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

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Reactions of $[RuCl_2(COD)]_n$ (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, $Ru_2Cl_4(BINAP)_2(NEt_3)$ and $Ru_2Cl_4(p\text{-tolyl-BINAP})_2(NEt_3)$ respectively, which serve as excellent catalysts for asymmetric hydrogenation of alkenes and some cyclic anhydrides.

In the last decade a number of rhodium complexes co-ordinated 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%.[1] 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.[2] This is possibly because only a limited number of chiral bidentate phosphine ruthenium complexes, such as Ru_2Cl_4-$(DIOP)_3$ (**1**),[2a] $RuHCl(DIOP)_2$ (**2**),[2b] [DIOP = 2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane] and some cyclopentadienyl complexes[3] 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.

$Ru_2Cl_4(DIOP)_3$ (**1**) $\qquad$ $RuHCl(DIOP)_2$ (**2**)

A conventional method, the ligand exchange reaction of $RuCl_2(PPh_3)_3$ 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, $Ru_2Cl_4(DIOP)_3$ (**1**). We found that $[RuCl_2(COD)]_n$ (**3**)[4] (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).

$$[RuCl_2(COD)]_n + (-)\text{-BINAP} \xrightarrow[(3)]{} Ru_2Cl_4[(-)\text{-BINAP}]_2(NEt_3) + RuHCl[(-)\text{-BINAP}]_2 \quad (1)$$
(**4**) (**5**)

The complex (**4**) can be recrystallized from CH_2Cl_2–diethyl ether to give an orange microcrystalline product. N.m.r. (^1H, ^{31}P, and ^{13}C) spectra as well as the elemental analysis data of

Table 1. Hydrogenation of α-acylaminoacrylic acids using Rh- and Ru-BINAP complexes.[a]

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

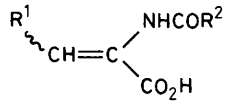
[a] Hydrogenation reaction was carried out with [substrate] = 0.08 M and [Ru] = 0.001 M in the presence of triethylamine under 2 atm of hydrogen at 35 °C in ethanol–tetrahydrofuran (1:1) for 24 h. [b] $[Rh\{(-)\text{-BINAP}\}]ClO_4$ or $[Rh\{(-)\text{-BINAP}\}(MeOH)_2]ClO_4$, A. Miyashita, H. Takaya, T. Souchi, and R. Noyori, *Tetrahedron*, 1984, **40**, 1245.

the complex (**4**) are consistent with the formulation.† In the ^1H n.m.r. spectrum of (**4**), the methyl and methylene protons of triethylamine appear, respectively, at δ 1.3 as a triplet and at δ 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, $RuHCl[(-)\text{-BINAP}]_2$, on the basis of ^1H n.m.r. and i.r. spectral analyses as well as by analogy with the known DIOP complex (**2**). Similarly, (−)-*p*-tolyl-BINAP gave $Ru_2Cl_4[(-)\text{-}p\text{-tolyl-BINAP}]_2(NEt_3)$ (**6**) and $RuHCl[(-)\text{-}p\text{-tolyl-BINAP}]_2$ (**7**). This synthetic method should be widely applicable to other chiral bidentate phosphine ligands such as DIOP, BPPM, BPPFA, and chiraphos.‡[5a]

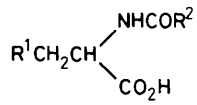
$Ru_2Cl_4[(-)\text{-}p\text{-tolyl-BINAP}]_2(NEt_3)$
(**6**)

$RuHCl[(-)\text{-}p\text{-tolyl-BINAP}]_2$
(**7**)

The complexes (**4**) or (**6**) should provide a co-ordinatively unsaturated ruthenium species, $RuCl_2L_2$ (L = phosphine ligand), which is a rare structure for Ru^{II} phosphine complexes[6] 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 hydrogenation of alkenes. As can be seen in Table 1, the asymmetric hydrogenation of α-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*-α-benzoylaminocinnamic 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,[2c] the configuration determining step of the system catalysed by (**4**) seems to be *via* a hydride species,[5] 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'.[2c] 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.[2b]



(**8**)



(**9**)

a; R^1 = Ph, R^2 = Me
b; R^1 = R^2 = Ph
c; R^1 = H, R^2 = Me

The complex (**4**) was also found to catalyse the asymmetric hydrogenation of prochiral or meso cyclic anhydrides to give the corresponding chiral lactones.[2e] 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-δ-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.[1b] 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

† All new complexes obtained here gave satisfactory elemental analyses. (**4**) $^{31}P\{^1H\}$ N.m.r., 62 [d, ^2J(PP) 35 Hz], 57 p.p.m. [d, ^2J(PP) 35 Hz] (downfield is positive from external PPh_3); (**5**) ^1H n.m.r., δ −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 $[RuCl_2(PPh_3)_2]_2$ (see ref. 6).

‡ 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-bisdiphenylphosphinobutane (chiraphos) provide $Ru_2Cl_4(DIOP)_3$, $RuCl_2(BPPM)$, $RuCl_2(BPPFA)$, and $RuCl_2(chiraphos)_2$ respectively while in ethanol, BPPM gives $RuH_2(BPPM)_2$ (unpublished results).

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

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