Tetrahedron: Asymmetry Vol. 4, No. 10, pp. 2219-2228, 1993
Printed in Great Britain

0957-4166/93 $6.00+.00
Pergamon Press Ltd

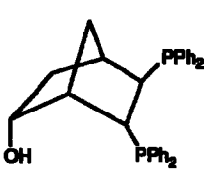
A BORON ANALOG OF DIOP : SYNTHESIS AND PROPERTIES

A. BÖRNER[1a], J. WARD, K. KORTUS[1b], H. B. KAGAN*
Laboratoire de Synthèse Asymétrique[2]
Institut de Chimie Moléculaire d'Orsay
Université Paris-Sud, 91405 Orsay, France

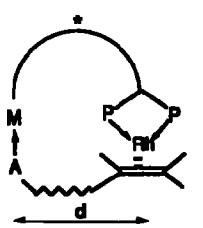
(*Received in UK 2 August* 1993)

Summary: A rhodium complex of a boron analog of DIOP, which is a model for a tailored bimetallic catalyst possessing dual functions, is an active catalyst for hydrogenation and hydrosilylation.

Recently we described the synthesis of hydroxy NORPHOS **1**, with the aim of using the hydroxyl group for the introduction of a Lewis acid while the diphosphine system is bonded to a soft metal such as rhodium[3]. Our intention is to prepare dual chiral ligands for achieving asymmetric catalysis with substrate specificity and increased enantioselectivity, thanks to a secondary interaction between chiral ligands and substrates[4]. Thus, a prochiral substrate (a C=C double bond for example) with a distant basic function (ether, carbonyl group, etc...) should be able to interact with the tailored ligand not only at the catalytic center but also with the pendant Lewis acid (as in **A**). We wish to present a first example of a chiral bimetallic catalyst **6** based on an analog of (R,R)-DIOP **2**[6], namely boron compound **4** as illustrated in Scheme 1[7].



