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Asymmetric transfer hydrogenation of acrylic acids catalyzed by rhodium(I) complexes of diphosphine ligands

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Abstract

A number of chiral 1,2 1,3 and 1,4-diphosphines have been investigated as ligands for the rhodium catalyzed hydrogen transfer from formic acid and its salts to acrylic substrates. The results reveal a strong dependence of the activity and selectivity of the catalytic system on the size of the chelate ring and rigidity of the ligand, the reaction medium, as well as the nature of the substrate. © 1998 Elsevier Science S.A.

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1. Introduction

The asymmetric hydrogenation of prochiral olefins is one of the main applications of chiral homogeneous transition metal catalysts [1–4]. Catalytic hydrogen transfer reduction, where adequate molecules are used as H-donors instead of molecular hydrogen, has become a rapidly growing area of interest in the past couple of decades [5–7], following a process first observed by Knoevenagel [8] in the beginning of the century. Several types of H-donors can be used, namely, primary and secondary alcohols, alkanes, formic acid, formates, and hydrazine [5,6]. When an olefin is the substrate, formic acid or its salts are very efficient hydrogen donors in the presence of rhodium–phosphine catalysts. These are both active in the hydrogen abstraction from formic acid, as well as in the activation of the olefin [9].

The first enantioselective transfer reductions of acrylic acids using formic acid in the presence of sodium formate were reported by Brunner and Kunz [10]. In that work, enantiomeric excess (ee) up to 50% were achieved with Rh(I) complexes of selected 1,2-diphosphines. However, ee higher than 90% were obtained in a different catalytic system for the asymmetric transfer reduction of itaconic acid (**2**), using Rh(I)/[(2*R*,4*S*)-*N*-*t*-butoxycarbonyl-4-diphenyl-phosphino-2-dipenylphosphinomethylpyrrolidine] (bppm) formic acid/triethylamine as hydrogen source and DMSO as solvent [11,12]. The most striking difference between the two catalytic systems is that the first one operates only at temperatures around 100°C, while the second is active even at room temperature.

We have undertaken a systematic study to compare the activity and enantioselectivity of the two referred catalytic systems, varying the size of the metal-diphosphine chelate, the flexibility of the backbone, the solvent, and the nature of the substrate.

2. Experimental

2.1. Apparatus

NMR spectra were recorded on a Bruker 250 or 300 MHz, using $CDCl_3$ as solvent and TMS as internal standard. For ^{31}P spectra, 85% H_3PO_4 was used as external standard. Gas chromatography was carried out on a Hewlett-Packard 5890A instrument using a capillary column (ultra2-crosslinked 5% PhMeSilicone). Optical rotations of isolated products were measured on an Optical Activity AA-5 electrical polarimeter. Melting points were measured on a Leitz-Wetzler microscope

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with heated plate and values are uncorrected. Mass spectra were recorded under electron impact at 70 eV on a HP-5899. Infrared spectra were recorded on a Phillips PU 9800 FTIR spectrometer. Elemental analyses were carried out on a Fisons EA 1108.

2.2. Synthesis of ligands

The 1,2-bis(diphenylphosphino)ethane (dppe), (2*S*,3*S*)-2,3-bis(diphenylphosphino)butane (chiraphos), 1,4-bis(diphenylphosphino)butane (dppb), 1,3-bis(diphenylphosphino)propane (dppp), (2*R*,4*R*)-2,4-bis(diphenylphosphino)pentane (bdpp), were commercial samples. A sample of [Rh(cod)(deguphos)]BF_4 (cod = 1,5-cyclooctadiene; deguphos = (3*R*,4*R*)-*N*-benzyl-3,4-bis(diphenylphosphino)pyrrolidine) was kindly supplied by Degussa Iberica. 1,2-bis[(diphenylphosphino)methyl]benzene (dppmb) [13] and (2*R*,3*R*)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)-butane (diop) [14] were prepared by similar literature procedures and the characterization was in agreement with the reported data.

