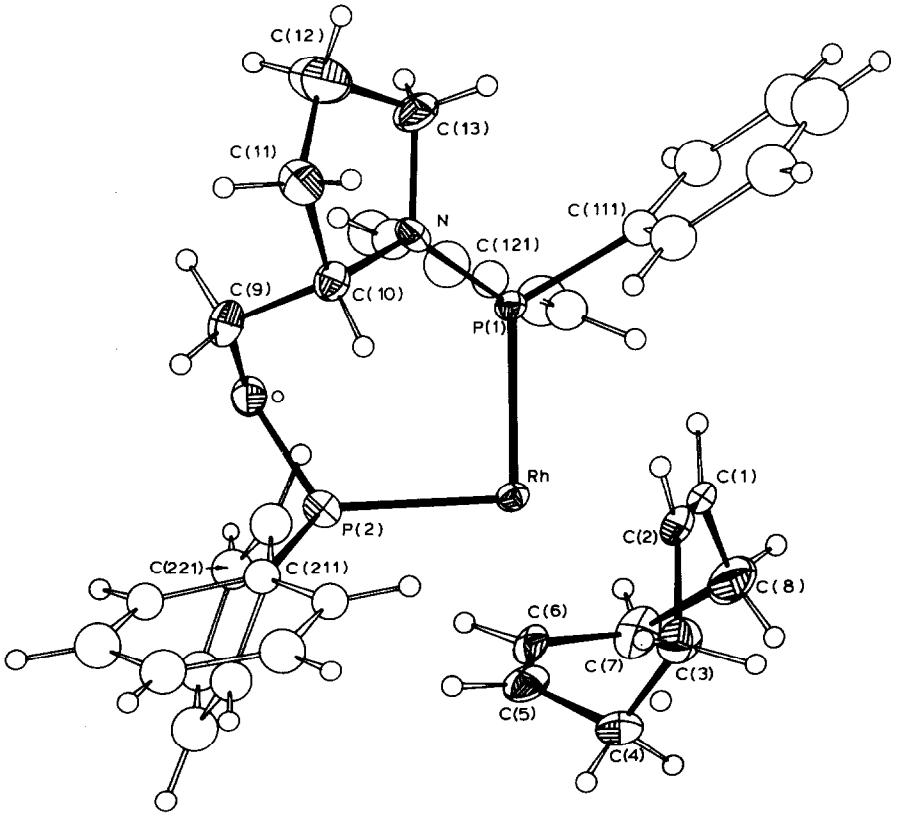


Fig. 1. A view of the cation [Rh(COD)((*S*)-Prolophos)]$^+$.

TABLE 4

DEVIATIONS FROM THE Rh–P(1)–P(2) PLANE (Å)

C(111)	−0.499	N	−0.804
C(121)	1.734	C(10)	−1.718
C(211)	−1.471	C(9)	−1.046
C(221)	1.420	O	0.101

distances (mean 2.277 Å) are comparable to those found in similar complexes $[Rh(COD)(LL)]^+$; for instance, when LL = *trans*-1,2-bis(diphenylphosphinamido)-cyclohexane (LLC) the mean value is 2.300 Å [14] and when LL = (2*S*,3*S*)-2,3-bis(diphenylphosphino)butane (LLB) it is 2.270 Å [15]. In the LLC analogue there is a seven-membered chelate ring fused with a six-membered cyclohexane ring, and the P–Rh–P angle is 89.91°. In our compound there is a seven-membered metallocycle fused with the five-membered proline ring. The proline ring is directly connected to the P(1) atom and this implies an increased rigidity of the metallocycle reflected in the larger P–Rh–P angle (93.0(1)°).

The P(1)–N bond distance is 1.638(10) Å and the coordination around the N atom is essentially planar (the sum of the angles at the N atom is 357.7° and this atom is out of the plane C(10)–C(13)–P(1) of 0.13 Å).

