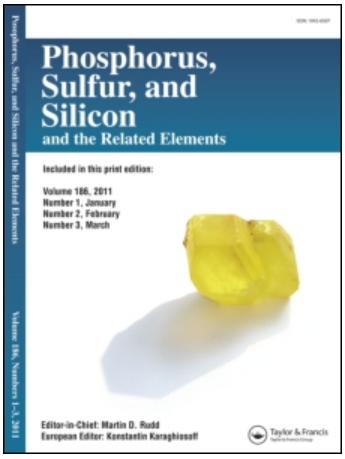

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PHOSPHINE- AND PHOSPHITE-SUBSTITUTED 3,3'-BI-INDOLIZINES- NEW ATROPISOMERIC LIGANDS

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Communication
PHOSPHINE- AND PHOSPHITE-SUBSTITUTED 3,3′-BI-INDOLIZINES- NEW ATROPISOMERIC LIGANDS

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For the first time enantiomerically pure phosphine- or phosphite-substituted 1,1′-alkyl-3,3′-bi-indolizines were obtained. In situ prepared rhodium complexes of these compounds were tested in hydroformylation of styrene and methylstyrene.

Keywords: bi-indolizines; bisphosphine ligands; bisphosphite ligands; hydroformylation

Chiral ligands with C_2-symmetry have become an important tool for developing enantioselective syntheses catalysed by transition metals. One of the most successful ligands of this type proved to be binaphthyl derivatives. [1-5] But also biheteroaryls, such as bithienyls [6] and biindolyls [7] have been examined for their use in asymmetric synthesis.

As our work is engaged in the bi-indolizine system, we also tried to prepare biindolizine ligands. Recently we reported on the lipase-catalysed resolution of the diol **1** [8] and its chlorination to **3**. [9] Now, we wish to present the reaction of these chiral bi-indolizine derivatives to give bisphosphites **2a,b** and bisphosphines **4a,b** and **5**.

The bisphosphites **2a,b** were obtained by reaction of the diols **1a,b** with chlorophosphite prepared from enantiomerically pure (*S*)-binaphthol in the presence of triethylamine (Scheme 1).

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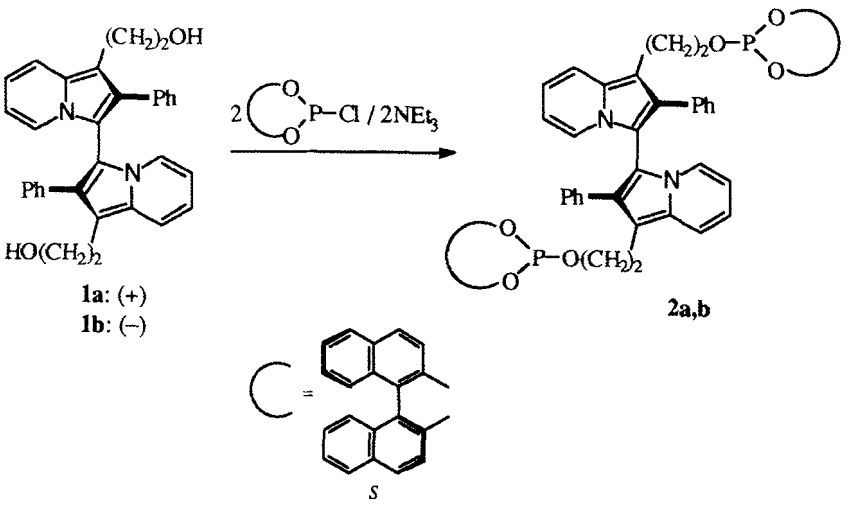


1a: (+)
1b: (–)

