Tetrahedron: Asymmetry Vol. 4, No. 3, pp. 575-590, 1993
Printed in Great Britain

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

Chiroptical, Structural and Catalytic Properties of S-α-Methyl-[1-(substituted phenyl)-2-(2'-pyrido)-1-ethylidene] benzylamines and their Rh(I) and Cu(I) Complexes

Vitomir Šunjić*, Dragan Šepac, Biserka Kojić-Prodić, Rudolf Kiralj, Kata Mlinarić-Majerski and Vladimir Vinković

"Ruder Bošković" Institute, P.O.B. 1016, 41001 Zagreb, Croatia

(*Received in UK* 4 *January* 1993)

Key Words: Chiral 1,5-bidentate nitrogen ligands; CD spectra; X-ray crystal and molecular structure; conformation and imine-enamine equilibrium

Abstract: S-α-Methyl-[1-(substituted-phenyl)-2-(2'-pyrido)-1-ethylidene]benzylamines **15-21** and their Rh(I) complexes **22-28** are prepared and their chiroptical and conformational properties are studied. Free ligands are present as enamines in the solution and in the solid state, but are bound to Rh(I) in the imine form. The CD spectra confirm that complexation of **15-21** induces both structural change and strong conformational perturbations. The molecular structures in the crystal are reported for the chiral 1,5-bisnitrogen ligand **18**, and its Rh[(norbornadiene)$_2$] perchlorate complex **25**. The absolute conformation of the chromophore in **18** inverts on binding to Rh(I) in **25**. The value of the torsional angle about C10-C9-C16-C21 bond (-69.7°) in **18**, which defines the twisted stilbene-like chromophore, turns for **25** into 75.0°. Chiral S-(-)-methylbenzyl subunit in **18** has a C1-N1-C9-C10 torsional angle of 175.2°, whereas on binding to Rh(I) in **25** this angle changes to -178.4°. The absolute conformation around the styrene-like arrangement of the bonds in **15-21** can be deduced from the strong positive Cotton effect at *ca.* 350 nm. Cyclopropanation of styrene with ethyl diazoacetate, in the presence of *in situ* generated Cu(I) complexes of chiral 1,5-bidentate ligands **15-21**, yielded *cis/trans* 2-phenylcyclopropan-1-carboxylic acid ethylesters with 5-21% e.e. Though generally low, the enantioselectivity was somewhat higher for *ortho*-(**16-18**) than for *para*-(**19-21**) substituted phenyl derivatives.

INTRODUCTION

The role played by weak π-donor bisnitrogen ligands is critical for stabilizing and fine tuning of the reactivity of the metal centre in catalysis. 1,4- and 1,5-bisnitrogen compounds are generally considered to be both good σ- and π-donors. Those with C_2-symmetry are topologically best suited for enantioface differentiation in some catalytic reactions, *e.g.* cyclopropanation[1-3], hydrosilylation[4-6], alkylation[7,8], and hydrogen transfer[9,10]. Aratani's chiral Cu(I) catalytic complexes, although they lack C_2 symmetry, exhibited very high enantioselectivity in the cyclopropanation of the chrysanthemic acid precursors[11,12]. Bolm *et al.* demonstrated[13,14] for some chiral 1,4-bisnitrogen ligands, derivatives of 2-substituted-6-phenylpyridine, that C_2 symmetry was not essential for high asymmetric induction in some catalytic reactions.

Dedicated to the memory of Prof. Günter Snatzke, deceased on 14 January 1992.

We have been interested in Rh(I) catalysts with chiral 1,4- and 1,5-bisnitrogen ligands, attempting to correlate their chiroptical properties, which reflect degrees of distortion of the chiral chromophore, with the enantioselectivity induced by complex in some standard catalytic reactions[15,16]. Here we report on preparation of some chiral 1,5-bisnitrogen ligands and their Rh(I) complexes, structural data for a selected ligand and its Rh(I) complex, and the results of the enantioselective cyclopropanation of styrene with the *in situ* generated Cu(I) complexes of these ligands.

RESULTS AND DISCUSSION

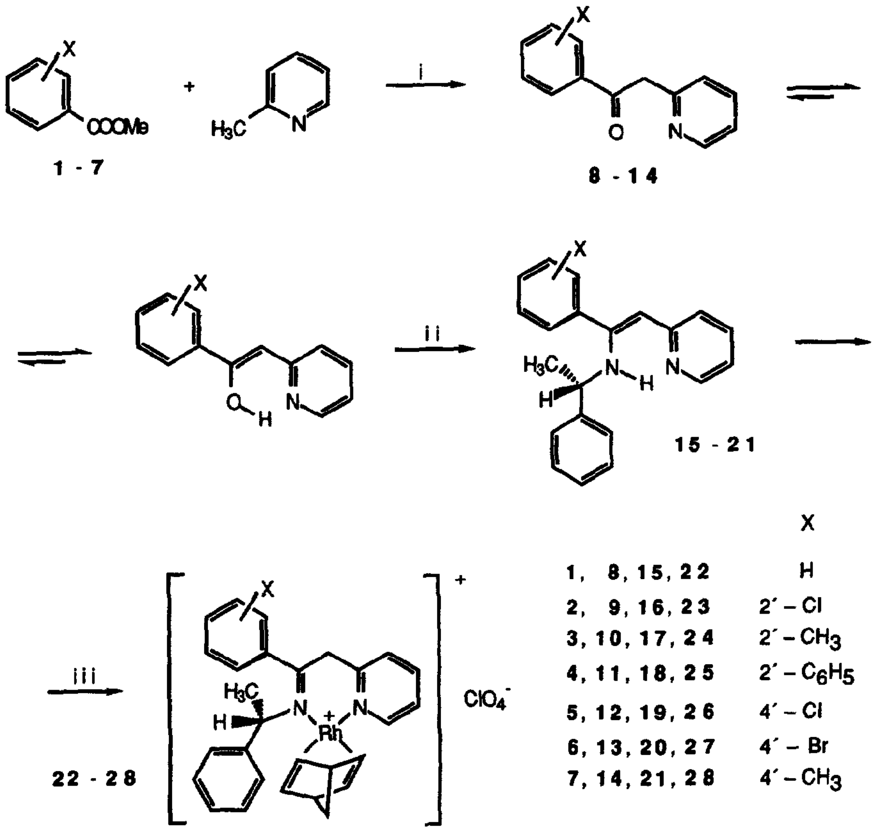
Synthesis. 1,5-Bisnitrogen ligands are prepared in two steps from commercially available materials (Scheme 1). In the first step screening of the bases was required, since sodium amide in liq. ammonia[17] proved unsatisfactory for the preparation of most of the ketomethylpyridines. Best results were obtained with lithium diisopropylamide-THF complex in cyclohexane[18]. Ketomethylpyridines **8-14** behave as bidentate O,N-ligands, and some chiral congeners afford stable Rh(I) complexes[19]. In solution these ketones are present as the keto-enol tautomeric mixture (Scheme 1.); according to the NMR data in chloroform-d_1, enols are present in *ca.* 30-80%. No enaminone tautomers can be detected, although they have been found for ketomethylquinolines, as the preferred form, in solution[20]. The formation of ketimines **15-21** required prolonged reaction times and continuous elimination of water from the high-boiling solvent. Other methods; use of the strong acid in the presence of molecular sieves[19], $TiCl_4$ in benzene[21], $AlCl_3$ in benzene[22], template synthesis in the presence of Ni(II), or Cu(II)[23], were inefficient. The best yields were obtained according to the protocol that uses phosphorous penthoxide on the inert support for binding water in the condensate, and *para*-toluenesulphonic acid as catalyst in boiling toluene. In the ^{1}H-NMR spectra all ligands exhibited a doublet for the nitrogen proton at 9.8-10.3 ppm, and a singlet for the enaminic (N-C=CH) proton at 4.9-5.3 ppm. In the ^{13}C-NMR off-resonance spectra a doublet for the enamine carbon(=CH) at 86.84-100.34 ppm was present.