2.2.1. (2R,3R)-2,3-dihydroxi-1,4-bis(diphenylphosphino)butane (diop–diol)

The diphosphine diop (2 g, 4.36 mmol) was dissolved in CH_2Cl_2 (50 ml) and 4 ml of 70% aqueous $HClO_4$ were added. After stirring vigorously for 30 min at room temperature, a saturated aqueous solution of $NaHCO_3$ is added until neutralization and the organic phase separated. The aqueous phase is further extracted with dichloromethane and the combined organic extracts dried over $MgSO_4$ and concentrated to give an oil which crystallizes from ethanol as a white solid. (3.05 mmol, 70% yield). M.p. 104–105°C. $[\alpha]_D^{22}$ − 35(*c*1.0, $CHCl_3$). ^{1}H NMR: 2.32 (d, 4H, *J* 6.27); 2.63 (bs, 2H); 3.65–3.71 (m, 2H); 7.22–7.41 (m, 20H). ^{13}C NMR: 33.6 (d, $J_{(CP)}$ 13.0, $\underline{C}H_2$); 72.1 (dd, $J_{(CP)}$ 8.3, 14.4, $\underline{C}H$); 128.3–128.8 (m, C_m, C_p); 132.6 (d, $J_{(CP)}$ 18.5, $\overline{(C}_o)$); 133.0 (d, $J_{(CP)}$ 19.0, C_o); 137.7 (d, $J_{(CP)}$ 11.7, P–$\underline{P}$Ph(C_i)); 138.1 (d, $J_{(CP)}$ 10.7, P–$\underline{P}$Ph (C_i)); ^{31}P NMR: − 22.6. *m*/*z*: 459 (M^+, 1%), 458 (3), 457 (0.6), 381 (26), 273 (100), 255 (18), 185 (57), 183 (57); IR(cm^{-1}, KBr): 3283, 3069, 3048, 1480, 1431, 1082, 1069, 1026, 737, 694. Anal. Calc. $C_{28}H_{28}O_2P_2$: C, 73.35; H, 6.16. Found: C, 73.34; H, 6.30.

2.2.2. (2R,3R)-2,3-dibenzyloxy-1,4-bis(diphenylphosphino)butane (diop–bz)

A solution of (2*S*,3*S*)-2,3-benzyloxy-1,4-ditosylbutane [15,16] (1 g, 1.64 mmol) in dry THF (10 ml) was added dropwise, under N_2, at 0°C, to (7.2 ml, 3.6 mmol) of potassium diphenylphosphide in THF (0.5 M) with stirring. The resulting solution was brought slowly to room temperature, and stirred for an additional 2–3 h with tlc monitoring until reaction was complete. After filtering with celite and concentrating the filtrate, a white solid was obtained which was recrystallized in isopropanol/dichloromethane to give the pure diphosphine. M.p. 114–116°C, $[\alpha]_D^{22}$ − 15 (*c*1.0, CH_2Cl_2). ^{1}H NMR: 2.32 (m, 2H); 2.54 (m, 2H); 3.65 (m, 2H); 4.24 (d, 2H, *J* 11.4, AB system); 4.36 (d, 2H, *J* 11.4, AB system); 7.10–7.42 (m, 30H). ^{13}C NMR: 29.2 (d, $J_{(CP)}$ 13.8, P–$\underline{C}H_2$); 72.3 (s, Ph–$\underline{C}H_2$); 76.6 (m, $\underline{C}H$–CH_2); 127.5–128.7 (m, P–$\underline{P}$h ($\overline{C}_{m,p}$), $OCH_2\underline{P}\overline{h}$ ($C_{o,m,p}$)); 133.3 (d, $J_{(CP)}$ 16.7, P–$\underline{P}$h ($\overline{C}_o$)); 132.5 (d, $J_{(CP)}$ 18.6, P–$\underline{P}$h (C_o)); 138.0 ($OCH_2\underline{P}$h(C_i)); 138.3 (d, $J_{(CP)}$ 13.1, P–$\underline{P}$h (C_i)); 139.1 (d, $J_{(CP)}$ 12.9, P–$\underline{P}$h (C_i)); ^{31}P NMR: − 23; IR(cm^{-1}, KBr): 3066, 3053, 3027, 2884, 1480, 1455, 1431, 1360, 1204, 1105, 1086, 1076, 1067, 1026. m/z 639 (M^+, 1%), 561 (14), 453 (15) 347 (47), 239 (26), 185 (56), 121 (21), 108 (41), 91 (100). Anal. calc. $C_{42}H_{40}O_2P_2$: C, 78.98; H, 6.31. Found: C, 78.86; H, 6.03.