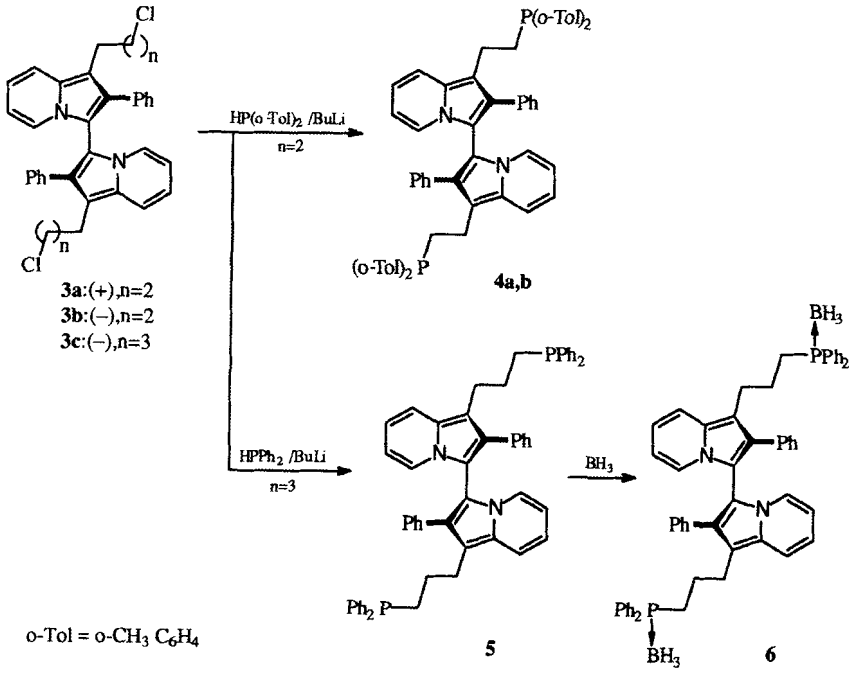
2a,b

S

The phosphine-substituted bi-indolizines **4a,b** were obtained by reaction of the dichlorides **3a,b** (n = 2) with lithium di-o-tolylphosphide. In the case of the dichloride **3** (n = 3) we only used the (−)-enantiomer **3c** for the introduction of the phosphine groups, because the resolution of the racemic starting diol gave the (−)-enantiomer with >99% ee, but the (+)-enantiomer only with 34% ee. [8] Therefore, only (−)-**3c** was converted into the bisphosphine **5** by reaction with lithium diphenylphosphide (Scheme 2). For analytical purposes the stable phosphine-borane **6** was synthesized. An attempt to determine the absolute configuration of one of the bi-indolizine derivatives by X-ray analysis failed because the crystals obtained were not suitable. Hence, compounds **2a,b**; **4a,b** and **5** were characterised by their optical rotation value.

The capability of the new chiral ligands for enantioselective synthesis was tested in the rhodium catalysed hydroformylation of styrene and 2-methylstyrene (Scheme 3). The catalytic complex was prepared *in situ* (18 mL toluene, $Rh(CO)_2acac$:ligand 1:4). In contrast to the known rhodium complexes of BINAP and similar phosphines a formation of a basket with rhodium in the middle of the handle and above the bi-indolizine plane would be imagined.

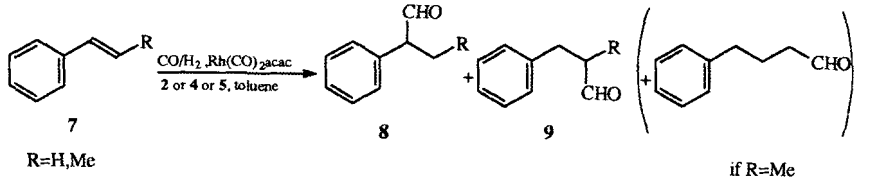
The branched aldehydes **8** (R=H,Me) and **9** (R=Me) were obtained with good regioselectivity (81 to 94% branched aldehyde) but the enantiomeric excess of the formed 2-phenyl-propanal **8** (R=H) (between 2 and 6 %) or 2-phenyl-butanal **8** (R=Me) and 2-methyl-3-phenylpropanal **9** (R=Me) (between 4 and 15%, depending on the ligand) was poor.



In future efforts to achieve better results in enantioselectivity will concentrate on checking further catalytic reactions.

EXPERIMENTAL

All reactions and operations were carried out under argon atmosphere using oxygen-free dry solvents. NMR spectra were recorded on Bruker MSL 400 (^{31}P NMR, $CHCl_3$), Varian Gemini 300 (^{13}C, $CDCl_3$), and Bruker WP200SY (^{1}H, $CDCl_3$), respectively. The chemical shifts are given in ppm; the coupling constant J in Hz. Mass spectra were recorded on HP 5985 B Fisons-Instruments



VG AutoSpac. Optical rotations were measured on a Perkin-Elmer 241 polarimeter, and are given in units of 10^{-1} deg cm^2 g^{-1}. Satisfactory microanalyses of products **2a,b**; **4a,b** and **6** were obtained.

