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Optically active pheniramine by enantioselective hydrogenation of unsaturated amines, esters and acids using Ru(II)-complexes with BINAP as catalytic precursors

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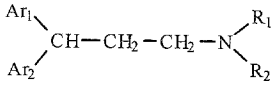
Abstract

Pheniramine (**3a**) was prepared through enantioselective hydrogenation of various precursor compounds catalyzed by Ru(II)/BINAP complexes. In the case of *N,N*-dialkyl-3-phenyl-3-(2-pyridyl)allylamines (**1** and **2**) only the (*Z*)-isomer shows a satisfactory reactivity; moreover the chemoselectivity is affected by the hydrogenolysis of the alkylamino group of the substrate. The enantioselectivity did not exceed 50%. 3-Phenyl-3-(2-pyridyl)acrylic acids (**9** and **10**) and their ethyl esters (**5** and **6**) gave good chemical yields only at reaction temperature $\geqslant 50°C$; also in this case poor enantioselectivities (up to 35%) were achieved. © 1997 Elsevier Science B.V.

1. Introduction

Several active principles of important drugs showing antihistaminic, antiallergic, spasmolytic and choleretic activity present the 3,3-diaryl-*N,N*-dialkylpropylamine framework (Fig. 1) [1].

Often Ar_1 is structurally different from Ar_2 so that the molecule has a stereogenic center which gives rise to a couple of enantiomers, that generally display a different therapeutic activity [2,3]. Hence, the need for the development of synthetic strategies leads to the most biologically active enantiomer. Since the enantioselective hydrogenation of various olefinic substrates catalyzed by BINAP–Ru(II) complexes has been



Ar = aromatic or heteroaromatic group

R = alkyl group

Fig. 1. 3,3-diaryl-*N,N*-dialkylpropylamine framework.

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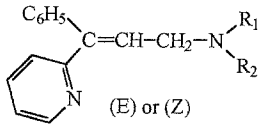


R_1, R_2 = alkyl group

Fig. 2. *N,N*-dialkyl-3-phenyl-3-(2-pyridyl)allylamine.

shown to be one of the most efficient methods for preparing chiral biologically active molecules [4], we want not only to get deeper insight into the stereochemical pathway of the previously reported catalytic reduction of *N,N*-dialkyl-3-phenyl-3-(2-pyridyl)allylamines [5], but also to investigate the same enantioselective process on suitable precursor compounds of *N,N*-dialkyl-3,3-diarylpropylamines. We have chosen *N,N*-dialkyl-3-phenyl-3-(2-pyridyl)allylamine as a model compound (Fig. 2) for our catalysis study.

2. Experimental

2.1. General methods and chemicals

$Ru(OCOCH_3)_2$[(*S*)-BINAP] was prepared according to a literature procedure [6,7]. $[(COD)RuCl_2]_n$, [(*R*)(+)-BINAP-(*p*-cymene)ClRu]Cl, (*S*)-BINAP, 2-benzoylpyridine, trimethylphosphono acetate, trimethylsilyl iodide, tetramethylene sulfone, were purchased from Aldrich. Triprolidine and pheniramine were Sigma products. (*Z*)- and (*E*)-*N,N*-dialkyl-3-phenyl-3-(2-pyridyl)allylamine were prepared by fractional crystallization of the corresponding neutral oxalates from ethanol following a well described procedure [8]. Elemental analyses and ^{1}H-NMR spectral data of the afore mentioned olefinic substrates were consistent with the expected structures.

Optical rotations were measured in a solution prepared using a suitable solvent on a digital polarimeter, Perkin Elmer model 241, using a 1 dm cell. Elemental analyses were performed with an elemental analyzer Perkin Elmer model 240C. ^{1}H NMR (300 MHz) spectra of $CDCl_3$ solutions were recorded using a Varian VXR 300s spectrometer.