Formation of the complexes **22-28** was hampered by the low purity of Rh[(norbornadiene)$_2$] perchlorate prepared in the usual manner[24]. An improved preparation in the sealed tube under argon afforded this precursor for the catalytic complexes in 63% yield, as the orange crystals. The ^{1}H-NMR spectra of the complexes **22-28** exhibited a singlet for the $N=C-CH_2$ group at 4.6-5.3 ppm, revealing the presence of ketimine form, found in the solid state for **25**, and confirmed by the UV-VIS spectra, discussed in the next paragraph.

Structural and chiroptical properties.- Ligand **18** and its complex **25** attracted our attention because of their peculiar conformational properties. The ORTEP plots of **18** and **25** are shown in Figures 1 and 2. The solid state structure of **18** revealed a chiral array of the biphenyl moiety, and also a chirally twisted benzene ring within the aza-stilbene subunit; the pyridine ring retains a nearly coplanar position relative to the central enamine double bond. The first torsional chirality is defined by the torsional angle between the disubstituted phenyl ring and the enamine double bond (-69.7°), and the second one by the torsional angle between the planes defined by two phenyl rings (-52.8°), Table 1. This chiral array is induced by the single stereogenic centre at C2 in the molecule, and looks promising for enantioselection in the binding of the substrate and reagent on the central metal atom of the complex in the course of the catalytic cycle.

Interatomic distances and bond angles of **18** and **25** are listed in Table 2. Selected torsional angles characteristic for the solid state conformations of these two compounds are given in Table 1. The molecule **18**

Scheme 1.



	X
1, 8, 15, 22	H
2, 9, 16, 23	2′ - Cl
3, 10, 17, 24	2′ - CH_3
4, 11, 18, 25	2′ - C_6H_5
5, 12, 19, 26	4′ - Cl
6, 13, 20, 27	4′ - Br
7, 14, 21, 28	4′ - CH_3

i. LDA x THF/cyclohexane, ii. S-(-)-methylbenzylamine/p-TsOH/toluene reflux.
iii. $Rh_2(NBD)_4ClO_4$/dichloromethane/r.t.

reveals an enamine C9=C10 bond. However, in the Rh(I) complex migration of double bond occurred, and the imino group was found in the crystal structure of **25**. These changes affect the relative orientation of the pyridine, and the phenyl ring on the stereogenic centre; the dihedral angle between these two planes in the ligand is 65°, whereas in the complex it is 21°. In the crystal structure of **25**, Rh(I) is coordinated to two nitrogen atoms: the imino group (N1), the pyridyl (N2), and the π-bonds of the norbornadiene ligand (Table 2., Fig.2). The distances Rh–C from two double bonds C28=C29 and C31=C32 are equal at the level of three standard deviations (Table 2). The molecular fragment Rh, N1, N2, and the centres of the olefinic bonds are planar (maximum deviation of 0.03Å), confirming the square planar geometry of the Rh(I) complex. A similar geometry is found for a 1,4-bisnitrogen ligand with the incorporated S-α-methylbenzylamine, the same chiral subunit[26].

To establish if the same chiral conformation of **18** and **25** is maintained in the solution, the analysis of electronic (UV-VIS) and CD spectra is performed. The electronic spectrum of **18** exhibits a strong K-band at

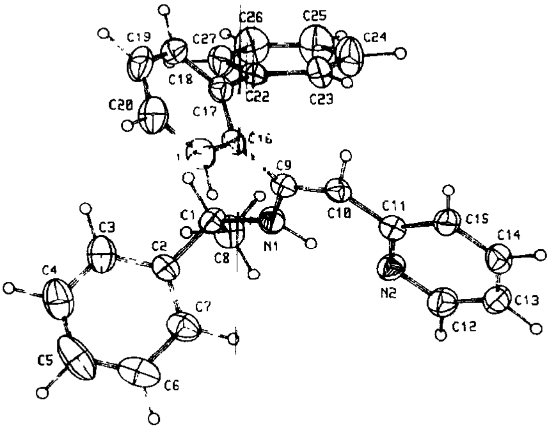


Fig. 1. Crystal structure of **18**; the ORTEP plot and atom labeling are shown.

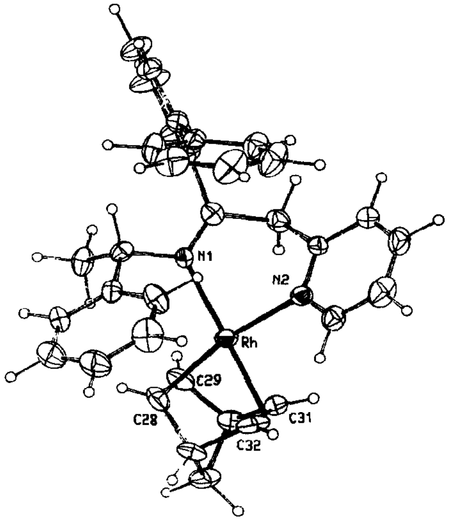


Fig. 2. Crystal structure of **25**; the ORTEP plot and atom labeling are shown.

355.5 nm (ε 16.780), and the shoulders at 307 nm (ε *ca.* 10.000) and at 230.8 nm (ε 18.800) (Fig 3). The CD spectrum exhibits two positive Cotton effects. The maximum of the first one (λ 356.0 nm, Δε +17.2) is at the same wavelength as the K-band; the second one is found at 228.5 nm (Δε +16.2) *i.e.* at the short-wavelength shoulder in the electronic spectrum. Another shoulder at 298 nm (Δε +7.2) is observed. The inflexion at 230 nm in the electronic spectrum rises strong CD band at 228.5 (Δε +16.2). This band and inflections in UV and CD at *ca.* 305 nm cannot be assigned with confidence.

The positive long-wavelength Cotton effect is probably due to the negative helicity of the torsional angle (-69.7°) between the aromatic ring and the styrene-like enamine double bond. As Crabbe has already established[27], chirally twisted styrenes exhibit opposite signs of the Cotton effect at *ca.* 270 nm to those of the helicity determined by the aromatic ring and double bond. Since the pyridine ring is situated in a nearly coplanar, *i.e.* achiral, position relative to the central double bond (torsional angle -6.1°), it cannot influence the sign of this band.

The electronic spectrum of the complex **25** exhibits a less intensive band at 340 nm (ε 4.860), than the free ligand, due to loss of conjugation between the two aromatic subunits. A new weak band at *ca.* 430 nm appears for the d→d* transition. The CD spectrum of the complex **25** differs significantly from that of the free ligand (Fig. 4). Here the d→d* transition band appears at 426 nm as a well defined Cotton effect (Δε +2.2). The medium wavelength CD band at 355 nm (Δε + 4.0) corresponds to the K-band in UV. There is also a third positive CD band at 264 nm (Δε +6.2) which is followed by the fourth, negative, short-wavelength band at 238.0 nm (Δε -1.8). The last two bands appear in the region where in the UV of phenylethylamine a very weak band is observed (258 nm, ε 130), and therefore a coupled excitone effect is excluded.