1



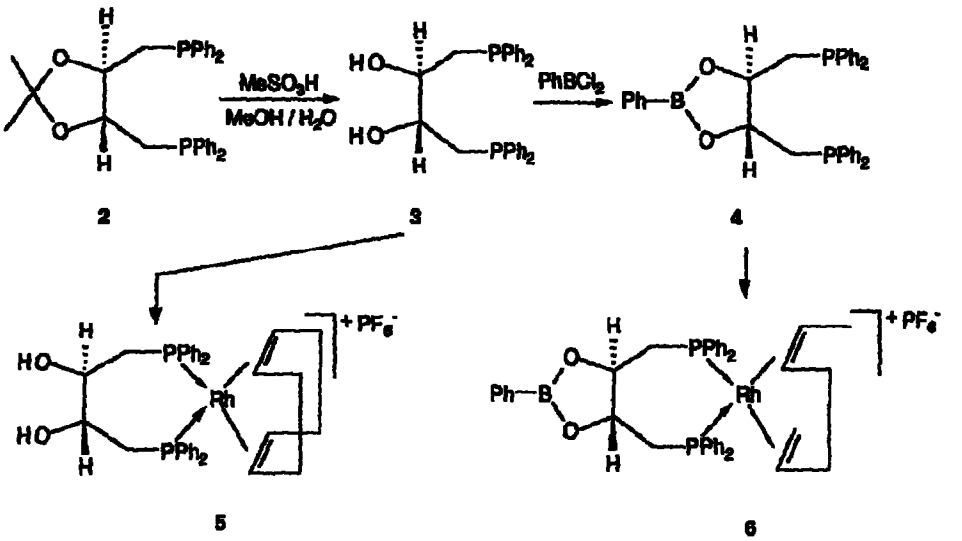
M : "hard" Lewis acid

A

Results and discussion

Preparation of ligand 4

Scheme 1



2 3 4

5 6

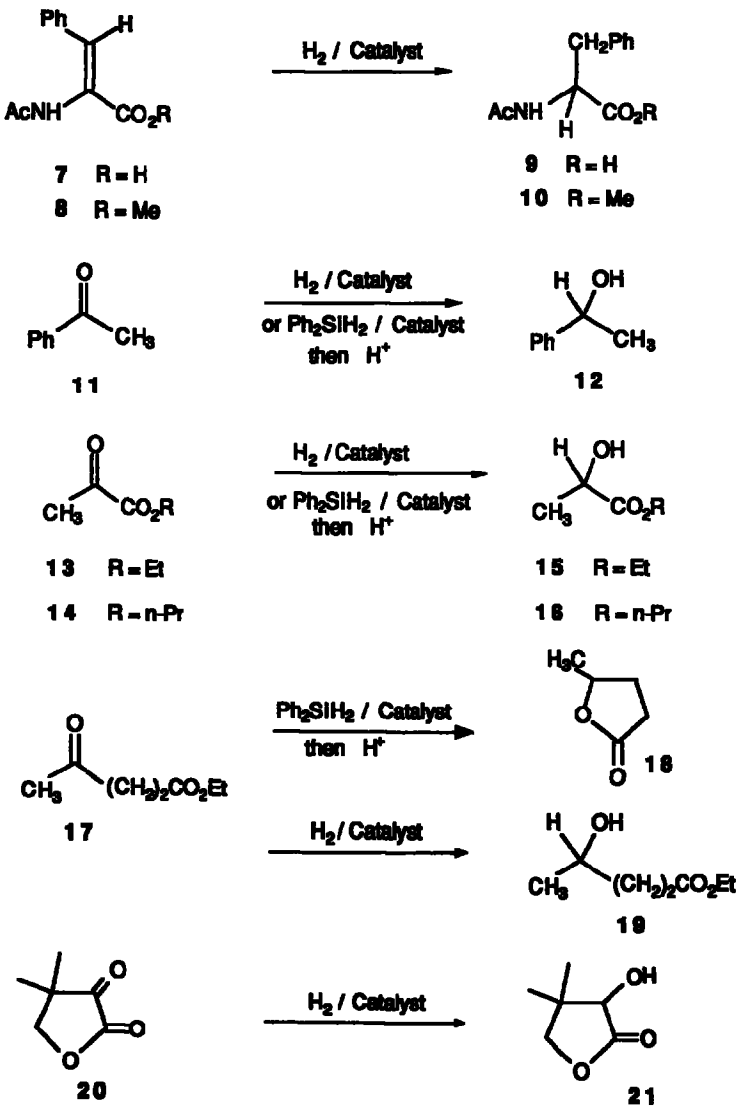
Acidic hydrolysis of DIOP 2 with aqueous HCl/MeOH gave 3, using the conditions described by Stille et al[8]. This procedure is quite simple, but provides a diphosphine which is always contaminated with considerable amounts of oxidation products. The yield of pure compound after recrystallisation was quite low. An improved procedure utilizing a catalytic amount of methanesulfonic acid was devised which gave after flash chromatography, (R,R)-3 as a crystalline compound [mp=92-94°C, $[\alpha]_D$=-35.8 (c=1, $CHCl_3$)]. This diphosphine has also been prepared by the method of Zhang et al[9], by double nucleophilic ring-opening of (R,R)-1,4-diepoxybutane by $LiPPh_2$.

The preparation of the boron analog of DIOP was easily achieved by mixing (R,R)-3 with dichlorophenylboron in dichloromethane at -78°C. Diphosphine (R,R)-4 (mp=121-122°C, $[\alpha]_D$=+3.8 (c=1, $CHCl_3$)) was isolated in 87%. This compound has been fully characterized, including ^1H, ^{31}P and ^{13}C NMR. It gives a cationic rhodium complex **6**, when treated with $(RhClCOD)_2$ and NH_4PF_6 in a mixture of dichloromethane and water. The rhodium complex **6**, $[Rh(COD)_2]PF_6$ was isolated in good yield after evaporation of the organic phase and characterized by ^1H, ^{31}P and ^{13}C NMR. An *in situ* neutral complex, formulated as $[RhCl(COD)_2]$ has been prepared by mixing $(RhClCOD)_2$ with two equivalents of 4 in methanol or dichloromethane. This complex was used directly in catalysis. A cationic rhodium complex **5** derived from dihydroxydiphosphine 3 was also prepared in a similar manner.

