Expanding the Scope of Atropisomeric Monodentate P-Donor Ligands in Asymmetric Catalysis: Hydrogen-Transfer Reduction of α,β-Unsaturated Acid Derivatives by Rhodium/Ph-binepine Catalysts

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Dedicated to Professor *Giambattista Consiglio*, a good friend and excellent chemist, for his remarkable contributions to the advancement of stereoselective catalysis

A range of α,β-unsaturated acids and esters have been selectively reduced to the corresponding saturated acid derivatives by hydrogen transfer. As the reducing agent, formic acid was used in the presence of Rh^I complexes formed with the powerful chiral ligand Ph-binepine (**1**), an axially chiral binaphthalene-type monodentate P-donor ligand. Very high stereoselectivities (up to 97% ee) were obtained in the case of itaconic acid (**2a**).

Introduction. – The reduction of unsaturated functional groups by means of transition-metal-mediated hydrogen transfer from a suitable hydrogen donor such as i-PrOH or HCOOH has experienced increasing success over the last years [1]. This mild methodology represents a viable alternative to catalytic hydrogenation by molecular H_2 due to its operational simplicity and reduction of the risks associated with the use of an easily inflammable gas of high diffusibility. Significant advances in this area have been achieved in the asymmetric reduction of ketones and imines with catalysts of excellent activity/selectivity based on Ru and Rh complexes with monotosyl-substituted diamines or amino alcohols as chiral modifiers [1a].

Less efforts have been devoted to the transfer hydrogenation of C=C bonds. Although this process is thermodynamically favored, even when alcohols are used as H-donors, only the reduction of conjugated C=C bonds is of practical significance, while simple alkenes and dienes are poorly reactive. A perusal of the literature shows that transfer hydrogenation of conjugated acid derivatives such as itaconic acid and α-(acetamido)cinnamic acid selectively takes place at the C=C bond, and stereoselectivities higher than 90% can be sometimes attained in this reaction when performed in the presence of Ru [2] or Rh complexes [3] with chiral bidentate diphosphines such as binap [2], bppm [3a–f], or deguphos [3g]. No example of the application of monodentate phosphines as chiral inducers in this reaction has been reported thus far, in spite of the excellent performances displayed by binaphthalene-templated monodentate P-ligands [4], such as phosphonites [5], phosphites [6], and phosphoramidites [7], in the Rh-catalyzed hydrogenation of a wide variety of substrates.

Pursuing our long-lasting interest in the application of axially chiral phosphacyclic P-donor ligands in asymmetric catalysis [8], in the course of the last years, we have focused our attention on the scope of the 'phenyl binaphthophosphepine' (Ph-binepine; **1**)[1]) ligand in transition-metal-catalyzed stereoselective reactions (*Fig. 1*). The monodentate phosphine ligand **1** had been synthesized for the first time in 1994 by one of us [9]. In the meantime, *Beller* and co-workers [10], *Zhang* and *Chi* [11], and ourselves [12] have exploited this ligand with remarkable success in a range of metal-catalyzed reactions. These results have prompted us to expand the scope of Rh^I complexes with **1** to the hydrogen transfer reduction of conjugated acid derivatives. The results of this study are reported in this paper.

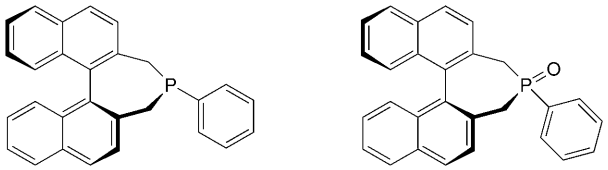
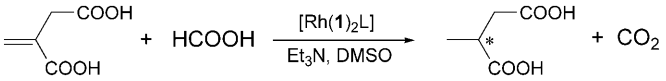


Fig.1. *Structures of the phosphepine ligand Ph-binepine* ((*S*)-**1**) *and of its oxide*

Results and Discussion. – The reduction of itaconic acid (=2-methylidenebutanedioic acid; **2a**) with Et_3N/HCOOH (TEAF) in DMSO has been selected as the benchmark reaction of this investigation (*Scheme 1*). The commercially available azeotrope of TEAF (Et_3N/HCOOH 5:2) was consistently used as the reducing agent throughout this study, and all catalytic experiments were performed with a substrate/Rh ratio of 66.7:1 and a substrate/HCOOH ratio of 1:5. These conditions allowed us to apply strictly homogeneous conditions.