Table 1. Selected torsion angles [°] for **18** and **25**.

	18	**25**
C2 - C1 - N1 - C9	-91.2 (8)	-139.6(8)
C1 - N1 - C9 - C10	175.2 (7)	-178.4(8)
C1 - N1 - C9 - C16	-4(1)	-3(1)
N1 - C9 - C10 - C11	4(1)	-63(1)
N2 - C11 - C10 - C9	-6(1)	57(1)
C10 - C9 - C16 - C17	109.9(7)	-110.5(9)
C9 - C16 - C17 - C22	0.6(9)	9(1)
C16 - C17 - C22 - C23	-52.8(9)	-119(1)
C10 - C9 - C16 - C21	-69.7(8)	75(1)
N1 - C9 - C16 - C21	109.2(7)	-101(1)
N1 - C1 - C2 - C7	-46.6(9)	-144.3(8)
N1 - C1 - C2 - C3	139.7(7)	37(1)
C9 - N1 - C1 - C8	146.6(7)	94(1)
C11 - C10 - C9 - C16	-177.2(7)	121.2(8)

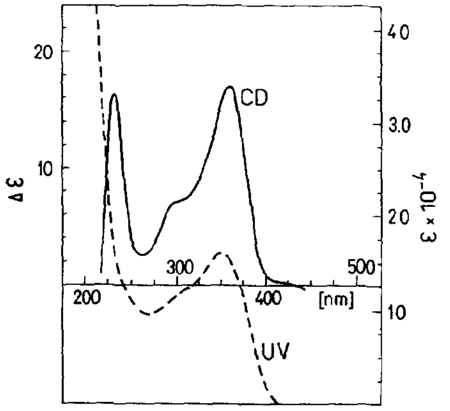


Fig. 3. UV and CD spectra of **18** in MeCN.

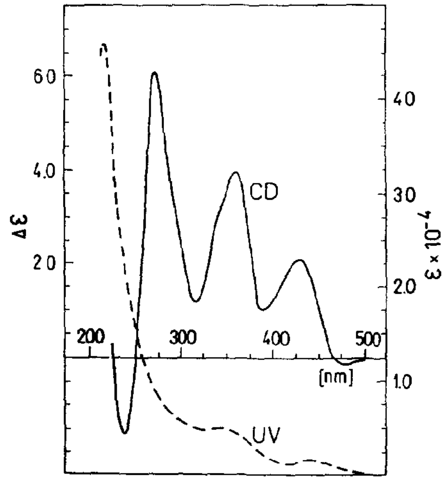


Fig. 4. UV and CD spectra of **25** in MeCN.

Cyclopropanation.- *In situ* formed Cu(I) complexes of the ligands **15-22** are examined in cyclopropanation of styrene, according to the known protocol[28,29]. Results are presented in the Table 3. They

Table 2. Selected bond lengths [Å] and angles [°] for **18** and **25**.

	18	**25**		
		Ligand	Coordination sphere	
C1 - C2	1.512(10)	1.528(13)	Rh - N1	2.119 (7)
C1 - C8	1.545(10)	1.519(14)	Rh - N2	2.111 (7)
C1 - N1	1.465 (8)	1.492(11)	Rh - C28	2.139(10)
N1 - C9	1.366 (8)	1.261(11)	Rh - C29	2.137 (8)
C9 - C10	1.351 (9)	1.524(12)	Rh - C31	2.107(10)
C10 - C11	1.448 (9)	1.513(13)	Rh - C32	2.119(11)
C11 - N2	1.341 (8)	1.344(11)	N1 - Rh - N2	85.3(3)
N2 - C12	1.350(10)	1.342(12)	N1 - Rh - C28	105.7(4)
C12 - C13	1.357(12)	1.380(14)	N1 - Rh - C29	101.5(3)
C13 - C14	1.372(11)	1.377(18)	N1 - Rh - C31	154.1(3)
C14 - C15	1.380(11)	1.359(16)	N1 - Rh - C32	166.0(4)
C15 - C11	1.397 (9)	1.391(14)	N2 - Rh - C28	164.0(3)
<C2 - C7>*	1.371(14)	1.382(15)	N2 - Rh - C29	152.9(3)
<C16 - C21>*	1.386(11)	1.387(15)	N2 - Rh - C31	96.9(3)
<C22 - C27>*	1.378(12)	1.378(17)	N2 - Rh - C32	100.6(4)
<N2 - C>*	1.346 (9)	1.343(12)	C28 - Rh - C31	78.2(4)

Table 2. Selected bond lengths [Å] and angles [°] for **18** and **25** (continued).

	18	**25**		
		Ligand	Coordination sphere	
<C11 - C12>*	1.377(11)	1.377(16)	C28 - Rh - C32	66.1(4)
C1 - N1 - C9	125.6 (6)	119.2 (7)	C29 - Rh - C31	65.8(4)
N1 - C1 - C2	113.4 (6)	107.9 (7)	C29 - Rh - C32	79.0(4)
N1 - C1 - C8	106.8 (6)	109.2 (7)		
C2 - C1 - C8	110.7 (5)	115.7 (8)		
N1 - C9 - C10	122.7 (6)	118.4 (8)		
N1 - C9 - C16	117.1 (5)	126.5 (8)		
C10 - C9 - C16	120.2 (6)	115.0 (7)		
C9 - C10 - C11	128.2 (6)	112.0 (7)		
C11 - N2 - C12	117.8 (6)	119.5 (8)		
<C2 - C7>*	120.0 (9)	120 (1)		
<C16 - C21>*	120.0 (7)	120 (1)		
<C22 - C27>*	120.0 (8)	120 (1)		
<C11 - C12>*	119.3 (7)	120 (1)		

*Average values of bond lengths and angles of aromatic rings reveal low enantioselectivity of the catalytic complexes, with somewhat higher average optical yields obtained for the *ortho*-substituted ligands. The low enantioselectivity with Cu complex of **18** was particularly surprising, because of the well defined conformational chirality of the ligand. Presumably, in the Cu(I) complexes this arrangement is lost; higher enantioselectivities can be expected for Cu complexes with more restricted conformational mobility controlled by the third binding site, an anionic hydroxy group or amino group, in the ligand.

Table 3. Enantioselective Cyclopropanation of Styrene

Ligand	Yield (%)	*cis/trans*	Ester e.e (%)[a] *cis*[b]	*trans*[b]
15	70	39/61	8	10
16	50	41/59	21	13
17	59	39/61	10	5
18	53	40/60	11	5
19	53	42/58	9	10
20	32	41/59	9	10
21	64	42/58	9	7
nill	59	53/47	0	0

[a]Given % of yields and e.e.'s are the average values of the two experiments that differ *ca.* ±1%; [b]Enantiomer with 1S configuration was regularly in excess.

Conclusions.- The 1,5-bisnitrogen ligands **15-21** form stable Rh(I) complexes **22-28** with the well defined conformational properties. Their structure and conformation in solution can be deduced from the spectral and chiroptical data, and related to the solid-state data for the ligand **18**, and its Rh(I) complex **25**. An "inversion" of the most relevant torsional angles in the ligands occur on binding to Rh(I).

In spite of the well defined conformational chirality of **15–21**, their Cu(I) complexes, prepared *in situ*, exhibited low enantioselectivity in cyclopropanation of styrene. In order to improve enantioselectivity of their Cu(I) catalytic complexes the preparation of the congeners of **15-21** with a "third arm" is in course.

