

## Synthesis of Novel Chiral Ruthenium Complexes of 2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl and their Use as Asymmetric Catalysts

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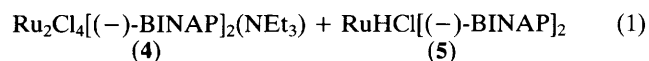
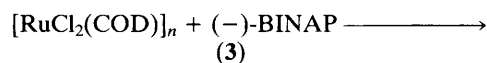
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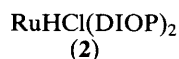
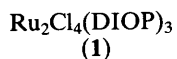
Reactions of  $[\text{RuCl}_2(\text{COD})]_n$  (COD=cyclo-octa-1,5-diene) with the chiral bidentate phosphine ligands 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl, BINAP, and 2,2'-bis(di-*p*-tolylphosphino)-1,1'-binaphthyl, *p*-tolyl-BINAP, give new chiral ruthenium(II) complexes,  $\text{Ru}_2\text{Cl}_4(\text{BINAP})_2(\text{NEt}_3)$  and  $\text{Ru}_2\text{Cl}_4(p\text{-tolyl-BINAP})_2(\text{NEt}_3)$  respectively, which serve as excellent catalysts for asymmetric hydrogenation of alkenes and some cyclic anhydrides.

In the last decade a number of rhodium complexes coordinated with chiral bidentate phosphine ligands have been prepared, and employed as catalysts for asymmetric reactions to give products with enantiomeric excesses as high as 99%.<sup>1</sup> In contrast, little is known with regard to the asymmetric reactions catalysed by chiral ruthenium complexes in spite of the well documented catalytic activity of ruthenium catalysts.<sup>2</sup> This is possibly because only a limited number of chiral bidentate phosphine ruthenium complexes, such as  $\text{Ru}_2\text{Cl}_4(\text{DIOP})_3$  (1),<sup>2a</sup>  $\text{RuHCl}(\text{DIOP})_2$  (2),<sup>2b</sup> [DIOP = 2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane] and some cyclopentadienyl complexes<sup>3</sup> have been available. This communication reports a convenient synthetic method for new ruthenium complexes having the chiral bidentate phosphine ligands, BINAP, 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl, or *p*-tolyl-BINAP, 2,2'-bis(di-*p*-tolylphosphino)-1,1'-binaphthyl, and their uses in catalytic asymmetric reactions.

A conventional method, the ligand exchange reaction of  $\text{RuCl}_2(\text{PPh}_3)_3$  with a chiral bidentate phosphine ligand, could not be used for the preparation of the bidentate phosphine complexes except for the preparation of the DIOP complex,  $\text{Ru}_2\text{Cl}_4(\text{DIOP})_3$  (1). We found that  $[\text{RuCl}_2(\text{COD})]_n$  (3)<sup>4</sup> (COD = cyclo-octa-1,5-diene) was an excellent starting material for the rapid synthesis of a wide range of ruthenium chiral phosphine complexes. The reaction of (3) with (–)-BINAP (1 : 1.2) in the presence of triethylamine under toluene reflux conditions affords an orange-red complex (4) (85% yield), and a small amount of a yellow complex (5) (equation 1).



The complex (4) can be recrystallized from  $\text{CH}_2\text{Cl}_2$ -diethyl ether to give an orange microcrystalline product. N.m.r. (<sup>1</sup>H, <sup>31</sup>P, and <sup>13</sup>C) spectra as well as the elemental analysis data of

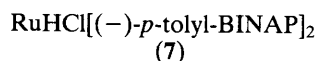
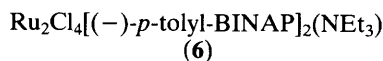


**Table 1.** Hydrogenation of  $\alpha$ -acylaminoacrylic acids using Rh- and Ru-BINAP complexes.<sup>a</sup>

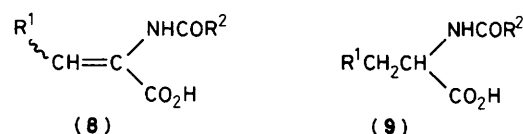
Substrate	Catalyst	Product	o.p./%	Configuration
Z-(8a)	Rh-( <i>-</i> )-BINAP <sup>b</sup> (4)	(9a)	84 86	( <i>R</i> ) ( <i>S</i> )
Z-(8b)	Rh-( <i>-</i> )-BINAP <sup>b</sup> (4)	(9b)	96—100 92	( <i>R</i> ) ( <i>S</i> )
(8c)	Rh-( <i>-</i> )-BINAP <sup>b</sup> (4)	(9c)	67 76	( <i>R</i> ) ( <i>S</i> )
E-(8b)	Rh-( <i>-</i> )-BINAP <sup>b</sup> (4)	(9b)	87 65	( <i>S</i> ) ( <i>S</i> )

<sup>a</sup> Hydrogenation reaction was carried out with [substrate] = 0.08 M and [Ru] = 0.001 M in the presence of triethylamine under 2 atm of hydrogen at 35 °C in ethanol-tetrahydrofuran (1:1) for 24 h. <sup>b</sup> [Rh{(*-*)-BINAP}ClO<sub>4</sub>] or [Rh{(*-*)-BINAP}(MeOH)<sub>2</sub>]ClO<sub>4</sub>, A. Miyashita, H. Takaya, T. Souchi, and R. Noyori, *Tetrahedron*, 1984, **40**, 1245.