2.2.3. Catalytic reactions

The rhodium complex $[Rh(cod)Cl]_2$ was prepared according to the usual procedure [17]. In the tables, conversions are measured by relative peak areas of GC. For the identification of the reaction products, pure samples of the reduced acrylic acids were prepared by catalytic hydrogenation and characterized by the usual methods (NMR, IR and elemental analysis) all being known compounds. The ee were calculated by using the following reported values [18] for the optically pure compounds: *N*-acetyl-(*R*)-alanine $[\alpha]_D^{22}$ + 66.5 (*c*2, H_2O); *N*-acetyl-(*S*)-phenylalanine $[\alpha]_D^{22}$ + 46.8 (*c*1.06, EtOH 95%); Methyl-(*R*)-succinic acid $[\alpha]_D^{22}$ + 15.5 (*c*2.82, EtOH).

2.2.4. General procedure for transfer reductions using formic acid / triethylamine in dimethylsulphoxide

DMSO (3.75 ml) was added to a degassed mixture of 30 μmol $[Rh(cod)Cl]_2$, 72 μmol of the diphosphine ligand and 4 mmol substrate, under nitrogen. In the case of deguphos, 60 μmol of [Rh(cod)(deguphos)]BF_4 were used. The solution was stirred for 15 min at 28°C, after which triethylamine (8 mmol) and 96% formic acid (20 mmol) were added. Reactions were monitored by removing aliquots at regular intervals, treating with diazomethane, and examining the product conversion by gas chromatography. After complete conversion, 10% NaOH was added to the reaction mixture and the precipitated catalyst was filtered. Acidification with 10% HCl was followed by extraction with ether and drying of combined organic extracts ($MgSO_4$). The solidified product was obtained by evaporation from ethylacetate/hexane before measuring optical rotation.

2.2.5. General procedure for transfer reduction using formic acid / sodium formate

20.3 μmol $[Rh(cod)Cl]_2$, 48.8 μmol of diphosphine ligand, except for deguphos where 40.5 mmol of

$[Rh(cod)(deguphos)]BF_4$ were used, 2 mmol substrate and 200 mg sodium formate were dissolved in 10 ml of aqueous formic acid (80%). Thus, the reaction was heated at the required temperature under nitrogen and it was monitored as in the previous case. The product was isolated as described above, after evaporation of formic acid.

3. Results and discussion

3.1. Ligand synthesis

We have chosen three sets of ligands which form five, six and seven member chelate rings with the metal center (Fig. 1). Of those forming five member chelate rings, dppe and chiraphos are representative of flexible backbone ligands, while deguphos has a rigid backbone. The nonchiral and chiral ligands, represented by dppp and bdpp, respectively, form six member chelate rings. Representing the flexible and rigid, chiral and nonchiral versions of seven member chelate rings are dppb, dppmb, diop, diop–diol and diop–bz, respectively. In order to compare the influence of ligands forming seven member chelate rings, we developed synthetic routes for diop–diol and diop–bz.

The diphosphine diop–diol has been cleanly obtained through hydrolysis of diop by treating it with perchloric acid [19] at room temperature for 30 min. After work-up the pure product is obtained by direct recrystallization in ethanol. Other acid catalysts (H_2SO_4, HCl, and *p*-toluenesulphonic acid, among others) were attempted, but they either do not catalyze the process or originate extensive degradation. An alternative hydrolysis of diop has been reported [20], but it requires further purification of the ligand.

The dimethyl ether of diop–diol was first reported by Kagan in his pioneering communication [14]. We were unable to reproduce this synthesis for which no experimental details were given. Alternatively, we have successfully prepared the similar ligand diop–bz. Starting from diethyl tartarate, by standard methods we prepared the (2*S*,3*S*)-2,3-dibenzyloxi-1,4-ditosylbutane [15,16]. This derivative was then treated with potassium diphenylphosphide in THF to give the new ligand diop–bz, which was fully characterized.

3.2. Transfer hydrogenation results

The effect of the rhodium chelate ring size on the catalytic asymmetric transfer reduction of olefins has been studied by Brunner et al. [12] and Brunner and Leitner [18,21]. We have expanded this study by using a larger number of diphosphine co-catalyst where the size of the chelate ring and the nature of the backbone of these ligands have been modified. The (*Z*)-α-acetylaminocinnamic acid (**1**) (Fig. 2) was used as model substrate both for reactions carried out in the aqueous formic acid (80%) and sodium formate system, as well as in the formic acid (96%) and triethylamine (molar ratio 5:2) in dimethylsulfoxide system. The results using these systems are summarized in Tables 1 and 2.