Under these conditions, the Rh complex selected as the catalyst precursor, $[Rh(nbd)Cl]_2$ (nbd=2,5-norbornadiene), displayed a modest, but not negligible, catalytic activity, and itaconic acid was converted into methylsuccinic acid in 15% yield after 24 h at 40° (*Table 1*, *Entry 1*). No separation of metallic Rh was noticed. While this background reaction has no practical influence on the results of the stereoselective experiments reported hereafter, its presence points out that DMSO has some protecting effect towards the Rh complex, likely due to the formation of some Rh/DMSO species [13].

Scheme 1. *Transfer Hydrogenation of Itaconic Acid* (**2a**)



2a

[1]) Systematic name of **1**: 4,5-dihydro-4-phenyl-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]phosphepine.

Table 1. *Hydrogen-Transfer Reduction of* **2a** *as a Function of Ligand-to-Metal Ratio.* Conditions: *in situ* generated catalyst from $[Rh(nbd)Cl]_2$ and **1** in DMSO, 24 h, 40°.

Entry	Ligand	Ligand/Rh ratio	Conversion [%]	ee [%]	Configuration
1	None	–	15	–	–
2	(*S*)-**1**	1.1 : 1	81	54	(*S*)
3	(*R*)-**1**	2.1 : 1	98	82	(*R*)
4	(*S*)-**1**	4.2 : 2	91	82	(*S*)
5	(*S*)-**1**(**O**)	2.1 : 1	15	0	racemic

Addition of 1 equiv. of Ph-binepine (**1**) to a solution containing the complex $[Rh(nbd)Cl]_2$ strongly increased the catalytic activity, and methylsuccinic acid was obtained in 81% yield, with 54% enantiomeric excess (ee) (*Table 1*, *Entry 2*). Both conversion and stereoselectivity could be further improved, up to 98 and 82%, respectively, when the reaction was run at a ligand/Rh ratio of 2 : 1 (*Entry 3*). However, when this ratio was further increased to 4 : 1, the yield decreased to 91%, the ee values basically remaining unchanged (*Entry 4*). These results point out that the ligand exerts a beneficial effect on the activity of the metal (ligand-accelerated catalysis) [14]. Thereby, the catalytically active species most likely features two monodentate P ligands per Rh center.

Because of the possibility that oxidation of Ph-binepine (**1**) may occur due to the long contact of the ligand with DMSO, a test was performed in the presence of the phosphepine oxide (*S*)-**1**(**O**) (*Fig. 1*) in place of (*S*)-**1**. This led to a 15% yield of *racemic* methylsuccinic acid (*Entry 5*), just as in the absence of ligand. This result, thus, confirms that no phosphepine oxide ligand is involved at any time in the catalytic process.

Table 2 summarizes the results of the reduction of **2a** (*Scheme 1*) in a range of different temperatures. As it frequently occurs, a decrease of the reaction temperature is accompanied by a net increase of the stereoselectivity. Indeed, the ee value increased from 82 to 94% when the reaction was performed at 22 instead of 40° (*Table 2*, *Entries 1 vs. 2*). Notably, this increase did not occur at the expense of the conversion, which remained almost quantitative, even when the reaction time was reduced from 24 to 4 h. A further decrease in temperature, however, diminished the rate of reaction well below practical application.

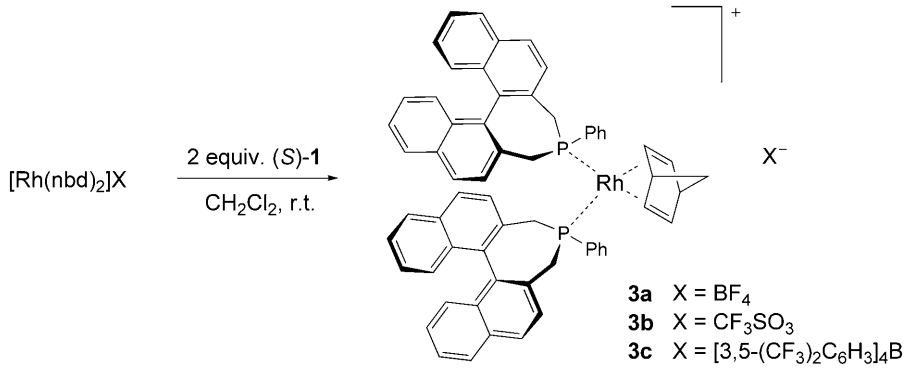
Table 2. *Hydrogen-Transfer Reduction of* **2a** *as a Function of Temperature and Solvent*