EXPERIMENTAL

^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ on Jeol FX 90Q FT spectrometer; shifts are given in ppm downfield from TMS as an internal standard. IR spectra were recorded on Perkin-Elmer 297 spectrophotometer. UV-VIS spectra were recorded on PU 8700 Series spectrophotometer. Rotations were determined on Optical Activity AA-10 Polarimeter.

Esters **1-7** were prepared from the commercially available acids (2.5 mmol) in the yields 90-95%, by esterification in abs. methanol (20 ml), to which thionylchloride (1.90 ml, 2.6 mmol) was added. Pure products were obtained by distillation *in vacuo*, or by crystallization.

Substituted-phenyl-2'-pyridylmethyl ketones (**8-14**)

2-Methylpyridine (310 mg, 3.3 mmol, distilled under argon before use) was dissolved in ether (20 ml), and LDA–THF complex (3.63 mmol, 1.5 mol solution in cyclohexane, Aldrich) was added dropwise at -50°C over 45 min. Resulting suspension was cooled to -10°C and 3.3 mmol of 2- or 4-substituted methylbenzoate (**1-7**) was added. The reaction was continued for 15 hr at ambient temperature, then water (30 ml) was added, organic phase separated and aqueous phase washed with ether (3x30 ml). Combined organic extracts were washed with dilluted hydrochloric acid, dried end evaporated to recover unreacted ester. Aqueous phase was adjusted to pH 8 with solid bicarbonate, extracted with ether (3x30 ml), dried *in vacuo* over conc. sulfuric acid, and purified by flash chromatography with chloroform-diisopropylether-light petroleum (1:7:2) as eluant. Pure product was obtained by final crystallization, or bulb-to-bulb distillation at *ca.* 250°C/0.01 mm Hg.

2-(2'-Pyrido)acetophenone (**8**) was crystallized from light petroleum, m. p. 57-59°C (lit^{31}. m. p. 59°C)

2-(2'-Pyrido)-2-chloroacetophenone (**9**) was purified by distillation at 250°C/10^{-3} mm Hg, and subsequent flash chromatography, yellow oil, yield 59.3%. IR (KBr); 1625, 1595, 1455, 1410, 1275, 1110, 800, 740 cm^{-1}. ^{1}H-NMR ($CDCl_3$); 8.55-6.86 (m, 8H), 5.90 (s, HC=C), 4.42 (s, CH_2). ^{13}C-NMR ($CDCl_3$); 195.37 (s, CO), 163.15, 158.02, 154.69, 149.38, 143.80, 139.45, 136.97, 136.35, 134.82, 134.60, 130.03, 128.67, 128.22, 126.58, 123.87, 121.79, 121.39, 118.40, 93.96 (d, HC=C), 48.20 (t, CH_2). Anal. calcd. for $C_{13}H_{10}NOCl$ (231.66): C 67.40%, H 4.35%, N 6.04%. Found: C 67.43%, H 4.46%, N 6.14%.

2-(2'-Pyrido)-2-methylacetophenone (**10**) was purified by distillation, yield 34.6%, pale-yellow oil. IR (KBr); 1630, 1600, 1550, 1475, 810, 765 cm^{-1}. ^{1}H-NMR ($CDCl_3$); 8.55-6.85 (m, 8H), 5.60 (s, HC=C), 4.40 (s, CH_2), 2.51 (s, CH_3). ^{13}C-NMR ($CDCl_3$); 199.38 (s, CO), 166.82, 157.79, 154.74, 148.65, 143.46, 137.98, 136.80, 136.35, 135.50, 131.27, 130.82, 130.03, 128.61, 127.99, 127.60, 124.89, 123.53, 121.00, 120.49, 117.84, 97.41 (d, HC=C), 50.00 (t, CH_2), 20.77 (q, CH_3). Anal. calcd. for $C_{14}H_{13}NO$ (211.24): C 79.60%, H 6.20%, N 6.63%. Found: C 79.50%, H 6.37%, N 6.46%.

2-(2'-Pyrido)-2-phenylacetophenone (**11**) was purified by distillation, yield 58.9%, yellow oil. ^{1}H-NMR ($CDCl_3$); 8.46-6.66 (m, 13H), 5.35 (s, HC=C), 3.80 (s, CH_2). ^{13}C-NMR ($CDCl_3$); 203.22 (s, CO), 166.76, 157.85, 154.57, 148.93, 143.40, 141.59, 140.13, 139.85, 136.63, 136.35, 135.90, 130.31, 129.85, 128.67, 128.45, 127.82, 127.71, 127.15, 126.81, 126.47, 123.21, 121.34, 120.83, 117.78, 98.82 (d, HC=C), 51.53 (t, CH_2). Anal. calcd. for $C_{19}H_{15}NO$ (273.31): C 83.49%, H 5.53%, N 5.12%. Found: C 83.43%, H 5.68%, N 5.09%.

2-(2'-Pyrido)-4-chloroacetophenone (**12**) was purified by crystallization from light petroleum, yield 45%, m.p. 89-90°C. IR (KBr); 1630, 1595, 1455, 1410, 1280, 1060, 800, 740 cm^{-1}. ^{1}H-NMR ($CDCl_3$); 8.55-6.86 (m, 8H), 6.00 (s, HC=C), 4.42 (s, CH_2). ^{13}C-NMR ($CDCl_3$); 195.37 (s, CO), 163.15, 158.02, 154.69, 149.38, 143.80, 139.45, 136.97, 136.35, 134.82, 134.60, 130.03, 128.67, 128.22, 126.58, 123.87, 121.79, 121.39, 118.40, 93.96 (d, HC=C), 48.20 (t, CH_2). Anal. calcd. for $C_{13}H_{10}NOCl$ (231.66): C 67.40%, H 4.35%, N 6.04%. Found: C 67.46%, H 4.29%, N 6.19%.

2-(2'-Pyrido)-4-bromoacetophenone (**13**) was purified by crystallization from acetone-water, yield 57.9%, yellow-greenish crystals, m. p. 96-98°C. IR (KBr), 1625, 1585, 1450, 1400, 1270, 1055, 800, 735 cm^{-1}. ^{1}H-NMR ($CDCl_3$); 8.55-6.86 (m, 8H), 6.01 (s, HC=C), 4.42 (s, CH_2). ^{13}C-NMR ($CDCl_3$); 200.06 (s, CO), 197.18, 195.43, 162.98, 157.78, 154.51, 149.21, 143.68, 136.91, 136.29, 135.11, 134.87, 131.55, 131.10, 129.97, 128.16, 126.98, 126.69, 124.72, 123.82, 123.08, 121.67, 121.34, 118.34, 103.23, 101.41, 93.91 (d, HC=C), 48.03 (t, CH_2). Anal. calcd. for $C_{13}H_{10}NOBr$ (276.12): C 56.54%, H 3.65%, N 5.07%.

Found: C 56.59%, H 3.66%, N 4.97%.

2-(2'-Pyrido)-4-methylacetophenone (**14**) was purified by crystallization from acetone-water, yellow crystals, yield 41.1%, m. p. 70-71°C. IR (KBr); 1630, 1600, 1550, 1465, 1060, 800, 740 cm^{-1}. ^{1}H-NMR ($CDCl_3$); 8.53-6.79 (m, 8H), 6.01 (s, HC=C), 4.42 (s, CH_2), 2.32 (s, CH_3). ^{13}C-NMR ($CDCl_3$); 195.88 (s, CO), 163.82, 154.97, 148.93, 143.57, 138.88, 136.57, 136.06, 133.58, 133.19, 128.84, 128.56, 128.39, 124.95, 123.76, 121.34, 121.00, 117.84, 93.12 (d, HC=C), 47.80 (t, CH_2), 21.16 (q, CH_3). Anal. calcd. for: $C_{14}H_{13}NO$ (211.24): C 79.60%, H 6.20%, N 6.63%. Found: C 79.52%, H 6.34%, N 6.50%.