Catalytic properties

The catalytic properties of the rhodium complexes derived from boron diphosphine **4** were examined under standard conditions with both the *in situ* neutral complex [RhCl(COD),4] and the cationic complex [Rh(COD),4]PF_6 (Scheme II).

Scheme II



Results on the hydrogenation of N-acetyl dehydrophenylalanine and its methyl ester are indicated in Table 1, which also includes for comparison data obtained with the

corresponding DIOP complex and with the complex 5 derived from the open diphosphine 3.

Table 1. Asymmetric hydrogenation of N-acetyl dehydro phenylalanine (7) and the methyl ester of N-acetyl dehydrophenylalanine (8).

Entry	Ligand[a]	Substrate	Solvent	Yield (%)[b] (time)	Ee (%)[c,d]
1[e]	2[f]	7	EtOH	100 (3 h)	81.0
2[e]	3[f]	7	EtOH	100 (> 10 h)	36.8
3[e]	3[g]	7	EtOH	100 (> 8 h)	36.6
4[e]	3[f]	7	MeOH	97 (> 4 h)	29.0
5[e]	4[f]	7	MeOH	100 (3 h)	73.0
6[e]	4[g]	7	MeOH	100 (4 h)	51.3
7[e]	2[f]	8	MeOH	100 (5 min)	66.9
8[e]	2[g]	8	EtOH	100	71.3[h]
9[i]	2[f]	8	CCl_4	0 (16 h)	
10[i]	2[f]	8	THF	66 (16 h)	36.0
11[i]	2[f]	8	CH_2Cl_2	100 (16 h)	29.4
12[i]	2[g]	8	CH_2Cl_2	100 (16 h)	56.0
13[e]	2[g]	8	CH_2Cl_2	100 (3 h)	76.2
14[e]	3[f]	8	MeOH	100 (> 7 h)	38.0
15[i]	3[g]	8	CH_2Cl_2	100 (23 h)	20.0
16[e]	3[g]	8	CH_2Cl_2	100 (3 h)	30.0
17[e]	4[f]	8	MeOH	100 (0.5 h)	67.0
18[i]	4[g]	8	CH_2Cl_2	100 (20 h)	48.4
19[e]	4[g]	8	CH_2Cl_2	100 (0.5 h)	73.0

[a] (S,S) configuration. [b] Determined by ^1H NMR. [c] Measured on the crude product: gc with chiral columns for N-acetyl phenylalanine 9 after esterification with diazomethane and for methyl ester of N-acetyl phenylalanine 10 with XE 60-L-valine tert-butylamide, 150 °C. [d] configuration (S). [e] p=1 bar, T=25°C, [Rh]=3×10^{-3} M, [Substrate]/[Rh]=50. [f] Neutral catalyst: prepared *in situ* from $(RhClCOD)_2$ and diphosphine. [g] Cationic catalyst: prepared as described in the experimental section. [h] see ref. 10. [i] p=10 bar, T=25°C, [Rh]=3×10^{-3} M, [Substrate]/[Rh]=50.

It is satisfying to see that the boron analog of DIOP produces catalytically active complexes for hydrogenation. Moreover, it consistently gives higher enantioselectivities than the acyclic diphosphine (R,R)-3 (compare entries 5 and 4). It is slightly less stereoselective than (R,R)-DIOP itself, but the absolute configurations of products are the same with the both ligands.

Asymmetric hydrogenations are usually performed in alcohols (ethanol or methanol) or in solvent mixtures including an alcohol. Reactions in aprotic solvents

or in solvents of low basicity were sought in order to give to the boron site a better chance to provide a secondary interaction with the substrate. We were pleased to see that catalytic hydrogenation is indeed possible in dichloromethane, toluene or THF (entries 9-19).

The asymmetric hydrogenation and hydrosilylation, respectively, of ketones was also investigated (Table 2 and Table 3). Marko et al. showed that acetophenone can be reduced to 1-phenyl-ethane-1-ol with ee's up to 80% by rhodium/DIOP complex in presence of a base (entries 1-3, Table 2)[11-13].