Entry	Ligand	Solvent	*T* (°)	Conversion [%]	ee [%]	Configuration
1[a])	(*R*)-**1**	DMSO	40	98	82	(*R*)
2[b])	(*S*)-**1**	DMSO	22	>99	94	(*S*)
3[a])	(*S*)-**1**	–	40	87	53	(*S*)
4[b])	(*S*)-**1**	–	22	>99	91	(*S*)

[a]) Catalyst formed *in situ* from $[Rh(nbd)Cl]_2$ and 2 equiv. of **1**; 24 h. [b]) With preformed $[Rh(nbd)\{(S)\text{-}\mathbf{1}\}_2]^+ CF_3SO_3^-$; 4 h

When the above reaction was run in neat TEAF (in the absence of DMSO), a slightly lower, but still respectable, ee value of 91% was achieved at 22° (*Table 2*,

Scheme 2. *Preparation of Cationic Rh Complexes with Ligand* **1**



Entry 4). Note, however, that there is a beneficial effect of the co-solvent on the lifetime of the catalyst: when the reaction was run in neat TEAF at 40°, both conversion and ee were considerably lower than in the presence of DMSO as a co-solvent (*Entry 1 vs. 3*). Because of this, DMSO was used in all subsequent experiments.

There is increasing evidence that the activity, lifetime, and stability of a charged transition-metal catalyst, as well as the corresponding product selectivity, are significantly influenced by the nature of the counter-ion [15a]. For instance, it has been shown that in the asymmetric hydrogenation of imines [15b] and olefins [15c] promoted by cationic Rh diphosphine catalysts, both activity and enantioselectivity change on varying the nature of the counter-ion. To probe the influence of weakly coordinating anions [16] on the efficiency of transfer hydrogenation, a range of Rh complexes of the type $[Rh\{(S)\text{-}\mathbf{1}\}_2(nbd)]^+ X^-$ ($X^- = BF_4^-$, $CF_3SO_3^-$, $[3,5\text{-}(CF_3)_2C_6H_3]B^-$) have been prepared by reaction of $[Rh(nbd)_2]^+ X^-$ with 2.1 equiv. of (*S*)-**1** to afford the complexes **3a**–**c**, respectively (*Scheme 2*).

Since the ^{1}H- and ^{31}P-NMR spectra of the three complexes showed only minor variations due to the counter-ion, the discussion of the NMR data will be limited to the spectra of **3b**.

In the ^{31}P-NMR spectrum (in $CDCl_3$ solution), coordination of the ligand to the metal was confirmed by the presence of a *doublet* at *ca.* δ(P) 35, with a downfield shift of nearly 27 ppm compared to the free ligand. The splitting is due to the coupling between the coordinated P- and ^{103}Rh-atoms, with a ^1J(P,Rh) coupling constant of *ca.* 155 Hz. In the corresponding ^{1}H-NMR spectrum, four signals, each accounting for two H-atoms, were observed for the coordinated norbornadiene (nbd). The allylic (δ(H) 3.60) and olefinic (δ(H) 3.91, 5.58) signals were observed as broad *singlet*s, and the bridging *nbd* CH_2 group resonated as a sharp *singlet* at δ(H) 1.33. Four signals, each integrating for two H-atoms, were assigned to the four benzylic CH_2 groups on each coordinated ligand: δ(H) 1.90 (*d*, J = 12.1), 2.51 (*d*, J = 14), 3.18 (*d*, J = 14), 2.35 (*t*-like *m*). In the spectrum of the free ligand **1**, the diastereoisotopic H-atoms of the CH_2 groups give rise to two sets of eight lines for each methylene group at δ(H) 2.66 and 2.82. Upon coordination to Rh, the chemical shifts of the latter signals are spread over a wider range (δ(H) 1.90 and 3.18). Selective decoupling of the three *doublet*s shows that there is a ^1J(H,H) coupling, and that coupling to the P-atom is no longer present[2]). For the resonance at δ(H) 2.35, on the contrary, irradiation of the corre-

[2]) Geminal P,H coupling constants have a *Karplus*-like dependence from the H–C–P electron-pair dihedral angle. Upon coordination to the metal, a change of the electron density and of the hybrid-

sponding geminal H-atoms turned the *multiplet* into a *doublet* whose splitting arises from a residual coupling. This is most probably due to an agostic interaction of one pseudo-axial H-atom with the metal, as pointed out by inspection of molecular models. Several *multiplet*s, roughly corresponding to eight *doublet*s and four *triplet*s at δ(H) 6.8 and 8.7, and integrating for 34 H-atoms, finally accounted for the aromatic H-atoms. In summary, these data support C_2-symmetric $[Rh\{(S)\text{-}\mathbf{1}\}_2(nbd)]^+ X^-$ complexes.