the complex (4) are consistent with the formulation.<sup>†</sup> In the <sup>1</sup>H n.m.r. spectrum of (4), the methyl and methylene protons of triethylamine appear, respectively, at  $\delta$  1.3 as a triplet and at  $\delta$  3.1 and 3.3 as two complex multiplets. The latter becomes a characteristic AB quartet by homonuclear decoupling of the methyl protons, indicating that the triethylamine co-ordinates to the ruthenium metal which has a chiral environment that makes the enantiotopic methylene protons inequivalent. The complex (5) was also prepared almost quantitatively by the reaction of complex (3) with (*-*)-BINAP (1:2) in the presence of triethylamine under ethanol reflux conditions. The complex (5) was determined to have a monohydride structure, RuHCl[(*-*)-BINAP]<sub>2</sub>, on the basis of <sup>1</sup>H n.m.r. and i.r. spectral analyses as well as by analogy with the known DIOP complex (2). Similarly, (*-*)-*p*-tolyl-BINAP gave Ru<sub>2</sub>Cl<sub>4</sub>[(*-*)-*p*-tolyl-BINAP]<sub>2</sub>(NEt<sub>3</sub>) (6) and RuHCl[(*-*)-*p*-tolyl-BINAP]<sub>2</sub> (7). This synthetic method should be widely applicable to other chiral bidentate phosphine ligands such as DIOP, BPPM, BPPFA, and chiraphos.<sup>‡5a</sup>



The complexes (4) or (6) should provide a co-ordinatively unsaturated ruthenium species, RuCl<sub>2</sub>L<sub>2</sub> (L = phosphine ligand), which is a rare structure for Ru<sup>II</sup> phosphine complexes<sup>6</sup> and can be expected to serve as an asymmetric catalyst for hydrogenation of alkenes. The complex (4) exhibits excellent catalytic activity and a high stereoselectivity for the



a; R<sup>1</sup> = Ph, R<sup>2</sup> = Me  
b; R<sup>1</sup> = R<sup>2</sup> = Ph  
c; R<sup>1</sup> = H, R<sup>2</sup> = Me

hydrogenation of alkenes. As can be seen in Table 1, the asymmetric hydrogenation of  $\alpha$ -acylaminoacrylic acids (8) using the complex (4) as the catalyst in the presence of triethylamine under relatively mild conditions provided almost quantitatively *N*-acylamino acids (9) with the (*S*) isomer in excess. An optical yield of 92% has been achieved in the hydrogenation of *Z*- $\alpha$ -benzoylaminoacinnamic acid *Z*-(8b). The complex (5) also exhibits high stereoselectivity in the absence of triethylamine. Interestingly, the chirality induced in the products by the use of (4) is opposite to that obtained by a Rh-(*-*)-BINAP catalyst in similar solvent systems. Based on these results, as well as the established mechanism for the hydrogenation of alkenes catalysed by ruthenium complexes,<sup>2c</sup> the configuration determining step of the system catalysed by (4) seems to be *via* a hydride species,<sup>5</sup> in which the chiral induction of the product should result from the preferential co-ordination of one face of the alkene, rather than an 'unsaturated route'.<sup>2c</sup> It should be noted that under the same conditions the DIOP complex (1) exhibited no catalytic activity for this hydrogenation, presumably because of the stereochemical problems as mentioned by James and co-workers.<sup>2b</sup>

The complex (4) was also found to catalyse the asymmetric hydrogenation of prochiral or meso cyclic anhydrides to give the corresponding chiral lactones.<sup>2c</sup> The complex (4) was more effective than (1) for the hydrogenation of the prochiral glutaric anhydrides. The hydrogenated products of 3-methyl- and 3-phenyl-glutaric anhydrides, (3*R*)-3-methyl- and (3*R*)-3-phenyl- $\delta$ -valerolactone, have 39% and 33% optical purity (o.p.), respectively.

The enantioselectivity of this Ru complex (4) for hydrogenation of alkenes is comparable to the Rh-BINAP system.<sup>1b</sup> To our knowledge this is the first system to attain such a high stereoselectivity in the asymmetric hydrogenation of alkenes catalysed by chiral ruthenium complexes. This synthetic reaction should provide a general method for preparing ruthenium complexes of known chiral bidentate phosphine

<sup>†</sup> All new complexes obtained here gave satisfactory elemental analyses. (4) <sup>31</sup>P{<sup>1</sup>H} N.m.r., 62 [d, <sup>2</sup>J(PP) 35 Hz], 57 p.p.m. [d, <sup>2</sup>J(PP) 35 Hz] (downfield is positive from external PPh<sub>3</sub>); (5) <sup>1</sup>H n.m.r.,  $\delta$  -16.2 (septet). Molecular conductivity, the limited solubility, and the i.r. spectrum suggest that complex (4) has a dimeric structure with bridging Cl ligands as in the complex [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (see ref. 6).

<sup>‡</sup> In toluene DIOP, (2*S*,4*S*)-*N*-t-butoxycarbonyl-2-[(diphenylphosphino)methyl]-4-(diphenylphosphino)pyrrolidine (BPPM), (*S*)-*N*,*N*-dimethyl-1-[(*R*)-1',2-bis(diphenylphosphino)ferrocenyl]ethylamine (BPPFA), and (*S*,*S*)-2,3-bis(diphenylphosphino)butane (chiraphos) provide Ru<sub>2</sub>Cl<sub>4</sub>(DIOP)<sub>3</sub>, RuCl<sub>2</sub>(BPPM), RuCl<sub>2</sub>(BPPFA), and RuCl<sub>2</sub>(chiraphos)<sub>2</sub> respectively while in ethanol, BPPM gives RuH<sub>2</sub>(BPPM)<sub>2</sub> (unpublished results).

complexes leading to development of asymmetric reactions catalysed by these ruthenium complexes.

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