The enantiomeric excesses were determined using chiral HPLC methodology. The chromatographic system consisted of a Jasco 887-PU pump and a Jasco Multi 340 UV multi channel detector. The eluates were also monitored by using a Jasco J 710 spectrometer equipped with a micro HPLC cell (8 μl volume), and lenses to focus the light beam in the sample compartment. This detection system allows the absorption and the circular dichroism (CD) signal to be simultaneously detected. A reodyne model 7125 injector with 20 μl loop was used. The chromatographic retentions of the solutes were followed at 265 nm and reported as the capacity factor (k'), where $k' = (t_{analyze} - t_0)/t_0$ ($t_{analyze}$ = retention time of the fraction; t_0 = retention of non retained solute). The enantioselectivity (α), where $\alpha = k'_1/k'_2$, was also calculated, k'_2 and k'_1 are the capacity factors of the second and first eluted enantiomers, respectively.

The chromatographic resolution of compound **7** was obtained with a Chiralcell AD (Daicel 25 × 0.4 cm i.d.) at room temperature. The mobile phase was hexane/2-propanol (90/10, v/v), 0.6 ml/flow. The chromatographic resolution of compound **11** was obtained with a Chiracel OJ (Daicel 25 × 0.4 cm i.d.) at room temperature. The mobile phase was hexane/2-propanol/acetic acid (70/30/0.5, v/v/v), 0.5 ml/min flow.

2.2. Synthesis of (Z)- and (E)-ethyl-3-phenyl-3-(2-pyridyl)acrylate (5 and 6)

Compounds **5** and **6** were prepared as a mixture of (*Z*)- and (*E*)-isomer in 40 to 60 molar ratio following the experimental procedure described in the literature [9]. Sodium metal (0.021 mol, 0.49 g) was added to ethyl alcohol (25 ml) under stirring in an inert atmosphere at 0°C. After sodium dissolution trimethylphosphono acetate (0.022 mol, 3.5 ml) and ethyl alcohol (25 ml) were introduced in the reaction

vessel. The mixture was stirred overnight and 2-benzoylpyridine (16 mmol, 3.0 g) was slowly added at RT. After 3 h reflux the reaction mixture was quenched with ice–water and the organic phase separated, dried (Na_2SO_4) and the solvent was removed. The two geometrical isomers **5** and **6** were separated by subjecting the above mixture to flash-chromatography using petroleum ether/ethylacetate 1:1 as eluant. The analytical data and ^{1}H-NMR spectral data were in agreement with those reported in the literature [9].

2.3. Synthesis of (Z)- and (E)-3-phenyl-3-(2-pyridyl)acrylic acids (9 and 10)

Compounds **9** and **10** were obtained by a two-steps hydrolysis of the corresponding ethyl esters under neutral condition by conversion of **5** and **6** into the corresponding trimethylsilylesters by treatment with trimethylsilyl iodide in sulpholane followed by reaction with water [10,11].

Compound **9**: m.p. 168–172°C, ^{1}H-NMR (DMSO-d_6) δ 8.68 (d, 1H, J = 5.2) 7.59 (dt, 1H, J_1 = 7.5, J_2 = 1.8), 7.55–6.95 (m, 7H, aromatics), 6.43 (s, 1H).

Compound **10**: m.p. 170–173°C, ^{1}H-NMR (DMSO-d_6) δ 8.65 (d, 1H, J = 5.2) 7.79 (dt, 1H, J_1 = 7.5, J_2 = 1.8), 7.36–7.22 (m, 7H, aromatics), 6.43 (s, 1H).

2.4. General procedure for enantioselective hydrogenation

The catalytic complex was placed in a stainless steel 150 ml pressure reactor. The reactor was evacuated to 0.01 mm Hg and a solution of the substrate in the appropriate solvent was introduced by suction. The vessel was charged at the desired pressure with H_2 and heated and stirred for the required time. After gas-release the reaction solution was filtered through a short-path column (5 cm) containing silica, to remove the catalyst, and the solvent evaporated. The hydrogenation product was purified by flash chromatography and the pure hydrogenated products were characterized by the usual analytical and spectroscopical determination.

Compound **3a**: The physical constants, ^{1}H-NMR and elemental analysis data were consistent with those obtained from a commercial sample.