Whichever cationic complex **3** was used, the reduction of itaconic acid (**2a**) at room temperature was found to be complete within 4 h (*Table 3*). However, there was a significant influence of the nature of the counter-ion on stereo-induction The ee values increased from 82 to 89 to 94 and, finally, to 97% for $X = Cl^-$ [18], $[3,5\text{-}(CF_3)_2C_6H_3]B^-$, $CF_3SO_3^-$, and BF_4^-, respectively (*Table 3*). Comparison of the enantioselectivities obtained at 40° with the *in situ* generated catalyst $[Rh(nbd)Cl]_2$ (*Table 3*, *Entry* 4; 82% ee) and with preformed $[Rh\{(S)\text{-}\mathbf{1}\}_2(nbd)]^+ BF_4^-$ (*Entry* 5; 89% ee) confirms the role of the counter-ion in determining the stereoselectivity. As the coordinating ability of the counter-ions decreases in the order $Cl^- > CF_3SO_3^- > BF_4^- > [3,5\text{-}(CF_3)_2C_6H_3]_4B^-$, a direct correlation between this property and the trend in stereoselectivity is not immediately apparent.

Table 3. *Hydrogen-Transfer Reduction of* **2a** *with Catalysts of the Type* $[Rh(nbd)\{(S)\text{-}\mathbf{1}\}_2]^+X^-$ *as a Function of Counter-Ion* (X^-)*, Temperature, and Reaction Time*

Entry	X^-	T [°]	t [h]	Conversion [%]	ee [%]	Configuration
1	BF_4^-	22	4	> 99	97	(*S*)
2	$CF_3SO_3^-$	22	4	> 99	94	(*S*)
3	$[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$	22	4	> 99	89	(*S*)
4	[a])	40	24	> 99	82	(*S*)
5	BF_4^-	40	24	> 99	89	(*S*)

[a]) Catalyst made from 1/2 $[Rh(nbd)Cl]_2$ and two equiv. of (*S*)-**1**.

This behavior is in strong contrast with what was observed in the reduction of the same substrate with molecular H_2, where changing the counter-ion has a dramatic effect on the activity of the catalyst [19]. When the hydrogenation was performed in CH_2Cl_2, conversions of 39%, 84%, and > 99% within 1 h were observed for **3c**, **3a**, and **3b**, respectively. The effect on enantioselectivity was otherwise negligible.

For the sake of comparison with other monodentate P-donor ligands of similar design, the transfer hydrogenation of itaconic acid (**2a**) was also performed with *in situ* prepared catalysts with a range of chiral monodentate ligands such as the phosphite (*R*)-**4** [6], the phosphonite (*R*)-**5** [5], the phosphoramidite (*R*)-**6** (MonoPhos) [7], and the dithiaphosphepine (*R*)-**7**[3]) (*Fig. 2*). The first three ligands are, in general, as efficient as Ph-binepine (**1**) in Rh-catalyzed asymmetric hydrogenations of α,β-unsaturated acid derivatives (ee values of 90–99%).

In *Table 4*, the results obtained by screening the above different ligands are reported, together with the best results scored with Ru and Rh catalysts modified by

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ization at the P-atom give rise to a change in the bond angles, which is reflected in a change of the associated coupling constants [17].

[3]) This ligand has been prepared in our laboratory. Its synthesis will be reported elsewhere.