S-α-Methyl-[1-(substituted phenyl)-2-(2'-pyrido)-1-ethylidene]benzylamines (**15-21**)

Ketone **1-7** (11.0 mmol), and S-(-)- benzilmethylamine (2.67 g, 22 mmol, Aldrich), and few crystals of *para*-toluenesulphonic acid, dissolved in toluene (50 ml), were heated under reflux for 90 hr. The apparatus was set up in the way that the vapours pass a side-arm connecting reaction vessel and reflux condenser, whereas condensate returns passing through the glass-tube filled with P_2O_5 on inert support (Fluka). Toluene was azeotropically evaporated with chloroform (2x200 ml), and crude product purified by crystallization from methanol.

S-α-Methyl-[1-(phenyl-2-(2'-pyrido)-1-ethylidene]benzylamine (**15**) yield 98%, colourless crystals, m. p. 47°C, $[\alpha]_D$ +730 (c 1.0, $CHCl_3$). IR (KBr); 1620, 1590, 1550, 1490, 1470, 1415, 1140, 770, 700 cm^{-1}. ^{1}H-NMR (C_6D_6); 10.20 (d, NH), 8.35 (d, 1H), 7.46-6.42 (m, 13H), 5.31 (s, HC=C), 4.68-4.34 (m, CH), 1.44 (d, CH_3). ^{13}C-NMR (C_6D_6); 160.78, 155.36, 147.86, 147.07, 139.67, 135,95, 128.95, 128.61, 126.58, 122.74, 117.78, 100.341 (d, HC=C), 54.97 (d, CH), 25.62 (q, CH_3). Anal. calcd. for $C_{21}H_{20}N_2$ (300.39): C 83.96%, H 6.71%, N 9.33%. Found: C 83.89%, H 6.90% N 9.15%.

S-α-Methyl-[1-(2-chlorophenyl)-2-(2'-pyrido)-1-ethylidene]benzylamine (**16**) colourless crystals, m. p. 52-53°C, $[\alpha]_D$ +784 (c 1.0, $CHCl_3$). IR (KBr) 2980, 2880, 1625, 1585, 1545, 1410, 1310, 1140, 800, 760, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$); 10.14 (d, NH), 8.46 (d, 1H), 7.54-6.75 (m, 12H), 4.98 (s, HC=C), 4.18 (q, CH), 1.51 (d, CH_3) ^{13}C-NMR ($CDCl_3$); 159.71, 150.62, 147.24, 136.74, 135.27, 130.93, 129.01, 128.05, 126.24, 126.02, 125.68, 121.67, 116.87, 86.84 (d, HC=C), 53.78 (d, CH), 24.83 (q, CH_3). Anal. calcd. for: $C_{21}H_{19}N_2Cl$ (334.83): C 75.32%, H 5.72%, N 8.37%. Found: C 75.54%, H 5.61%, N 8.20%.

S-α-Methyl-[1-(2-methylphenyl)-2-(2'-pyrido)-1-ethylidene]benzylamine (**17**) yield 89.4%, colourless crystals, m. p. 53-54°C, $[\alpha]_D$ +955 (c 1.0, $CHCl_3$). IR (KBr); 1620, 1590, 1550, 1470, 1415, 1350, 1140, 800, 760, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$); 10.15 (d, NH), 7.47-6.65 (m, 12H), 4.95 (s, HC=C), 4.10 (m, CH), 2.46 (s, CH_3), 1.47 (s, CH_3). ^{13}C-NMR ($CDCl_3$); 161.46, 148.59, 139.00, 136.63, 131.27, 130.36, 129.46, 129.18, 127.60, 127.15, 126.41 122.86, 118.17, 117.95, 97.91 (d, HC=C), 55.08 (d, CH), 26.52 (q, CH_3), 20.66 (q, CH_3). Anal. calcd. for $C_{22}H_{22}N_2$ (314.42): C 84.03%, H 7.05%, N 8.91%. Found: C 84.01%, H 7.19%, N 8.83%.

S-α-Methyl-[1-(2-phenylphenyl)-2-(2'-pyrido)-1-ethylidene]benzylamine (**18**) yield 76.2%, colourless crystals, m.p. 124-125°C, $[\alpha]_D$ +760 (c 1.0, $CHCl_3$). IR (KBr); 2975, 1615, 1590, 1540, 1470, 1435, 1415, 1140, 795, 770, 745, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$); 9.82 (s, NH), 8.36 (s, 1H), 7.62-6.77 (m, 17H), 5.08 (s, HC=C), 3.96 (s, CH), 0.95 (s, CH_3). ^{13}C-NMR ($CDCl_3$); 159.90, 147.06, 135.03, 130.20, 127.72, 128.31, 127.92, 126.75, 126.03, 125.59, 121.41, 116.34, 97.66 (d, HC=C), 53.40 (d, CH), 24.05 (q, CH_3). Anal. calcd. for $C_{27}H_{24}N_2$ (376.48): C 86.13%, H 6.43%, N 7.44%. Found: C 86.26%, H 6.29%, N 7.48%.

S-α-Methyl-[1-(4-chlorophenyl)-2-(2'-pyrido)-1-ethylidene] benzylamine (**19**) yield 68.3%, colourless crystals, m.p. 105-107°C, $[\alpha]_D$ +707 (c 1.0, $CHCl_3$). IR (KBr); 2895, 1620, 1590, 1550, 1490, 1470, 1420, 1350, 1140, 1090, 825, 795, 765, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$); 9.93 (d, NH), 8.47 (d, 1H), 7.52-6.87 (m, 12H), 5.16 (s, HC=C), 4.37 (q, CH), 1.49 (d, CH_3). ^{13}C-NMR ($CDCl_3$); 159.22, 153.04, 147.136, 145.80, 136.91, 135.46, 137.71, 129.25, 128.13, 128.01, 126.29, 125.68, 122.03, 117.47, 99.64 (d, HC=C), 54.17 (d, CH), 24.76 (q, CH_3). Anal. calcd. for $C_{21}H_{19}N_2Cl$ (334.83): C 75.32%, H 5.72%, N 8.37%. Found: C 75.32%, H 5.93%, N 8.40%.

S-α-Methyl-[1-(4-bromophenyl)-2-(2'-pyrido)-1-ethylidene]benzylamine (**20**) yield 94.2%, colourless crystals, m.p. 99-101°C, $[\alpha]_D$ +563 (c 1.0 $CHCl_3$). IR (KBr); 2890, 1620, 1590, 1550, 1470, 1415, 1350, 1140, 1110, 820, 795, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$); 9.93 (d, NH), 8.46 (d, 1H), 7.51-6.86 (m, 12H), 5.16 (s, HC=C), 4.36 (q, CH), 1.48 (d, CH_3). ^{13}C-NMR ($CDCl_3$); 134.44, 128.28, 122.38, 121.01, 112.63, 110.702, 106.20, 104.79, 103.37, 101.53, 100.92, 97.27, 97.17, 92.73 (d, HC=C), 74.87 (d, CH), 29.41 (q, CH_3). Anal. calcd. for $C_{21}H_{19}N_2Br$ (379.29): C 66.50%, H 5.05%, N 7.39. Found: C 66.44%, H 5.13%, N 7.49%.