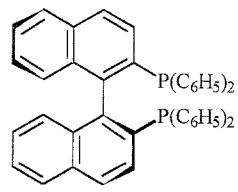
Compound **7**: The physical constants, ^{1}H-NMR and elemental analysis data were consistent with those reported in the literature [9].

Compound **11**: m.p. 160–162°C, ^{1}H-NMR (DMSO-d_6) δ 8.60 (d, 1H, J = 4.5); 7.69 (t, 1H, J = 7.2); 7.37–7.09 (m, 7H, aromatics); 4.60 (dd, 1H, J_1 = 8.2, J_2 = 3.2); 3.39 (dd, 1H, J_1 = 16.4, J_2 = 8.2); 3.07 (dd, 1H, J_1 = 16.3, J_2 = 3.2).

3. Results and discussion

3.1. Enantioselective catalytic hydrogenation of N,N-dialkyl-3-aryl-3-(2-pyridyl)allylamines (1 or 2)

It is known that the enantioselective hydrogenation of some classes of olefins containing various functionalities catalyzed by Ru(II)–diphosphine complexes may be considerably dependent on the stereochemistry of the starting olefin [12,13]. In fact, in the catalytic reduction of an (*E*)- and (*Z*)-mixture of *N,N*-dimethyl-3-phenyl-3-(2-pyridyl)allylamines **1a** and **2a** in the presence of $Ru(OCOCH_3)_2$[(*S*)-BINAP] (**I**) (Fig. 3) we observed that the (*Z*)-isomer **1a** was considerably more active than the (*E*)-isomer (Scheme 1) [5].



(S)-BINAP

Fig. 3. (*S*)-BINAP.

Thus the above (*E*)- and (*Z*)-mixture of **1a** and **2a** was separated by fractional crystallization of the corresponding oxalic acid salts [8] and the single isomers subjected to hydrogenation in the presence of complex **I** at 70 atm H_2 and 50°C.

Whereas the (*E*)-allylamine **2a** is only for 20% reduced into pheniramine **3a** after 200 h, the reaction with the (*Z*)-isomer proceeded more rapidly under the same conditions giving 50% of **3a** after 48 h. The chemoselectivity of both reactions did not exceed 60%, due to the simultaneous production of 1-phenyl-1-(2-pyridyl)propane (**4**) deriving from the hydrogenolysis of the carbon–nitrogen bond of **1a** and **2a**, respectively (Scheme 1). This undesired secondary reaction is enhanced considerably by increasing temperature: 20% of hydrogenolysis product **4** at 15°C, 30% at 40°C, 40% at 50°C. The enantiomeric purity of the isolated pheniramine **3a** was 50% and (*R*) was the prevailing configuration [14].

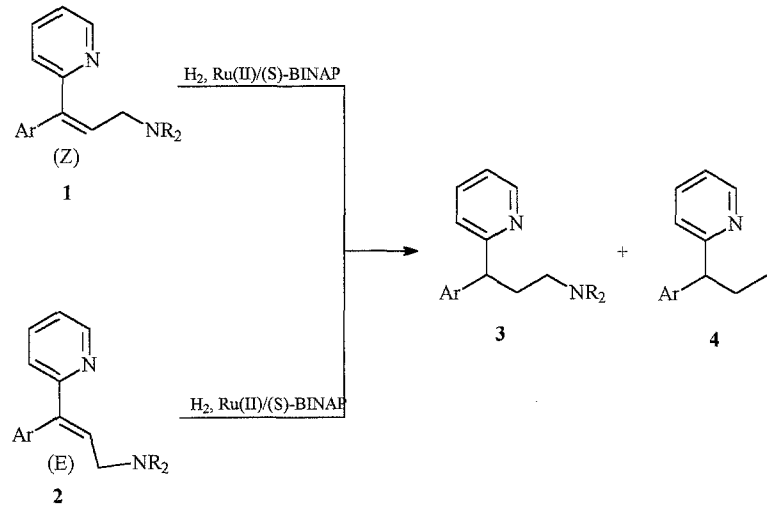
The fact that allylamine **2a** is sluggishly hydrogenated in the presence of the BINAP–Ru(II) complex was confirmed by the reduction of triprolidine (**2b**), a pharmacologically active commercially available compound having only (*E*)-configuration. Only about 10% of **2b** was reduced to **3b** after 96 h at 80 atm H_2 and 100°C, using complex **I** as the catalytic precursor.