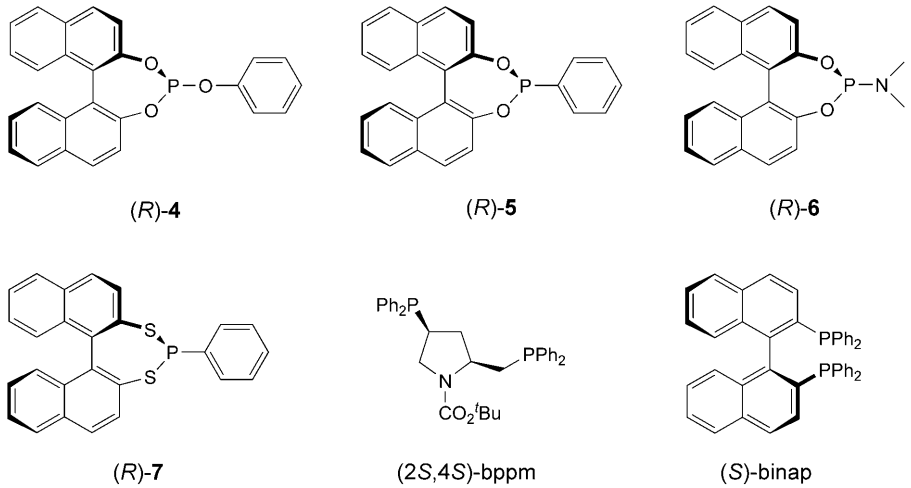

Fig. 2. *Structures of mono- and bidentate P ligands tested in transfer hydrogenations of* **2a**

the chiral diphosphine ligands binap [2b] and bppm [3c], respectively. Although the results are not fully comparable because of somewhat different experimental conditions (longer reaction times were necessary in some cases for a definite conversion to be observed), the superiority of ligand **1** over the other monodentate ligands in the reduction of **2a** is clearly evident. With ligands (*R*)-**4**, (*R*)-**5**, and (*R*)-**7**, the conversions were generally poor, with negligible or even null stereoselectivities. This might be due to ligand degradation. At variance, the Rh complex formed with (*R*)-**6**, which is known to be more stable than the complexes with the other ligands [7b], afforded quantitative conversions (*Table 4*, *Entries 5* and *6*), thus indicating that the relevant catalyst can tolerate these reaction conditions. However, (*R*)-**6** was found to be a poor chiral inducer, the ee values not exceeding 27%.

The excellent performance (97% ee) of Ph-binepine (**1**) in the reduction of **2a** (*Table 4*, *Entry 1*) was challenged only by some catalysts containing bidentate bisphos-

Table 4. *Hydrogen-Transfer Reduction of* **2a** *with Different Chiral Ligands*

Entry	Conditions[a])	Ligand	Conversion [%]	ee [%]	Configuration
1	*A*, *B*	(*S*)-**1**	>99	97	(*S*)
2	*A*, *C*	(*R*)-**4**	35	5	(*R*)
3	*D*, *C*	(*R*)-**4**	9	2	(*R*)
4	*D*, *C*	(*R*)-**5**	15	18	(*R*)
5	*A*, *C*	(*R*)-**6**	>99	24	(*R*)
6	*D*, *C*	(*R*)-**6**	>99	27	(*R*)
7	*A*, *C*	(*R*)-**7**	28	0	racemic
8	*E*	(2*S*,4*S*)-bppm	>99	92	(*S*)
9	*F*	(*S*)-binap	>99	97	(*R*)

[a]) *A*: Preformed Rh complex with BF_4^-; *B*: 4 h, 22°; *C*: 24 h, 40°; *D*: Rh complex formed *in situ*; *E*: $[Rh_2(OAc)_4]$ formed *in situ*, 5 h, 27°; *F*: $[RuH\{(S)\text{-binap}\}_2]PF_6$, i-PrOH, 24 h, 80–83°.

phines such as binap (97% ee) and bppm (92% ee) (*Entries 8* and *9*, resp). While in the first case the reaction conditions are completely different from ours (Ru catalyst, i-PrOH as H-donor), in the second case, both metal and H-donor were the same as in our case. Unfortunately, bppm is structurally not related at all to Ph-binepine (**1**), which prevents any meaningful comparison.

In the aim to explore the scope of this new catalyst and to get some insight into the reaction mechanism, a range of different substrates (*Fig. 3*) was tested in the hydrogen-transfer reduction in the presence of preformed or *in situ* generated **3a** ($X = BF_4^-$).