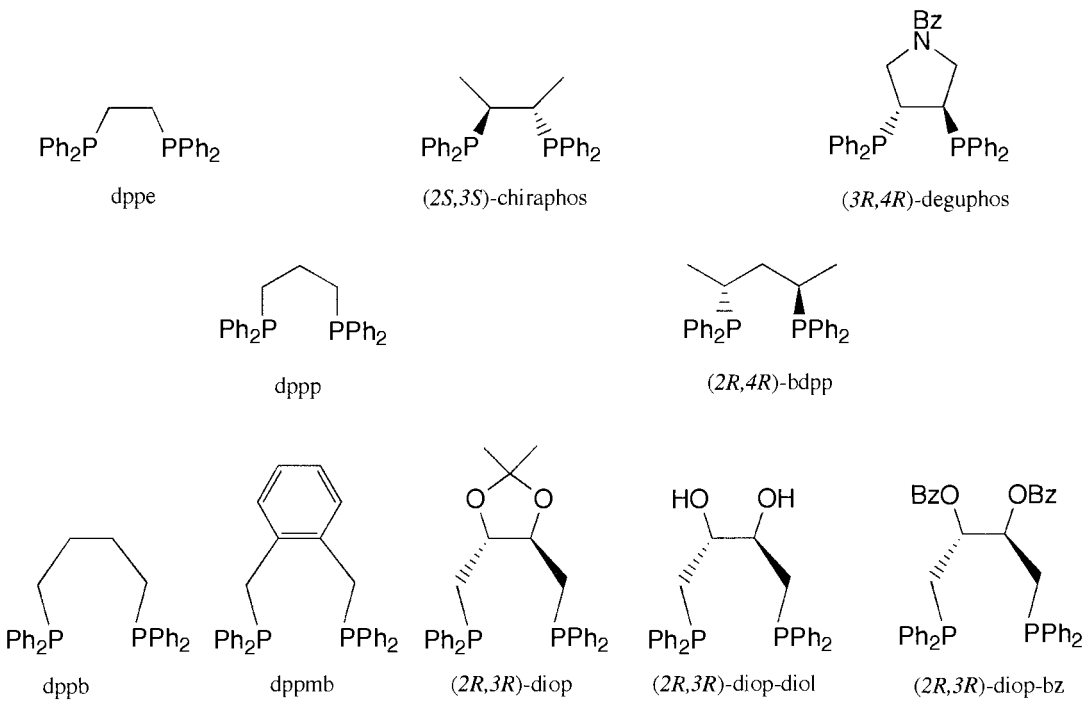
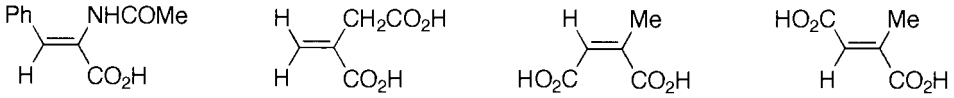


Fig. 1.



(Z)-(α)-Acetylamino cinnamic Acid (**1**) Itaconic Acid (**2**) Citraconic Acid (**3**) MesaconicAcid (**4**)

Fig. 2.

When formic acid/sodium formate was used as hydrogen source for the hydrogenation of (**1**), none of the Rh(I) catalysts of any of the selected ligands was active at room temperature. However, the same catalysts showed fairly good activities at temperatures above 90°C (Table 1). Meanwhile, some differences were observed in the activity of the wide variety of catalysts used. With the exception of diop–diol and diop–bz, the presence of rigid rings in the backbone structure of the ligand significantly lowers the activity of the catalyst (Table 1, experiments 1 and 2 vs. 4, or 8 vs. 9 and 10). These results are remarkably in contrast with the ones observed when DMSO was the solvent, under the second set of conditions (Table 2). In this case, the catalysts containing diphosphine ligands dppe, chiraphos and deguphos, that form five member chelate rings with the metal center, were nearly inactive at room temperature, although they become active at 120°C. Ligands which form six and seven member chelate rings showed complete conversions in about 24 h below 50°C, with the exception of the singular case of diop–diol. In this group of ligands there seems to be no significant influence of the rigidity of the backbone (Table 2, experiments 10–12). Therefore, regarding the activity of the system, the presence of a rigid ring in the backbone of the ligand seems to be relevant when formic acid/sodium formate is used, but the size of the chelate ring is crucial when formic acid/triethylamine/DMSO is employed. Only diop–diol ligand does not follow this general rule. The ligand which contains free alcohol groups is unable to catalyze hydrogen transfer at low temperatures, regardless of the catalytic system used. However the Rh(I) catalyst of this ligand is active even at room temperature in the reduction of acrylic acids using molecular hydrogen [19]. The fact that the closely related ligand diop–bz is active in formic acid/triehtylamine/DMSO at low temperatures, suggests that the hydroxyl groups of diop–diol interfere in the formic acid activation step.