S-α-Methyl-[1-(4-methylphenyl)-2-(2'-pyrido)-1-ethylidene]benzylamine (**21**) yield 98.8%, colourless crystals, m.p. 91-93°C, $[\alpha]_D$ +631(c.1.0, $CHCl_3$). IR (KBr); 2900, 1620, 1590, 1550, 1510, 1470, 1140, 790, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$); 9.97 (d, NH), 8.55 (d, 1H), 7.50-6.84 (m, 12H), 5.18 (s, HC=C), 4.45 (q, CH), 2.36 (s, CH_3), 1.48 (d, CH_3). ^{13}C-NMR ($CDCl_3$); 160.03, 154.87, 147.47, 146.43, 138.10, 136.00, 135.69, 128.89, 128.64, 128.45, 128.21, 126.54, 126.11, 122.19, 117.37, 99.15 (d, HC=C), 54.16 (d, CH), 24.94 (q, CH_3), 21.28 (q, CH_3). Anal. calcd. for $C_{22}H_{22}N_2$ (314.42): C 84.03%, H 7.05%, N 8.91%. Found.: C 84.22%, H 7.10%, N 9.09%.

Rh(I)-[S-α-Methyl-[(substituted phenyl)-2-(2'-pyrido)-1-ethylidene]benzylamine, norbornadiene] perchlorates (22-28)

Organometallic perchlorate salts are potentially explosive and extreme care must be taken with the handling of solid materials and of all residues.

Compounds **15-21** (0.9 mmole), were dissolved under argon atmosphere in dichloromethane (10 ml), and rhodium bisnorbornadiene perchlorate (254 mg, 0.9 mmol) was added from the Schlenk tube. After 16 hr stirring at ambient temperature, dichloromethane is evaporated in the stream of argon, and crude product was separated by thick-layer chromatography with dichloromethane-ethylacetate (8:2) as eluant. Pure product was washed from silica gel with dichloromethane-methanol (9:1). On evaporation of the solvent pure product was obtained by crystallization from ethanol (6 ml). On cooling to -20°C, collection on filter, and washing with ether (6x2 ml), precooled to -20°C, pure **22-28** were obtained. After drying *in vacuo* they were stored under argon.

Rh(I)-[S-α-Methyl-[(phenyl)-2-(2'-pyrido)-1-ethylidene]benzylamine, norbornadiene] perchlorate (**22**) yield 63.7%, m. p. 123-125°C, $[\alpha]_D$ -40 (c 0.1, MeOH). IR (KBr); 1600, 1475, 1445, 1305, 1085, 760,740, 700, 620 cm^{-1}. ^{1}H-NMR ($CDCl_3$); 8.03-7.07 (m, 14H), 5.06 (CH_2), 4.81 (q, $\underline{H}$C*CH_3), 4.04, 3.97 (2s, 4H, 2x$\underline{H}$C=C$\underline{H}$), 1.66, 1.60 (2 s+d, 5H, HC*C$\underline{H}_3$+2xCH(NBD)), 1.21 (s, CH_2 (NBD)). Anal. calcd. for $C_{28}H_{28}N_2RhClO_4$ (594.90): C 56.53%, H 4.74%, N 4.71%. Found: C 56.65%, H 4.93%, N 4.84%.

Rh(I)-[S-α-Methyl-[(2-chlorophenyl)-2-(2'-pyrido)-1-ethylidene]benzylamine, norbornadiene] perchlorate (**23**) yield 79.2%, m. p. 132-133°C. $[\alpha]_D$ -66 (c 1.0, MeOH). IR (KBr); 1625, 1600, 1470, 1445, 1430, 1410, 1305, 1090, 760, 745, 500, 620 cm^{-1}. ^{1}H-NMR ($CDCl_3$); 8.03-7.14 (m, 13H), 4.61 (CH_2), 4.58 (q, $\underline{H}C^*CH_3$), 3.79 (s, 4H, 2x$\underline{H}C=C\underline{H}$), 1.82 (s, 1H, CH (NBD)), 1.75 (s, 1H, CH (NBD)), 1.38 (d, $HC^*C\underline{H}_3$), 1.17 (s, CH_2 (NBD)). Anal. calcd. for $C_{28}H_{27}N_2RhClO_4$ (629.34): C 53.44%, H 4.32%, N 4.45%. Found: C 53.34%, H 4.17%, N 4.49%.

Rh(I)-[S-α-Methyl-[(2-methylphenyl)-2-(2'-pyrido)-1-ethylidene]benzylamine, norbornadiene] perchlorate **(24)** yield 82.8%, m. p. 125-126°C. $[\alpha]_D$ -58 (c 1.0, MeOH). IR (KBr); 1600, 1470, 1440, 1300, 1090, 760, 740, 700, 620 cm^{-1}. ^{1}H-NMR ($CDCl_3$); 8.0-6.97 (m, 13H), 5.0 (s, CH_2), 4.84 (q, $\underline{H}C^*CH_3$), 4.04, 3.92, 377 (3s, 4H, 2x$\underline{H}C=C\underline{H}$), 2.33 (s, CH_3), 1.64 (2 s+d, 5H, $HC^*C\underline{H}_3$+2xCH(NBD)), 1.18 (s, CH_2 (NBD)). Anal. calcd. for $C_{29}H_{30}N_2RhClO_4$ (608.93): C 57.20%, H 4.97%, N 4.60%. Found: C 57.24%, H 5.10%, N 4.64%.

Rh(I)-[S-α-Methyl-[(2-phenylphenyl)-2-(2'-pyrido)-1-ethylidene]benzylamine, norbornadiene] perchlorate **(25)** after crystallization from ethanol yield 32.9%, m.p 138-140°C, $[\alpha]_D$ -62 (c 1.0, MeOH). IR (KBr); 1620, 1600, 1475, 1440, 1305, 1090, 760, 740, 700, 620 cm^1. ^{1}H-NMR ($CDCl_3$); 7.93-6.78 (m, 18H), 5.30 (s, CH_2), 4.72 (q, $\underline{H}C^*CH_3$), 3.81, 3.74 (2s, 4H, 2x$\underline{H}C=C\underline{H}$), 1.60 (s, 1H, CH(NBD)), 1.29, 1.22, 1.13 (3s, 6H, $HC^*C\underline{H}_3$+CH_2 (NBD)+CH(NBD)). Anal. calcd. for: $C_{34}H_{32}N_2RhClO_4$ (671.00): C 60.86%, H 4.81%, N 4.17%. Found: C 61.02%, H 4.83%, N 4.13%.

Rh(I)-[S-α-Methyl-[(4-chlorophenyl)-2-(2'-pyrido)-1-ethylidene]benzylamine, norbornadiene] perchlorate **(26)** yield 60.1%, m.p. 129-131°C, $[\alpha]_D$ -20 (c 0.1, MeOH). IR (KBr); 1600, 1485, 1475, 1445, 1305, 1090, 1010, 760, 740, 700, 620 cm^{-1}. ^{1}H-NMR ($CDCl_3$); 7.80-6.98 (m, 13H), 5.08 (s, CH_2), 4.77 (q, $\underline{H}C^*CH_3$), 4.04, 4.02 (2s, 4H, 2x$\underline{H}C=C\underline{H}$), 1.67, 1.59 (2s, 5H, $HC^*C\underline{H}_3$+2xCH(NBD)), 1.21 (s, CH_2 (NBD)). Anal. calcd. for: $C_{28}H_{27}N_2RhCl_2O_4$ (629.34): C 53.44%, H 4.32%, N 4.45%. Found: C 53.68%, H 4.09%, N 4.52%.