3.2. Enantioselective catalytic hydrogenation of ethyl-3-phenyl-3-(2-pyridyl)acrylates (5 and 6)

The rather disappointing outcome of the enantioselective hydrogenation of allylamines **1a** and **1b** asked for a different preparative approach to **3a**: the chosen method, the key step of which consists of the asymmetric reduction of 3,3-diarylacrylic acid esters, is outlined in Scheme 2.

From the optically active hydrogenated ethyl ester **7** pheniramine **3a** is easily obtained by two classical steps (Scheme 2).

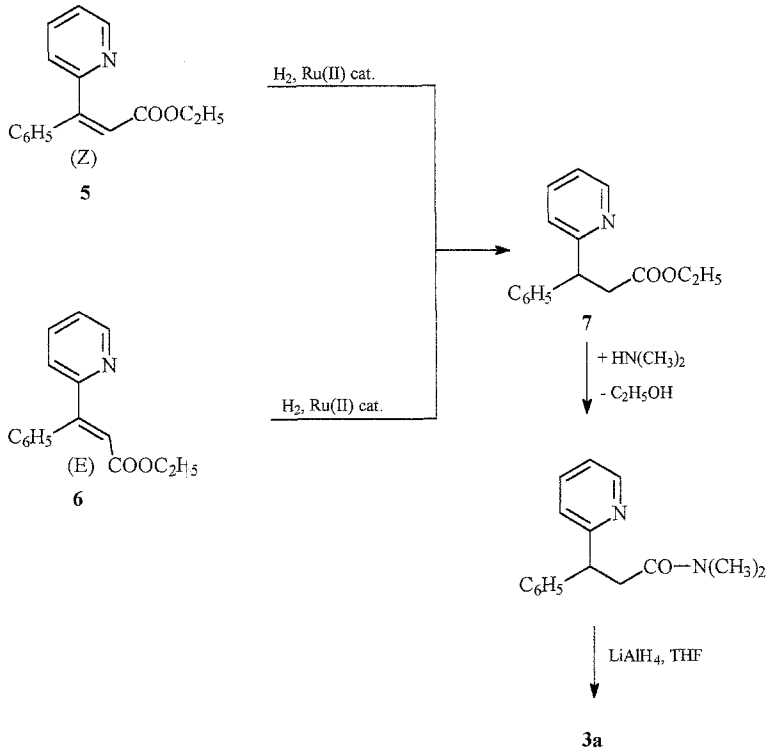
A mixture (60/40) of esters **5** and **6** was obtained in 80% yield from 2-benzoylpyridine by treatment with trimethylphosphonoacetate by



a) Ar = C_6H_5-; R_2N- = $(CH_3)_2N$-

b) Ar = *p*.$CH_3C_6H_4$-; R_2N- =

Scheme 1. Reduction of (*Z*)- and/or (*E*)-*N*,*N*-dialkyl-3-phenyl-3-(2-pyridyl)allylamine in the presence of Ru(II)/BINAP complexes.



Scheme 2. Asymmetric reduction of 3,3-diarylacrylic acid esters.

a Webb's modified Wittig–Horner reaction [9]. The two (*E*)- and (*Z*)-isomers were easily separated by flash-chromatography [9].