The difference between the activity of the catalyst with dppb and diop–bz, both forming flexible seven member chelates, is more pronounced when using formic acid/sodium formate as hydrogen source, but it is also significant in the case of formic acid/triethylamine/DMSO. No satisfactory explanation was found for this behavior.

In order to evaluate the effect of the solvent on these catalytic reactions, we have tried acetic acid, dimethylformamide and nitrobenzene instead of dimethylsulphoxide in the transfer reduction reaction of (**1**) with formic acid/triethylamine. The dppb co-catalyst was

Table 1
Influence of the ligand structure of the Rh(I) complex on the reduction of (*Z*)-(α)-acetylaminocinnamic acid (**1**) using formic acid/sodium formate as hydrogen source

Experiment	Ligand	*T* (°C)	Time (h)	Enantiomeric excess (%)
1	dppe	120	5	–
2	chiraphos	120	5	60 (*R*)
3	deguphos	90	48	91 (*S*)
4	deguphos	120	24	61 (*S*)
5	dppp	120	3	–
6	bdpp	90	12	92 (*R*)
7	bdpp	120	4	40 (*R*)
8	dppb	120	4	–
9	dppmb	120	30	–
10	diop	120	24	5 (*R*)
11	diop–diol	120	30	2 (*R*)
12	diop–bz	120	24	0

All experiments were run until full conversion, therefore the reaction time is an indication of the activity of the catalyst.
$[Rh(cod)Cl]_2$ /ligand/substrate = 1:2.2:50.

Table 2
Influence of the ligand structure of the Rh(I) complex on the reduction of (*Z*)-(α)-acetylaminocinnamic acid using formic acid/triethylamine as hydrogen source, in DMSO

Experiment	Ligand	*T* (°C)	Time (h)	Conversion (%)	Enantiomeric excess (%)
1[a]	dppe	28	93	6	–
2	dppe	120	4	100	–
3	chiraphos	28	24	0	–
4	chiraphos	120	24	100	0
5	deguphos	28	48	0	–
6	deguphos	120	48	100	0
7[a]	dppp	28	20	100	–
8	bdpp	28	30	56	–
9	bdpp	48	20	100	10 (*R*)
10[a]	dppb	28	24	100	–
11	dppmb	28	24	100	–
12[a]	diop	28	18	100	50 (*R*)
13	diop–diol	28	72	0	–
14	diop–diol	40	48	0	
15	diop–diol	120	30	100	40 (*R*)
16	diop–bz	40	24	100	0

[a] The results are consistent with the ones in Ref. [21].
$[Rh(cod)Cl]_2$ /ligand/substrate = 1:2.2:66.

chosen for this study since it likely forms the more flexible chelate ring among all the ligands used. The results of these experiments are shown in Table 3. Even at 90°C very low activity was observed for all solvents studied. To explain the dependence of the activities on the size of the chelate ring, Brunner and Leitner [18,21] invoked the minor stability of the six and seven member chelate rings comparatively to that of the five member ones as the reason for a dangling effect originated by the dissociation of one of the phosphorous atoms. Our observations also support that the coordination of DMSO facilitates this dangling, which is the key factor for the activation of the formate at low temperatures. Furthermore, DMSO seems to be unique as a solvent for this type of reaction. It could be also considered as an alternative explanation that the phosphine is oxidized by DMSO under reaction conditions. Thus, the vacancy in the coordination could be attributed to the weakness of the phosphine oxide ligand. However, this possibility can be discarded since Brunner et al. [12] have demonstrated that the co-catalyst remains intact during the hydrogen transfer reaction.

In the absence of DMSO, the dangling effect could be thermally activated. This step should be slower for ligands with rigid backbones, thus explaining the longer reaction times for the catalysts having that characteristic.