Rh(I)-[S-α-Methyl-[(4-bromophenyl)-2-(2'-pyrido)-1-ethylidene]benzylamine, norbornadiene] perchlorate **(27)** yield 42.4%, m. p. 129-130°C, $[\alpha]_D$ -46 (c 1.0, MeOH). IR (KBr); 1600, 1480, 1475, 1445, 1300, 1090, 1005, 760, 740, 620 cm^{-1}. ^{1}H-NMR ($CDCl_3$); 8.01-7.03 (m, 13H), 5.06 s, (CH_2), 4.76 (q, $\underline{H}C^*CH_3$), 4.05, 3.95 (2s, 4H, 2x$\underline{H}C=C\underline{H}$), 1.67, 1.63, 1.60 (2 s+d, 5H, $HC^*C\underline{H}_3$+2xCH(NBD)), 1.18 (s, CH_2 (NBD)). Anal. calcd. for $C_{328}H_{27}N_2RhClO_4$ (673.80): C 49.91%, H 4.04%, N 4.16%. Found: C 49.99%, H 4.19%, N 4.18%.

Rh(I)-[S-α-Methyl-[(4-methylphenyl)-2-(2'-pyrido)-1-ethylidene]benzylamine, norbornadiene] perchlorate **(28)** yield 94.2%, m. p. 124-125°C, $[\alpha]_D$ +16 (c 1.0, MeOH). IR (KBr); 1600, 1475, 1445, 1305, 1090, 810, 760, 740, 700, 620 cm^{-1}. ^{1}H-NMR ($CDCl_3$); 8.03-6.97 (m, 13H), 5.03 (s, CH_2), 4.89 (q, $\underline{H}C^*CH_3$), 4.04, 4.01 (2s, 4H, 2x$\underline{H}C=C\underline{H}$), 2.34 (s, CH_3), 1.67, 1.60 (2 s+d, 5H, $HC^*C\underline{H}_3$+2xCH(NBD)), 1.19 (s, CH_3 (NBD)). Anal. calcd. for $C_{29}H_{30}N_2RhClO_4$ (608.93): C 57.20%, H 4.97%, N 4.60%. Found: C 57.35%, H 5.10%, N 4.69%.

Enantioselective cyclopropanation-general procedure

To the slurry of copper (I) triflate (3.7 mg, 10 µmol) in styrene (0.52 g, 0.57 ml, 5.0 mmol), ligand was added (**14-21**), 15 µmol, 1.5 mol% related to diazoester), and suspension was stirred for 1 hr at ambient temperature under nitrogen. To the resulting mixture of the catalyst and olefine, ethyldiazoacetate (1mmol, 1ml of the 1M solution in 1,2–dichloroethane) was added over the period of 4.5 hr, using syringe pump. Thereafter the reaction mixture was stirred over night at ambient temperature. Diastereomeric mixture of *cis/trans* 2-phenylcyclopropan-1-carboxylic acid ethylesters were isolated by chromatography on silicagel column (1x15 cm) with ether-pentane (gradient 0-20%). Diastereomeric composition was determined on GLC capillary column DB-210, with biphenyl as an internal standard. Enantiomeric excess was determined on GLC chiral capillary column FS-Hydrodex b-PM (0.25 mm x 25 m), using initial temperature 120°C and 0.5°C/min gradient, 12 psi pressure of N_2, and split 1/150. Under above conditions retention times were as follows: *cis* (1S, 2R); 24.1 min, *cis* (1R, 2S); 24.7 min, *trans* (1R, 2R); 27.6 min, and *trans* (1S, 2S); 27.9 min.

CD measurements.-The CD measurements were performed on a Dichrograph Mark III (ISA-Jobin-Yvon) connected on-line to a PC. Noise was eliminated by curve-smoothing according to the Golay-Savitzky[27] algorithm (best parabola of degree 3 fitted to 25 consecutive points). Collected data are presented in the Table 4.

Table 4. CD Data for the Ligands **15-21**, and Compounds **25–28**.

Compound	$\lambda_{max}/\Delta\varepsilon$				
15	349.5/+22.9	296/+6.1 (sh)	236.5/+4.3	225.5/+2.2	
16	349.0/+27.3	300/+7.5 (sh)	243.2/+2.8	224.8/+1.73[a]	
17	348.0/+32.1	300/+8 0(sh)	238.5/+19.8	223.0/+8.4	
18	356.0/+17.2	298/+7.2 (sh)	228.5/+16.2		
19	351.6/+14.2	294.4/+4.0 (sh)	238.6/+7.5	228.0/+8.8	
20	349.5/+24.3	300/+8 (sh)	241.5/+8 (sh)	221.5/+14.1	
21	351.0/+28.6	300/+8 (sh)	230/+6 (sh)	222.0/+9.7	
25	426.0/+2.2	355.0/+4.0	264.0/+6.2	238.0/–1.8	
26	430.0/+0.9	349.0/+4.9	308.0/+2.5	277.0/+1.9	229.0/+1.4
27	~430/+1.1	349.0/+14.6	~300/+7.0(sh)	~230/+6.5(sh)	221.0/+10.4
28	433.0/+0.9	350.0/+8.6	~300/+3.5(sh)	278.0/+1.5	222.0/+0.8

[a] Broad band with fine-structure found between 220-260 nm

X-ray structure analysis.- The suitable crystals of **18** and **25** were obtained from ethanol over four days. Crystallographic data and details of data collection and refinement are listed in Table 5. Data reduction was performed by the ENRAF–Nonius SDP/VAX package[32]; Lorentz and polarization effects were corrected. An absorption correction for **25** was by the ψ–scan of the reflections $2\bar{1}\bar{2}$, $3\bar{2}\bar{3}$, $3\bar{2}\bar{4}$, $3\bar{2}\bar{5}$, $4\bar{2}\bar{4}$, $4\bar{3}\bar{4}$, $4\bar{3}\bar{5}$, $5\bar{3}\bar{5}$, $5\bar{4}\bar{5}$ and $6\bar{5}\bar{6}$. Minimum and maximum transmissions for **25** were 96% and 99%, respectively. No significant intensity variation for standard reflections in the course of the data collection was observed.

The structure of **18** was solved by direct methods using programme SHELX86[33]. The structure of **25** was solved by Patterson method with SHELX86. The rhodium scaterring factors and anomalous dispersion values were from *International Tables for X-ray Crystallography*, Vol. IV[34]. For other atoms the scattering factors were those included in the SHELX77 programme[35]. The H atom coordinates were introduced and refined under the constraints of pivot carbon atom geometry. The non–H atoms were refined anisotropically using SHELX77[35]; details of the refinement procedure are listed in Table 5. The ClO_4^- anion of compound **25** exhibits two different orientations; the population parameter of oxygen atom O1 being presented in both orientations was assigned value of 1 whereas other oxygen atoms (O2 to O7) have reduced site population to 0.5. During the chemical reaction the S–enantiomer was used and thus the absolute configuration to C1 in **18** and **25** was assigned as S. Molecular geometry was calculated by the programme package EUCLID[36].

Table 5. Crystal data and summary of experimental details and refinement for **18** and **25**.