Table 2. Asymmetric hydrogenation of acetophenone (11), ethyl pyruvate (13) and ketopantolactone (20).

Entry	Ligand	Substrate	Solvent	Yield (%)[a] (time)	Ee (%)[b]
1[c]	(S,S)-2[d]	11	MeOH	39 (100 h)	51.0
2[e]	(S,S)-2[d]	11	MeOH	14 (6 h)	53
3[f]	(S,S)-2[d]	11	PhH	64 (6 h)	80
4[g]	(R,R)-3[d]	11	MeOH	75 (7 d)	3
5[g]	(R,R)-4[d]	11	MeOH	41 (5 d)	3.6
6[h]	(R,R)-2[d]	$MeCOCO_2Me$	MeOH	95 (90 h)	18.2 (R)
7[h]	(R,R)-2[d]	$MeCOCO_2Me$	THF	98 (20 h)	41.2 (R)
8[i]	(S,S)-2[d]	13	$MeOH/PhCH_3$	100	24.0 (S)
9[j]	(S,S)-2[k]	13	CH_2Cl_2	97 (3 d)	38.6 (R)
10[j]	(S,S)-2[d]	13	THF	100 (2 d)	38.2 (S)
11[j]	(R,R)-3[d]	13	$MeOH/PhCH_3$	100 (3 d)	23.4 (R)
12[j]	(R,R)-3[k]	13	CH_2Cl_2	99 (3 d)	21.7 (S)
13[j]	(R,R)-3[d]	13	THF	100 (3d)	34.9 (R)
14[j]	(R,R)-4[d]	13	$MeOH/PhCH_3$	92 (4 d)	15.7 (R)
15[j]	(R,R)-4[k]	13	CH_2Cl_2	95 (3 d)	0.8 (S)
16[j]	(R,R)-4[d]	13	THF	100 (3 d)	32.0 (R)
17[l]	(S,S)-2[d]	20	THF	100	52.0 (S)
18[m]	(R,R)-3[d]	20	THF	80 (3 d)	51.8 (R)
19[m]	(R,R)-4[d]	20	THF	100 (3d)	54.3 (R)

[a] Determined by gc on the crude product. [b] Measured on the crude product by gc with chiral columns: 1-phenyl-ethane-1-ol 12, ethyl lactate 15 and pantolactone 21 with 50m Cyclodex IP at 125°C, 100°C and 150°C respectively. [c] p=50 bar, T=50°C, ref. 11. [d] Ligand for the neutral catalyst: prepared *in situ* from $(RhClCOD)_2$ and diphosphine. [e] p=70 bar, T=50°C, NEt_3, ref. 12. [f] p=70 bar, T=50°C, NEt_3, ref. 13. [g] p=50 bar, T=25°C, [Rh]=2.6×10^{-3} M, [Substrate]/[Rh]=170. [h] p=20bar, T=25°C, ref. 14. [i] p=20 bar, T=25°C, ref. 15. [j] p=20 bar, T=25°C, [Rh]=2.6×10^{-3} M, [Substrate]/[Rh]=50. [k] Ligand for the cationic catalyst: prepared as described in the experimental section. [l] p=50 bar, T=50°C, ref. 16. [m] p=50 bar, T=50°C, [Rh]=2.6×10^{-3} M, [Substrate]/[Rh]=100.

Rhodium complexes **5** and **6** are much less efficient (entries 4 and 5, Table 2). Asymmetric reduction of methyl or ethyl pyruvate in presence of rhodium/DIOP complexes has been also described (entries 6-8, Table 2)[14,15] with ee's up to 40%. The behavior of complexes **5** and **6** in various aprotic solvents was checked (entries 12, 13, 15 and 16 in Table 2), ee's remained low (<35%). Interestingly, the use of dichloromethane gives the opposite configuration of the product, compared to reaction performed in THF or methanol (for example entries 9, 10 and 12, 13 in Table 2). Ketopantolactone **20** was also reduced in presence of a rhodium/DIOP catalyst[16]. The use of complexes **5** and **6** with this substrate gives similar results to the DIOP catalyst (entries 17-19, Table 2)