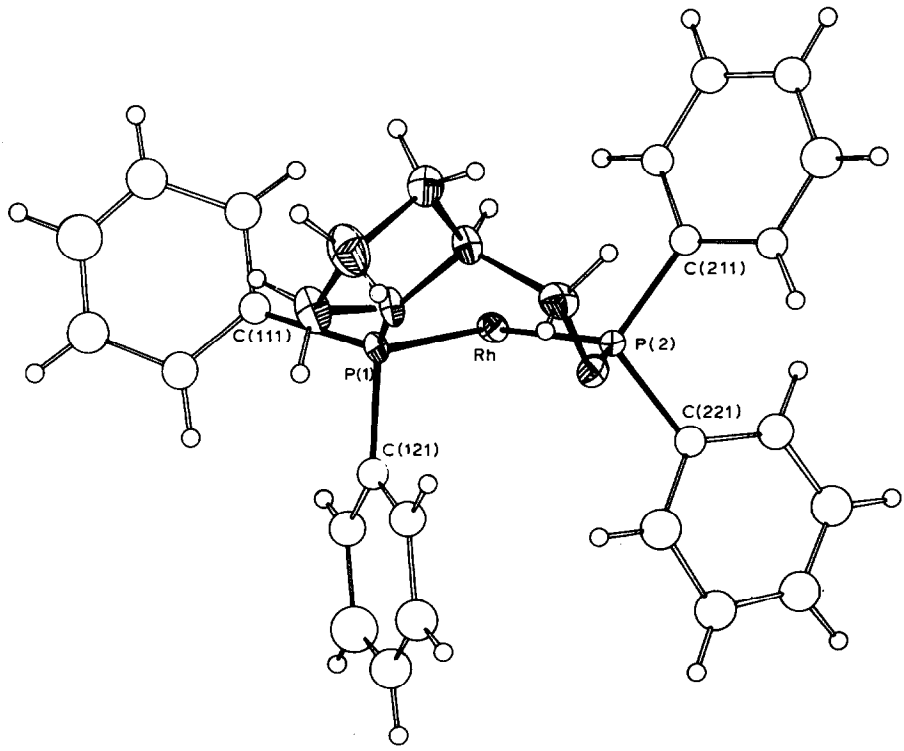


Fig. 2. A view of the dispositions of the phenyl groups. The COD molecule is omitted for clarity.

The seven-membered chelate ring has a boat conformation, with the oxygen atom in the plane P(1)–Rh–P(2) (its out-of-plane displacement being 0.10 Å only, see Table 4).

The conformations of the seven-membered rings of this type have been discussed recently by Kagan et al. [16] examining the structure of the complex [Fe(η^5-Cp)((−)DIOP)I]. The analysis was based on the comparison with the conformations of cycloheptane, and cannot be simply extended to (*S*)-Prolophos complexes since this diphosphine differs from DIOP in not possessing a C_2 local symmetry and in containing an atom in the ring (N) which is closer to sp^2 than sp^3 hybridization. The structural data for DIOP complexes indicate a preferred chair conformation, but examples of boat conformation are also known [16 and references therein]. For (*S*)-Prolophos an analysis based on models suggests that a chair or a chair-twisted conformation would give lead larger steric repulsions than the boat conformation which is present in the solid state.

The phenyl rings bonded to the P(2) atom (Fig. 2) are symmetrically displaced with respect to the P(1)–Rh–P(2) plane (apart from the torsion angles around the P–C bonds) and the out-of-plane displacement for the first carbon atoms is −1.47 and +1.42 Å respectively. In contrast the phenyl groups bound to P(1) are unsymmetrically disposed, and the out-of-plane displacements are −0.50 and +1.73 Å, respectively. The bond parameters within the phenyl rings as well as those within the COD molecule, although somewhat scattered, can be considered normal. The good optical yields given by the rhodium(I) complexes with these new ligands demonstrate that a single asymmetric center is enough to lead to a high stereodifferentiating ability of a catalyst, not only when this single chiral center is in a five-membered ring but also when it is in a seven-membered ring provided the higher flexibility of the latter is suppressed by a fused ring.

Our results justify studies on the use of these readily available chelating aminophosphine-phosphinite ligands in reactions other than carbon–carbon double bond hydrogenations.

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