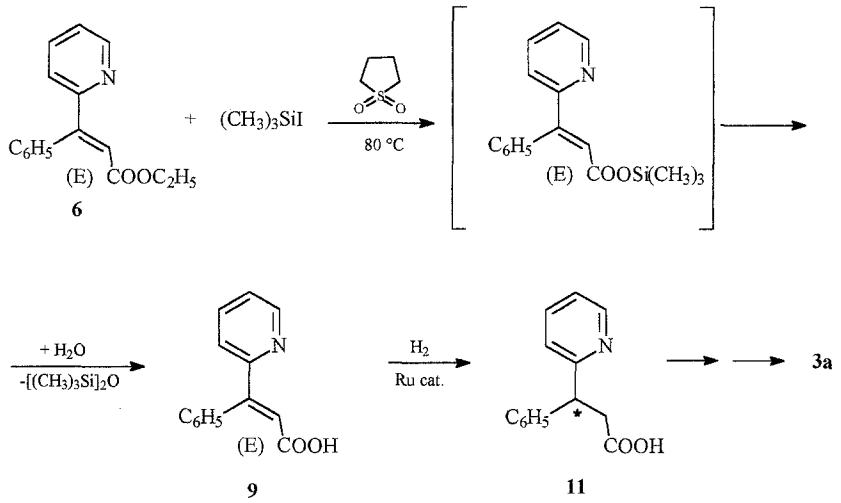
Results and experimental conditions of the hydrogenations of **5** and **6** are reported in Table 1: the data obtained using complex **I** and the commercially available [(*R*)(+)-BINAP-(*p*-cymene)ClRu]Cl (**II**) [15] are compared.

From these data the following comments can be made: (i) both reaction rate and chemoselectivity are satisfactory for all four experiments, thus overcoming the troubles encountered in the hydrogenation of allylamines **1a** and **1b**; (ii) enantiomeric purity of the saturated ester **7** is rather low in all cases; (iii) the catalytic precursor **I** gave the highest optical yield even at 100°C (up to 35% ee); (iv) complex **I** showed to be catalytically more active than complex **II**; (v) both enantioselectivity and prevailing configuration of the reduction product depend on the

Table 1
Enantioselective hydrogenation of the ethyl 3-phenyl-3-(2-pyridyl)acrylates (**5** and **6**)

Substrate	Catalytic precursor	Reaction time (h)	*T* (°C)	Yield [a] (%)	$[\alpha]_D^{25}$	ee (%)
5	$Ru(OCOCH_3)_2$[(*S*)-BINAP]	20	100	98	+55.6	35
6	$Ru(OCOCH_3)_2$[(*S*)-BINAP]	20	100	80	+10.4	6
5	[(*R*)(+)-BINAP-(*p*-cymene)ClRu]Cl	69	50	99	−44.5	28
6	[(*R*)(+)-BINAP-(*p*-cymene)ClRu]Cl	48	50	98	+17.1	11

Other reaction conditions: P_{H_2} = 60 atm, substrate/catalyst = 150:1, solvent: methanol (ca. 0.2 M).
[a] The hydrogenation product was purified by flash-chromatography (silica gel, eluant petroleum ether/ethyl acetate = 1:1).



Scheme 3. Hydrolysis of (*E*)-ethyl-3-phenyl-3-(2-pyridyl)acrylates to (*E*)-3-phenyl-3-(2-pyridyl)acrylic acids and its enantioselective catalytic hydrogenation.

stereochemistry of the substrate: in particular, using complex **II** opposite configuration is achieved for (*E*)- with respect to (*Z*)-isomer.

3.3. Enantioselective catalytic hydrogenation of 3-phenyl-3-(2-pyridyl)acrylic acids (9 and 10)

It is known from the results reported in the recent literature that unsaturated prochiral carboxylic acids give generally very high enantiomeric excesses when hydrogenated in the presence of BINAP–Ru(II) complexes [15–18]; the carboxylic group seems to play a key-role in the formation of an efficient substrate–catalyst adduct [19], which should promote a very high enantioselection.

Therefore, we decided to subject also (*E*)-**9** or (*Z*)-**10** to enantioselective reduction with complex **II** at 50°C and 70 atm. The catalytic precursor **I** showed low activity in the reduction of the unsaturated acids **9** and **10**. These substrates were prepared from the corresponding esters by a two-steps hydrolysis [10,11] under neutral conditions as outlined in Scheme 3, to avoid the tedious separation and purification of the amphoteric compounds **9** and **10**. However, the overall yields of the transformation **5** to **9** and **6** to **10** through the intermediate trimethylsilylesters did not exceed 70% (Scheme 3) [10,11].