Table 3. Asymmetric hydrosilylation of ketones with diphenylsilane

Entry	Ligand	Substrate	Solvent	Yield (%)[a] (time)	Ee (%)[b]
1[c]	(S,S)-2	11	PhH	99 (24 h)	28.5 (R)
2[d]	(S,S)-2	11	$PhCH_3$	90 (3 h)	28.8 (S)
3[d]	(R,R)-3	11	$PhCH_3$	63 (2 h)	13.7 (R)
4[d]	(S,S)-4	11	$PhCH_3$	83 (1.5 h)	21.0 (S)
5[e]	(S,S)-2	14	PhH	82	76.5 (S)
6[d]	(S,S)-2	14	$PhCH_3$	85 (6 d)	32.0 (S)
7[d]	(R,R)-3	14	$PhCH_3$	98 (8 d)	10.1 (R)
8[d]	(R,R)-4	14	$PhCH_3$	100 (7 d)	10.4 (R)
9[e]	(S,S)-2	17	PhH	100	38.1 (S)
10[f]	(S,S)-2	17	$PhCH_3$	98	31.9 (S)
11[f]	(R,R)-3	17	$PhCH_3$	100	7.3 (R)
12[f]	(S,S)-4	17	$PhCH_3$	100	18.9 (S)

[a] Determined by gc on the crude product. [b] Measured on the crude product by gc with chiral columns: 1-phenyl-ethane-1-ol **12** with 50m Cyclodex IP, n-propyl lactate **16** with 25m Lipodex E and 4-methyl-γ butyrolactone **18** with 50m Lipodex C. [c] ref. 17. [d] T=25°C, [Rh]=3.3×10^{-3} M, [Substrate]/[Rh]=500, [Silane]/[Substrate]=1.1. [e] Ref.18. [f] [Rh]=5.5×10^{-3}M, [Substrate]/[Rh]=300, [Silane]/[Substrate]=1.1.

We are currently studying the asymmetric hydrogenation of bifunctional substrates with variable distances between the prochiral double bond and a basic group[19], with the hope to see enhanced reactivity and stereoselectivity for substrates able to interact at both rhodium and boron.

Experimental Section

General Data: All reactions were performed under argon, using conventional Schlenk techniques owning to the sensitivity of compounds to oxygen. Solvents were purified and dried by standard techniques. All glassware used was oven dried. ^{1}H, ^{31}P, ^{13}C and ^{11}B NMR were recorded on a Bruker AM 250 instrument operating at 250, 101, 63 and 80 MHz respectively. Chemical shifts are reported in ppm downfield from internal TMS (^{1}H and ^{13}C), external 85% H_3PO_4 (^{31}P) and external BF_3-Et_2O (^{11}B). Mass spectra (chemical ionisation by NH_3) were obtained with a Riber Mag R10-10 instrument. Elemental analysis were performed by the Service de Microanalyse, Gif-sur-Yvette, France. GC analysis of chiral products were performed at Rostock on a HP 5890 Series II gas chromatograph. IR spectra were recorded on a Perkin Elmer 88 instrument. Substrates for catalytic reactions were synthesized by known methods or purchased by commercial suppliers. A conventional apparatus for hydrogenation under atmospheric pressure was used. Hydrogenations under 10-50 bar pressure were performed in a 50 mL autoclave.