3,3'-Bis[1-(3-(dinaphtho[2,1-d;1',2'-f)1,3-dioxa-2-phosphepinyl)oxyethyl)-2-phenylindo lizine] **2a,b**: 0.5 mmol of the diol **1** and 1.1 mmol triethylamine were dissolved in 30 mL of toluene. To this stirred mixture a solution of 1 mmol *(S)*-2-chloro-dinaphtho[2,1-d;1',2'-f)1,3-dioxa-2-phosphepine in 10 mL toluene was added dropwise. Stirring was continued overnight, then the precipitate was filtered off and the solvent was evaporated. The yellow residue was purified by column chromatography (acetone/hexane 1:4).

2a (from **1a**): $C_{72}H_{50}N_2O_6P_2$ (1101.2); 50% yield; yellow solid; mp 189°C,dec.; $[\alpha]_D^{20}$ = +561.8 (c = 1.0; toluene); ee > 99%; ^{1}H-NMR: 3.10(t, 4H, CH_2), 3.85, 3.98(2dt,4 H,CH_2O), 6.27(t,2H, $CH_{indoliz}$), 6.54(dd,2H, $CH_{indoliz}$), 6.73(dd,4H, $CH_{indoliz}$),6.94-7.45, 7.76-7.94(m, 34H, CH_{phenyl}); ^{13}C-NMR [10]: 26.4(CH_2); 65.6(OCH_2): ^{31}P-NMR:137.5ppm; MS(LSIMS): m/z 1100 (M^+). **2b** (from **1b**):55% yield; yellow solid; mp 193-194°C,dec.; $[\alpha]_D^{20}$ = +610.82 (c = 1.0; toluene); ee 90%; ^{1}H-NMR: 3.12(t,4H,CH_2), 3.86,4.00(2dt,4 H,CH_2O), 6.27(t,2H, $CH_{indoliz}$) 6.53(dd,2H, $CH_{indoliz}$), 6.79(dd,4H, $CH_{indoliz}$), 7.01-7.45, 7.74-7.96(m, 34H, CH_{phenyl}); ^{13}C-NMR [10]: 26.4(CH_2);65.5 (OCH_2), ^{31}P-NMR:139.0.

3,3'-Bis[1-(3-di-o-tolyl-phosphinoethyl)-2-phenylindolizine] **4a,b**. A solution of 2 mmol lithium di-o-tolylphosphide in 10 mL THF was added to 1 mmol of the chloro-substituted bisindolizine **3** dissolved in 20 ml THF, at 0°C. The mixture was stirred for 2 hours at this temperature and then allowed to stand overnight at room temperature. The solvent was removed in vacuo, and the residue was chromatographed on a short column (acetone/hexane 1:5).

4a (from **3a**): $C_{60}H_{54}N_2P_2$(865.04); 46% yield; yellow syrup; $[\alpha]_D^{20}$ = −24.6(c = 0.83;toluene); ee > 87%; ^{1}H-NMR:2.12, 2.84(2m, 2 × 4H, CH_2), 2.50(s, 12H, CH_3),6.39-7.27(m, 34H, CH_{arom}); ^{13}C-NMR [10]:20.6 (CH_2, J = 50.2), 20.7 (CH_3, J = 21.2),28.3(CH_2, J = 13.7); ^{31}P-NMR: −37.5; MS: 865 (M^+ + 1)(apci). **4b** (from **3b**): $[\alpha]_D^{20}$ = +43.7 (c = 1.0; toluene); ee > 90%.

3,3'-Bis[1-(3-diphenyl-phosphinopropyl)-2-phenylindolizine] **5**. **5** was prepared from **3c** with lithium diphenylphosphide according to the same procedure as described above for **4**.

67% yield; $[\alpha]_D^{20}$ = +7.63(c = 1.77; toluene); ee 98%; ^{31}P-NMR: −17.3;

3,3'-Bis[1-(3-(diphenyl-boranyl-phosphino)-propyl)-2-phenylindolizine] **6**. 1 mmol of **5** was dissoluted in 5 ml THF and 4ml of 1m borane-tetrahydrofuran solution in THF was added. The mixture was stirred for two days, then the solvent was evaporated and the viscous residue was extracted four times with hot

diisopropyl ether. After cooling yellow crystals precipitated which were collected on a glass filter.

$C_{58}H_{56}B_2N_2P_2$ (864.7);46% yield, mp 87-89°C; ^{1}H-NMR:1.52(dt,4H,CH_2), 2.14(m,4H,CH_2), 2.88(t,4H,CH_2), 6.33-7.53(m,38H,CH_{arom}); ^{13}C-NMR [10]: 23.21(J = 37.8), 3.6(J = 127.7), 24.3; ^{31}P-NMR: 16.0; MS: 865 (M^+ + 1) (LSIMS);

Acknowledgements

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