The present work demonstrates that ee higher than 90% can be obtained in the reduction of (**1**) at temperatures above 90°C, namely when the Rh(I) complexes of deguphos and bdpp, which form five and six member chelate rings, are used in the formic acid/sodium formate system (Table 1, experiments 3 and 6) at 90°C. On the contrary, ligands which form seven member chelates give very poor ee under the same conditions (Table 1, experiments 10–12).

When the system DMSO/formic acid/triethylamine is used, a marked influence of the size of the chelate ring on the enantioselectivity is observed. Ligands which form five member chelates are active only above 120°C, and they exert no enantioselection on the reaction products (Table 2, experiment 4 and 6). These results may be explained considering that a monodentate diphosphine intermediate is the dominant species in the enantioselective discrimination step, when DMSO is present at high temperatures.

Table 3
Influence of the solvent on the reduction of (*Z*)-(α)-acetylaminocinnamic acid, with formic acid/triethylamine, using the Rh(I) complex of dppb

Solvent	*T* (°C)	Time (h)	Conversion (%)
DMSO	28	24	100
AcOH	28	19	0
AcOH	90	48	15
DMF	28	24	0
DMF	90	48	18
$PhNO_2$	28	24	0
$PhNO_2$	90	48	5

Reaction conditions are those of Table 2.

Table 4
Transfer hydrogenation of acrylic acids catalyzed by Rh(I) complex of deguphos using the system formic acid/sodium formate

Experiment	Substrate	*T* (°C)	Time (h)	Conversion (%)	Enantiomeric excess (%)
1	**1**	90	48	100	91 (*S*)
2	**1**	120	24	100	61 (*S*)
3	**2**	90	48	100	57 (*R*)
4	**2**	120	18	100	57 (*R*)
5	**3**	90	72	48	–
6	**3**	120	20	100	11 (*R*)
7	**4**	120	72	50	–

Reaction conditions are those of Table 1.

The diphosphine bdpp, which forms a six member chelate, is active near room temperature in DMSO. However, the ee is significantly lower than the one observed in the formic acid/sodium formate system, 10% and 92%, respectively. The ligand therefore shows a intermediate behavior between the ones of the ligands forming five and seven member chelates.

The ligands diop and diop–diol, which form seven member chelates, gave ee of 50% and 40%, respectively, in DMSO/formic acid/triethylamine. These values are significantly higher than those obtained in formic acid/sodium formate. The reaction requires, however, higher temperatures for diop–diol. The reason why the Rh(I) complex of diop–bz does not induce chirality in either of the two systems studied is not yet clear. [1]

Table 4 shows the results for the transfer hydrogenation of several acrylic acids in the presence of the Rh(I) complex of deguphos in formic acid/sodium formate system. Lowering the temperature from 120°C to 90°C raised the ee in the reduction of (**1**) from 61 to 91%. On the contrary, with substrate (**2**), the 57% ee obtained was unchanged at lower temperatures. With substrate (**3**) the ee was significantly lower, 11% at 120°C, while at 90°C very low conversions were obtained. With substrate (**4**) there was only 50% of conversion after 72 h, even at 120°C.

The low activities and selectivities observed with substrates (**3**) and (**4**) are likely to be due to the lower stability of the *quasi*-four member chelates, which they form with the metal center, in contrast to the *quasi*-5 member chelates formed by substrates (**1**) and (**2**) [22].

[1] The hydrogenation of (**1**) with Rh/diop–bz using molecular hydrogen yields only 10% ee. Unpublished results.

The overall results point to a strong specificity of the catalyst with respect to the structure of the substrate.

4. Conclusion

Chiral five and six member chelate diphosphine ligands (chiraphos, deguphos and bdpp) form active and high enantioselective rhodium catalysts for the reduction of (*Z*)-α-acetylaminocinnamic acid (**1**) with formic acid/sodium formate, while ligands forming seven member chelates (diop, diop–diol and diop–bz) show nearly no enantioselective discrimination. In all these catalytic systems, the rate of the reaction depends on the presence of a rigid ring on the backbone of the diphosphine ligand. On the other hand, seven member chelate ligands (diop, and diop–diol) show moderate enantioselectivity when the reaction medium was formic acid/triethylamine/DMSO, while the five and six member chelate diphosphines form much less active catalysts, and they show very low or no chiral induction. Finally, the catalytic results strongly depend on the solvent and the nature of the acrylic substrate.

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