(-)-(R,R)-2,3-dihydroxy-1,4-bis(diphenylphosphino)-butane [(-)-3] (R,R)-DIOP (-)-2 (1.7 g, 3.4 mmol), methanol (50 mL), water (5.6 mL) and methanesulfonic acid (85 mL) were refluxed for 4 h under argon. The solution was cooled to room temperature and the solvent was removed under reduced pressure. The white foamy residue was purified by flash chromatography utilizing a mixture of CH_2Cl_2/ethyl acetate (9/1) as eluent to yield 3 (1.42 g, 71%): mp. 92-94 °C. $[\alpha]_D$= -35.8 (c 1, $CHCl_3$) [lit: mp. 99-100°C, $[\alpha]_D$= -34.2 (c 0.76, $CHCl_3$)][9]. ^{1}H NMR (δ, $CDCl_3$): 7.42-7.10 (m, 20H, aromat), 3.65 (m, 2H), 2.35 (d, 4H, J_{HH}=5.0 Hz), 2.20 (s, 2H, exchange with D_2O); ^{13}C NMR (δ, $CDCl_3$): 133.5-128.0 (aromat), 72.0 (q, CH, $^{2}J_{CP}$=14.8 Hz, $^{3}J_{CP}$=8.3 Hz), 33.7 (d, CH_2, $^{1}J_{CP}$=13.2 Hz); ^{31}P NMR (δ, $CDCl_3$): -23.0 (s, 2P). IR (KBr): 3377, 2925, 1639, 1433, 998, 736, 694, 552, 505, 380 cm^{-1}. Mass Spectrum, *m/e* (ion/relative intensity): 460(MH^++1;25.0) 459(MH^+;76.4) 273(10.5) 202(15.4) 188(15.4) 187(100). Anal. Calcd. for $C_{28}H_{28}O_2P_2$: C, 73.35; H, 6.11; P, 13.64; O, 6.98. Found: C, 73.70; H, 6.20; P, 13.15; O, 6.60.

(+)-(S,S)-2,3-dihydroxy-1,4-bis(diphenylphosphino)-butane [(+)-3] The procedure described for (-)-3 was applied: mp. 95-98°C. $[\alpha]_D$= +32.0 (c 1, $CHCl_3$).

(+)-(R,R)-2,3-O-phenylboron-dihydroxy-1,4-bis(diphenylphosphino-butane [(+)-4]. In a Schlenck tube was placed (-)-3 (194 mg, 0.42 mmol) in CH_2Cl_2 (10 mL) and cooled at -78°C. To this solution was transferred dropwise with stirring $PhBCl_2$ (56 µL, 0.43 mmol) in CH_2Cl_2 (5 mL), which had been cooled in another Schlenck tube also at - 78°C. The mixture was stirred for 45 min at -78 °C.

Stirring was continued for 2 h after warming up to room temperature. The solvent and the formed HCl were evaporated under vacuum. The resulting product was washed with hexane and dried to give 4 (160 mg, 87%) as a white solid: mp. 121-122°C. $[\alpha]_D$= 3.8 (c 1, $CHCl_3$). ^1H NMR (δ, $CDCl_3$): 7.80-7.20 (m, 25H, aromat), 4.51 (q, 2H), 2.52 (AB, 4H, J_{AX}=5.7 Hz, J_{BX}=6.3 Hz, J_{AB}=13.9 Hz); ^{13}C NMR (δ, $CDCl_3$): 136.0-127.6 (aromat), 81.5 (q, CH, $^2J_{CP}$=16 Hz, $^3J_{CP}$=8.3 Hz), 35.5 (d, CH_2, $^1J_{CP}$=9.5 Hz); ^{31}P NMR (δ, $CDCl_3$): -24.0 (s, 2P); ^{11}B NMR (δ, $CDCl_3$): 30.4 (s). IR (KBr): 3431, 2927, 1603, 1434, 1403, 1361, 1311, 1217, 1096, 1027, 987, 741, 696, 645, 501 cm^{-1}. Mass Spectrum, *m/e* (ion/relative intensity): 562(MNH_4^+;3.0) 547(MH^++2;12.7) 546(MH^++1;48.6) 545(MH^+;70.0) 544(19.1) 362(13.4) 361(34.4) 360(15.9) 359(16.5). Anal. Calcd. for $C_{34}H_{31}BO_2P_2$: C, 75.03; H, 5.70; P, 11.40; B, 1.98. Found: C, 75.00; H, 5.71; P, 11.10; B, 1.36.

(-)-(S,S)-2,3-O-phenylboron-dihydroxy-1,4-bis(diphenylphosphine butane [(-)-4]. The procedure described for (+)-4 was applied: mp. 118-120°C. $[\alpha]_D$= -4.3 (c 1.5, $CHCl_3$).