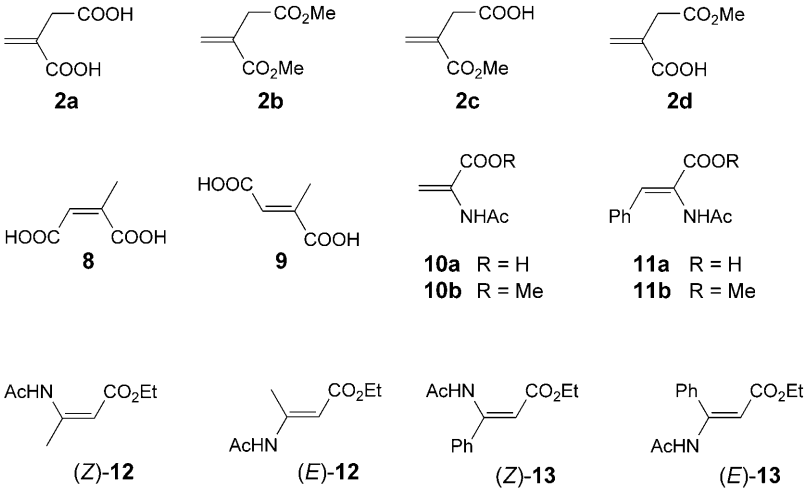

Fig. 3. *Structures of substrates tested in transfer hydrogenations*

First, we investigated the outcome of the reaction of the esters **2b**–**d** of itaconic acid, and the results are summarized in *Table 5*. It is known since long that these esters display different ligating properties towards Rh, and that the mode they bind the metal depends on the location of the substituents on the C=C bond. It is also recognized that the binding mode of these substrates is a critical factor in steering chiral induction by hydrogenation with molecular H_2 [20].

Table 5. *Transfer Hydrogenation of Itaconic and Butenedioic Acid Derivatives*

Entry	Ligand	Substrate	Conditions[a])	Conversion [%]	ee [%]	Configuration
1	(*S*)-**1**	**2a**	*A*	>99	97	(*S*)
2	(*S*)-**1**	**2b**	*A*	57	13	(*R*)
3	(*S*)-**1**	**2c**	*A*	99	81	(*S*)
4	(*S*)-**1**	**2d**	*A*	75	28	(*R*)
5	(*R*)-**1**	**8**	*B*	97	2	(*R*)
6	(*R*)-**1**	**9**	*B*	98	12	(*R*)

[a]) A: Preformed Rh complex with BF_4^-, 22°, 4 h; B: Rh complex formed *in situ*, 40°, 24 h.

Under the screening conditions used, the diacid **2a** and the α-monomethyl ester **2c** were quantitatively reduced, with excellent (97% ee) and good (81% ee) stereoselectivities, respectively, providing the corresponding (*S*)-configured methylsuccinates (*Table 5*, *Entries 1* and *3*). The reduction of the β-monomethyl and the dimethyl esters **2d** and **2b**, respectively, proceeded at a slower rate, with conversions as low as 75 and 57% after 4 h. At variance with the previous cases, the reduction products had the (*R*)-configuration, and their enantiomeric purities were modest (28 and 13% ee, resp.; *Entries 2* and *4*). In addition, during the reaction, partial double-bond migration in the diester **2b** from the terminal to the internal position was observed, resulting in the formation of the dimethyl ester of mesaconic acid (**9**), whose concentration was found to build up steadily in solution because of its low reactivity towards reduction.

A similar dichotomic behavior of itaconic acid derivatives had been observed several years ago in a Rh-catalyzed asymmetric hydrogenation [20]. It was attributed to the ability of the β-COOH group to support better the bidentate binding of the substrate to the metal through chelate coordination of the carboxylate arm. *Leitner* and *Lange* [3f] came to a similar conclusion when they performed transfer hydrogenations of the same substrates with the Rh catalyst formed with bppm as ligand. Based on labeling experiments, they pointed out the pivotal role of the free COOH group in addressing the addition of hydrogen across the C=C bond.

Further confirmation of the importance of this structural feature came from the results obtained in the hydrogen-transfer reduction of citraconic acid (**8**) and mesaconic acid (**9**). Both substrates gave rise to almost racemic products (*Table 5*), thus corroborating the strategic role of the β-COOH group in itaconic acid derivatives.