	18	**25**
Molecular formula	$C_{27}H_{24}N_2$	$C_{34}H_{32}N_2RhClO_4$
M_r	376.503	670.999
Crystal size [mm]	0.20 x 0.20 x 0.35	0.14 x 0.14 x 0.17
a [Å]	9.167(3)	10.505(2)
b [Å]	9.949(1)	16.959(9)
c [Å]	23.56(2)	17.18(1)
V [Å^3]	2149(2)	3060(3)
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
D_x [gcm^{-3}]	1.164	1.456
Z	4	4
$\mu(MoK_\alpha)$ [cm^{-1}]	0.6	6.8
$F(000)$	800	1376
T [K]	297	295
No. of reflections used for cell parameters and θ range [°]	25 6 – 17	25 8 – 18
θ range [°] for intensity measurement	2 – 25	2 – 25
hkl range	(-1, 10; -1, 11; -1, 28)	(0, 15; 0, 20; 0, 20)
scan	ω/2θ	ω/2θ
Δω	0.8 + 0.35 tanθ	0.8 + 0.35 tanθ
No. of measured reflections	2897	3119
No. of symm. independent refl.	1273 $I > 3\,\sigma(I)$	1906 $I > 2\,\sigma(I)$
No. of variables	277	436
R	0.047	0.040
R_w, $w^{-1} = k(\sigma F_o^2 + g F)$	0.055	0.038
Final shift / error	-0.229 (C10, y)	-0.613 (O7, x)
S	0.81	1.78
Residual electron density $(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ [e Å^{-3}]	0.18, -0.22	0.34, -0.39

Drawings were prepared by EUCLID and ORTEP II[37]. Calculation were performed on Micro–VAXII and IRIS–4D25G computers of the X–ray Laboratory, Ruđer Bošković Institute, Zagreb.

Acknowledgements.- The authors thank to Mr. U. Wagner, Ruhruniversität Bochum, for providing CD spectra. This work was supported by the Ministry of Science, Republic of Croatia, Projects no. 1-07-179 and 1-07-255, and in part by the Board for Scientific and Technological Cooperation, BR Deutschland (Jülich Programme).

REFERENCES

1. Mueller, D.; Umbricht, G.; Weber, B.; Pfaltz, A. *Helv. Chim. Acta*, **1991**, *74*, 232-240.
2. Bolm, C. *Angew. Chem. Int. Ed. Engl.*, **1991**, *30*, 542–543.
3. Lowenthal, R. E.; Abiko. A.; Masamune, S. *Tetrahedron Lett.* **1991**, *31*, 6005-6008.
4. Boteghi, C.; Schionato, A.; Chelucci, G.; Brunner, H.; Kurzinger. A.; Oberman, U. *J.Organomet. Chem.* **1989**, *370*, 17-31.
5. Nishiyama, H.; Kondo, M.; Nakamura, T.; Itoh, K. *Organometallics*, **1989**, *10*, 500-505.
6. Brunner, H.; Obermann, U. *Chem. Ber.* **1989**, *122*, 499-507.
7. Kobayashi, A.; Furuya, M.; Ohtsubo, A.; Mukaiyama, T. *Tetrahedron Asymmetry*, **1991**, *2*, 635-638.
8. Jansen, J. F. G. A.; Feringa, B. L. *J. Org. Chem.* **1990**, *55*, 4168-4172.
9. Kobayashi, S.; Shiina, J.; Izumi, J.; Mukayama, T. *Chem. Lett.* **1992**, 373-376.
10. Chelucci, G. *Gazz. Chim. Ital.* **1992**, *122*, 89-98.
11. Aratani, T.; Yoneyoshi, Y.; Nagase, S. *Tetrahedron Lett.*. **1977**, 2599-2602.
12. Aratani, T. *Pure and Appl. Chem.* **1985**, *57*, 1839-1844.
13. Bolm, C.; Schlingloff, G.; Harms, K. *Chem. Ber.* **1992**, *125*, 1191-1203.
14. Bolm, C.; Ewald, M.; Felder, M. *Chem. Ber.* **1992**, *125*, 1205-1215.
15. Čudić, P.; Klaić, B.; Raza, Z.; Šepac, D.; Šunjić, V. *Tetrahedron*, **1991**, *47*, 5295-5308.
16. Šunjić, V.; Raza, Z.; Šepac, D.; Klaić, B.; Marčec, R. Euchem Conference, "*Nitrogen Ligands in Organometallic Chemistry and Homogeneous Catalysis*", Alghero (Italy), 10-15. 05. **1992**, Book of Abstr., OC 17.
17. Weiss, M. J.; Hauser, C. R. *J. Am. Chem. Soc.* **1949**, *71*, 2023-2026.
18. Baroli, G; Cimarelli, C.; Palmier, G.; Bosco, M.; Dalpoizo, R. *Synthesis*, **1990**, 895-897.
19. Šepac, D. *M. Sc. Thesis*, University of Zagreb, **1993**.
20. Greenhill, J.V.; Loghmani–Khouzani, H.; Maitland, D. J. *J. Chem. Soc. Perkin Trans. I*, **1991**, 2831-2840.
21. Wingarten, H.; Chupp, J. P.; White, W. A. *J. Org. Chem.* **1967**, *32*, 3246-3249.
22. Armesto, D.; Horspool, W. M.; Apoita, M.; Gallego, M. G.; Ramos, A. *Synthesis*, **1989**, 448-451.
23. Hunter, J.; Nelson, J.; Harding, C.; McCann, M.; McKee, V. *J. Chem. Soc., Chem. Commun.* **1990**, 1148-1151.
24. Fryzik, M. D.; Bosnich, B. *J. Amer. Chem. Soc.* **1977**, *99*, 6262-6267.

25. Tulchinsky, M. L.; Demina, L. I.; Lindeman, S. V.; Tsivadze, A.Yu.; Struchkov, Yu. T. *J. Chem. Soc., Chem. Commun.* **1990,** 785–786.
26. Brunner, H.; Riepl, G.; Bernal, I.; Ries, W. *Inorg. Chim. Acta,* **1986,** *112*, 65-70.
27. Crabbe, P. *Chem. Ind.* **1969**, 917-918.
28. Lowenthal, R. E.; Abiko, A.; Masamune, S. *Tetrahedron Lett.* **1990,** *31*, 6005–6008.
29. Evans, D. E.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M. *J. Am. Chem. Soc.* **1991,** *113*, 726–728.
30. Corrected data given in Ziessow, D. *On-line Rechner in der Chemie*, Walter de Gruyter, Berlin, **1973**; p. 345.
31. Anschutz, R.; Berns, W. *Chem. Ber.* **1987**, *20*, 1392.
32. Frenz, A. B. *The Enraf–Nonius CAD4–SDP*. In *Computing in Crystallography*; Schenk, H.; Olthof–Hazenkamp, R.; Van Koningveld, H.; Bassi, G. C., Eds.; University Press, Delft, Holland, **1978**; pp. 64–71.
33. Sheldrick, G. M. SHELX86. In *Crystallographic Computing*, 3.; Sheldrick, G.M.; Krueger, C.; Goddard, R. Eds.; Oxford Univeresity Press, Oxford, **1985**.
34. *International Tables for X–ray Crystallography*, Vol. IV; Ibers, J. A.; Hamilton, W. C. Eds.; Kynoch Press, Birmingham, **1973**.
35. Sheldrick, G. M. SHELX77. In *Program for structure determination*, University of Cambridge, Cambridge, **1983**.
36. Spek, A. L. The EUCLID Package. In *Computational Crystallography*, Sayre, D. Ed.; Oxford, Clarendon Press, **1982**; p. 528.
37. Johnson, C. K. ORTEPII. In *Report ORNL–5138*, Oak Ridge National Laboratory, Tennessee, USA, **1976**.