The enantioselective hydrogenation on acids **9** and **10** was carried out under the same reaction conditions used for their ethyl esters: the results are reported in Table 2.

We have found that the catalytic activity of complex **II** towards the hydrogenation of unsaturated acids is comparable to that observed in the case of the corresponding ethyl esters. Unfortunately the obtained enantiomeric excesses

Table 2
Hydrogenation of (*E*)- and (*Z*)-3-phenyl-3-(2-pyridyl)acrylic acids (**9** and **10**)

Substrate	Catalytic precursor	Reaction time (h)	*T* (°C)	Yield (%)	$[\alpha]_D^{25}$	ee (%)
9	[(*R*)-BINAP-(*p*-cymene)ClRu]Cl	68	50	100	−18.5	27
10	[(*R*)-BINAP-(*p*-cymene)ClRu]Cl	30	50	77	+6.0	9

Other reaction conditions: P_{H_2} = 60 atm, substrate/catalyst = 75:1, solvent: CH_2Cl_2/methanol = 1:1 (ca. 0.2 M).
[a] The hydrogenation product was purified by flash-chromatography (silica gel, CH_2Cl_2/acetone = 1:1).

of reduction product **11** were unsatisfactory. The substrate having configuration (*E*)- gave rise to the levorotatory enantiomer as in the case of ester (Table 1).

3.4. Determination of enantiomeric excesses (ee) of optically active products by chiral HPLC techniques

The chromatographic resolution of **7** was obtained by HPLC upon a Chiralcel AD column. The method developed was efficient to determine the enantiomeric composition of samples of **7** obtained by catalytic hydrogenation of compound **5** (Table 1). The enantiomeric fraction showing negative CD at 265 nm was evaluated first on the Chiracel AD column.

A HPLC method was developed also for the resolution of **11**. A Chiralcel OJ column was successfully employed for the enantioselective analysis of this compound. Base line resolution was obtained and the enantiomeric excess of the analyzed samples was reliably determined. In Fig. 4 the chromatographic profiles of an enriched sample of **11** are reported, as an example. Both absorption (lower profile) and CD (upper profile) detection were used for monitoring the elutes. An ee of 27% was determined for the analyzed sample of **11** (Table 2). The enantiomeric fraction showing negative CD signal at 265 nm was eluted first on chiralcel OJ in the experimental conditions adopted.

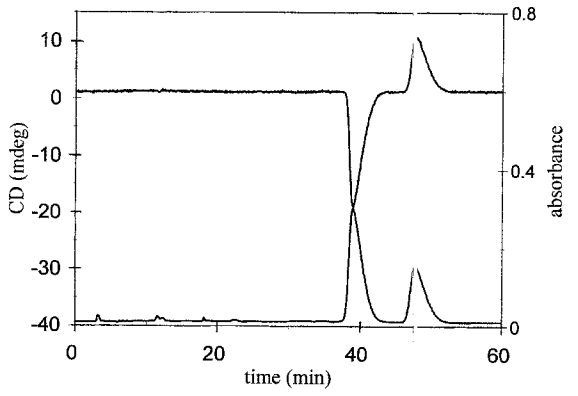
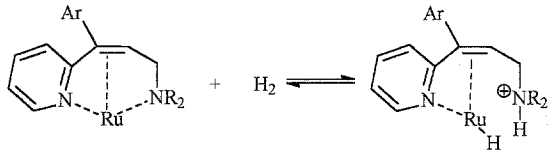


Fig. 4. HPLC resolution of an enriched sample of **11** on a Chiracel OJ column. CD (upper profile) and UV (lower profile) detection at 265 nm.