[Rh(COD),(-)-3]PF_6 [5]. The catalyst was prepared by the classic method starting from $(RhClCOD)_2$ (75 mg, 0.15 mmol), NH_4PF_6 (220 mg, 1.2 mmol) and (-)-3 (137 mg, 0.3 mmol) to give the rhodium complex (99 %): mp. 210-213 °C (decomposition). $[\alpha]_D$= - 7.7 (c 0.5, $CHCl_3$); $[\alpha]_D$= -7.5 (c=0.35, EtOH). ^1H NMR (δ, $CDCl_3$): 7.70-7.21 (m, 20H, aromat), 4.61 (m, 2H), 4.20 (m, 2H,); 3.81 (m, 2H), 3.20 (s, 2H, exchange with D_2O), 2.81-2.04 (m, 12H); ^{13}C NMR (δ, $CDCl_3$): 134.1-128.0 (aromat), 100.2, 97.7, 71.3 (CH), 33.0, 31.9, 28.4 (CH_2); ^{31}P NMR (δ, $CDCl_3$): 14.7 (d, 2P, J_{PRh}=142.4 Hz). Anal. Calcd. for $C_{36}H_{40}O_2P_3F_6Rh$: C, 53.08; H, 4.91. Found: C, 52.74; H, 4.91.

[Rh(COD),(+)-4]PF_6 [6]. The complex was prepared as described for [Rh(COD),(-)-3]PF_6 starting from $(RhClCOD)_2$ (43 mg, 0.086 mmol), NH_4PF_6 (130 mg, 0.7 mmol) and (+)-4 (94 mg, 0.17 mmol) to give the rhodium complex (91 %): mp. 165-170 °C (decomposition). $[\alpha]_D$= -4.8 (c 0.35, $CHCl_3$). ^1H NMR (δ, $CDCl_3$): 8.1-7.2 (m, 25H, aromat), 4.6 (m, 2H), 4.45 (m, 2H), 4.15 (m, 2H), 3.15-2.05 (m, 12H). ^{13}C NMR (δ, $CDCl_3$): 134.6-127.6 (aromat), 103.0, 99.4, 79.6 (CH), 34.6, 31.0, 29.4 (CH_2); ^{31}P NMR (δ, $CDCl_3$): 13.8 (d, 2P, J_{PRh}=143 Hz). ^{11}B NMR (δ, $CDCl_3$): - 0.8 (s). Anal. Calcd. for $C_{42}H_{43}BO_2P_3F_6Rh$: C, 56.03; H, 4.78; P, 10.33; B, 1.20. Found: C, 55.70; H, 4.77; P, 9.91; B, 0.93.

General procedure for asymmetric catalysis

Preparation of the catalyst solution

Neutral complex: to a solution of $(RhClCOD)_2$ in the appropriate solvent under argon, was added 2.1 equivalent of ligand. The solution was stirred 15 min.

Cationic complex: the isolated cationic complex was dissolved in the appropriate solvent.

Asymmetric hydrogenation

For hydrogenation at atmospheric pressure, the catalyst solution was placed in the hydrogenation flask under hydrogen, then the substrate, dissolved in the indicated solvent under argon, was added to the flask with a syringe; ([Rh]/[Substrate] as defined in Tables 1 and 2). Any contact with air was avoided. For hydrogenation under pressure (10-50 bar), the reaction was performed in an autoclave and the procedure is the same as above.

Isolation of the hydrogenation products

- N-acetyl phenylalanine **9**: after evaporation of the solvent, the residue was dissolved in 0.5 M NaOH and separated from the insoluble catalyst by filtration. The filtrate was acidified with dilute HCl, extracted with ether, and washed with a little water. The ethereal phase was dried over sodium sulfate and evaporated to dryness (isolated product 88-96%). The conversion was determined by NMR. After treatment with CH_2N_2, the ee's were determined by GC analysis as described in Table 1.

- N-acetyl phenylalanine methyl ester **10**: after evaporation of the solvent, the product was isolated by flash chromatography on silica gel with ethyl acetate as eluent (isolated product 95-98%). The conversion was determined by NMR. The ee's were determined by GC analysis as described in Table 1.

- 1-phenyl-ethane-1-ol **12**, ethyl lactate **15** and pantolactone **21**: after evaporation of the solvent, the conversion and the ee's were determined by GC on the crude product as described in Table 2.