3.5. Conclusive remarks

The previous paper on the enantioselective hydrogenation of *N*,*N*-dimethyl-3-phenyl-3-(2-pyridyl)allylamine to pheniramine catalyzed by the BINAP–Ru(II) complex left some questions still open [5]. In fact, we were not able to give a reasonable explanation to the unexpected low optical yields found in this catalytic process. One possible rationalization should be that we used as substrate a mixture of (*E*)- and (*Z*)-allylamine; therefore, the low enantiomeric excess could result from the possibility that hydrogenation of (*E*)- or (*Z*)-isomer produces pheniramine with a different enantiomeric purity or even with opposite configuration. The data of the present study confirm that the unsatisfactory optical yield achieved depends only on the intrinsically low enantioselection ability of catalytic precursor **I**. Moreover, it is to point out that the enantiomeric excess of pheniramine arises practically from the enantioselective reduction of the (*Z*)-allylamine. Several factors could be responsible for the low optical yields obtained, not only in the case of prochiral allylamines, but also of prochiral unsaturated esters and acids. In our opinion, the pyridine moiety plays a crucial role in determining both the reactivity of the substrate toward hydrogenation and the enantioselectivity of the catalytic process.

It is hard to individuate steric and/or electronic factors accounting for the fact that (*E*)-allylamine substrates are practically inert to the hydrogenation conditions with BINAP–Ru(II) catalysis. The mechanism of this reaction has not been completely elucidated [20] to date. However, if we assume that the rate determining step consists of the formation of a hydride–ruthenium species [19], the presence of two electron–donor coordinating groups available for the central metal atom only in the (*Z*)-form of allylamine substrate is beneficial for a more



III IV

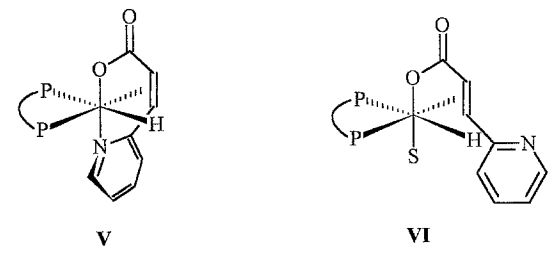
Scheme 4. Formation of a hydride–ruthenium species.

efficient heterolytic cleavage of H_2 molecule, as shown in Scheme 4.

Whereas the dialkylamino ligand, for instance, is involved in the step of H_2 activation, the pyridine ligand might still contribute to the stabilization of the intermediate hydride–ruthenium complex **IV**.

As for the reduction of the unsaturated esters [21] **5** and **6** and acids **9** and **10**, the pyridine system seems to interfere markedly in determining both the reactivity of the substrates and the catalytic pathway of the process. It is known that the olefinic bond activation in this type of substrates occurs through the formation of carboxylate complexes such as [22] shown in Fig. 5.

In the case of the (*Z*)-isomer the pyridine ligand is in a favorable position in complex **V** for coordinating to the metal, giving rise to a steric arrangement quite different from that of complex **VI** involving (*E*)-isomer. Therefore, a prevailing configuration of the hydrogenated product **11** results which is strongly dependent on the stereochemistry of the substrate (see Table 2); an analogous outcome was found in the hydrogenation of tiglic and angelic acid,



V VI

S = solvent

Fig. 5. Activation of the olefinic bond through the formation of carboxylate complexes.

which in the presence of $Ru(OCOCH_3)_2$(BINAP) afforded 2-methylbutanoic acid with opposite configuration [16].

It was emphasized that the success of the enantioselective hydrogenation of the α,β-unsaturated carboxylic acids depends on the carboxylate ability to bind the ruthenium(II) complexes so as to properly arrange and activate the substrate towards hydrogenation [19]. As matter of fact, whereas tiglic acid is smoothly reduced by this catalysts, its methyl ester is completely inert towards the H_2 addition [22]. The fact that both esters **5** and **6** react with H_2 in the presence of complex **I**, even at 100°C, indicates that the pyridine ligands plays an important role in the substrate activation step.

Finally, we must point out that the enantioselection ability of the BINAP–Ru(II) catalysts in the hydrogenation of substrates containing the 2-pyridyl group is surprisingly lower than in the case of structurally related substrates such as (*E*)-cinnamic acid [23]. Whereas in the case of unsaturated esters **5** and **6** and acids **9** and **10** this can be a consequence of the rather high reaction temperature required, which necessarily represses the optical yields, for (*Z*)-allylamine substrates the problem remains still open.

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