*Hydrosilylation of acetophenone **11**, n-propyl pyruvate **14**, and ethyl levulinate **17***

A mixture of substrate and diphenylsilane (1:1.1) in the appropriate solvent was added to the catalyst solution and stirred (neutral complex, [Rh]/[Substrate] as described in Table 3). The mixture was initially cooled with an ice-water bath for n-propyl pyruvate and ethyl levulinate; hydrosilylation of acetophenone and ethyl acetoacetate was performed at room temperature. The completion of the reaction was determined by GC analysis and ^1H NMR.

Isolation of the hydrosilylation products

- acetophenone: to the reaction mixture was added a mixture of acetone/10% HCl (80:20). After stirring for 2 h, the solvent was evaporated and the residue was extracted with ether and the extract was washed with water, dried and concentrated. The conversion to 1-phenyl-ethane-1-ol **12** and the ee's were determined by GC analysis on the crude product as described in Table 3.

- n-propyl pyruvate and ethyl levulinate: to the reaction mixture was added a 0.1% methanol solution of p-toluenesulfonic acid and the mixture was stirred for 10 min at 0°C and then at room temperature (0,5 h and 2 h respectively) before the solvent was evaporated. The conversion to n-propyl lactate **16** and 4-methyl-γ

butyrolactone 18 and the ee's were determined by GC analysis on the crude product as described in Table 3

Acknowledgments

This work was supported by CNRS and Procope. We acknowledge MRT and Ministery of Education for fellowships (to A. Börner and J. Ward respectively). We thank Mrs. G. Voß (Max Planck Group for Asymmetric Catalysis) for skilled technical assistance.

References

1a) Max Planck Society, Group for Asymmetric Catalysis on the University Rostock,
1b) Institute of Organic Catalytic Research Rostock,
Buchbinderstr. 5 u. 6, 18055 Rostock, Germany.
2) URA CNRS n° 1497
3) Ward, J.; Börner, A.; Kagan, H. B., *Tetrahedron:Asymmetry*, **1992**, 3, 849.
4) For a recent review on catalytic asymmetric synthesis involving a secondary interaction between chiral ligands and substrates, see ref. 5.
5) Sawamura, M.; Ito, Y., *Chem. Rev.*, **1992**, 92, 857.
6) Kagan, H. B.; Dang, T. P., *J. Am. Chem. Soc.*, **1972**, 94, 6429.
7) We learned from Professor Jacobsen (personal communication) that he has also prepared the boron analog of DIOP (see in this issue).
8) Descheneaux, R.; Stille, J., *J. Org. Chem.*, **1985**, 50, 2299.
9) Zhang, S. Q.; Zhang, S. Y.; Feng, R., *Tetrahedron :Asymmetry*, **1991**, 2, 173.
10) Brunner, H.; Schönhammer, B.; Steinberger, C., *Chem. Ber.*, **1983**, 116, 3530.
11) Törös, S.; Heil, B.; Marko, L., *J. Organomet. Chem.*, **1978**, 159, 401.
12) Heil, B.; Törös, S.; Bakos, J.; Marko, L., *J. Organomet. Chem.*, **1979**, 175, 229.
13) Törös, S.; Heil, B.; Kollar, L.; Marko, L., *J . Organomet. Chem.*, **1980**, 197, 85.
14) Ojima, I.; Kogure, T., *J. Chem. Soc., Chem. Commun.*, **1977**, 428.
15) Spindler, F.; Pittelkow, U.; Blaser, H. U., *Chirality*, **1991**, 3, 370.
16) Chiba, M.; Takahashi, H.; Morimoto, T.; Achiwa, K., *Tetrahedron Lett.*, **1987**, 28, 3675.
17) Dupont, W.; Poulin, J. C.; Dang, T. P.; Kagan ,H. B., *J. Am. Chem. Soc.*, **1973**, 95, 8295.
18) Ojima, I.; Kogure, T.; Kumagai, M., *J. Org. Chem.*, **1977**, 42, 1671.
19) From a molecular model of complex 6 one estimates that the distance d should be around 5-6 Å.