The results obtained in the transfer hydrogenation of a range of precursors of either α- or β-amino acids are collected in *Table 6*. Both α-(acetamido)acrylic acid (**10a**) and its methyl ester **10b** were found to be poor substrates for this reaction. Within 4 h at room temperature, the acid failed to react at all, and the ester suffered from low conversion (35%) and poor ee (33%) (*Table 6*, *Entry 4*). Although a higher temperature (40°) and longer reaction time (24 h) led to complete hydrogenation of both substrates (*Entries 1* and *2*), poor ee values were obtained (18 and 32%, resp., for **10a** and **10b**). Slightly better results were achieved with α-(acetamido)cinnamic acid (**11a**) and its methyl ester **11b**. These substrates are more reactive than the corresponding acrylic acid congeners, and fair conversions of 40 and 57%, respectively, were observed (*Entries 5* and *6*) after 4 h even at 22°. Stereoinduction was slightly better than before, but still remained far from being exciting (58 and 46% ee, resp.). Compared with the itaconic acid derivatives **2**, the derivatives of both **10** and **11** are less reactive, give lower ee values and, with the exception of methyl α-(acetamido)acrylate (**10b**), give rise to the enantiomer having the same configuration of the inducing ligand (*Table 6*).

Notably, regardless whether the reducing agent is molecular H_2 or HCOOH, the reduction of itaconic acid (**2a**) with Rh catalysts containing Ph-binepine (**1**) as ligand gave rise to methylsuccinic acid of the same configuration and of comparable enantiomeric purities. This supports the view that these processes rely on a common intermediate, and that the differences between the two processes must be restricted to the earliest stages of the reaction path, outside the catalytic cycle.

At variance, in the reduction of the substrates **10** and **11**, the configuration of the reduction product depends on the mode of reduction. With the sole exception of methyl

α-(acetamido)acrylate, the handedness of the reaction was found to be '*opposite*' (inducing ligand and reaction products having opposite configurations) with molecular H_2 [10c], but '*same*' (inducing ligand and product with identical configurations) in the case of HCOOH as reducing agent. This is a clear-cut indication that the chemistry involved in these two reductive processes, albeit similar, is far from being identical, and that the behavior of itaconic acid (**2a**) in hydrogen-transfer reduction is special compared with other structurally related substrates.

Enantioselective transfer hydrogenation has been applied for the first time to the reduction of the β-(acetamido)acrylates **12** and **13** with some success (*Table 6*). These are precursors of β-amino acids, a class of compounds of increasing interest for the pharmaceutical industry [21].

Table 6. *Transfer Hydrogenation of Precursors of α- and β-Amino Acids with Preformed [Rh(nbd){(S)-**1**}$_2$]$^+CF_3SO_3^-$.* Conditions: DMSO, 4 h, 22°.

Entry	Substrate	Conversion [%]	ee [%]	Configuration
1[a])	**10a**	>99	18	(*S*)
2[a])	**10b**	>99	32	(*R*)
3	**10a**	0	–	–
4	**10b**	35	33	(*R*)
5	**11a**	40	58	(*S*)
6	**11b**	57	46	(*S*)
7	(*Z*)-**12**	>99	12	(*S*)
8	(*E*)-**12**	97	46	(*S*)
9	(*E*)-**13**	36	4	(*R*)
10	(*Z*/*E*)-**13**[b])	78	2	(*R*)

[a]) *In situ* formed Rh complex, 40°, 24 h. [b]) (*Z*)/(*E*) 71:29.

The Me-substituted derivatives **12** were reduced almost quantitatively within 4 h at 22°, giving rise to the hydrogenated product of (*S*)-configuration (*same*), irrespective of the geometry of the C=C bond of the substrates. For the (*E*)-isomer, the ee was higher (46%) than for the (*Z*)-isomer (12%). This behavior contrasts with that observed by us in the hydrogenation of these substrates with molecular H_2 by Rh/Ph-binepine complexes, where the (*E*)-isomer is quite unreactive, while the (*Z*)-isomer gives the saturated product in more than 90% ee [19]. Notably, in this case, the configuration of the product does not change in moving from hydrogen transfer to hydrogenation, the relation being *same* in both cases. From this point of view, the behavior of β-amino acid precursors contrasts with that of α-(acylamino) acid precursors.

The configurational isomers of the phenyl-substituted substrates **13** displayed a quite different reactivity pattern: whereas (*E*)-**13** was found to be much less reactive than both (*Z*)-**13** and the corresponding Me derivative (*E*)-**12**, the hydrogenation rates for (*Z*)-**13** and (*Z*)-**12** were comparable. Whichever the geometry of the C=C bond of **13**, the stereoselectivity was miserable.

Recently, it has been shown that the combination of two different monodentate P-donor ligands, either both chiral, or one chiral and the other achiral, may, in some cases, produce a more-stereoselective and/or more-active catalyst [22]. This new strategy has

been exploited with some success in Rh-catalyzed asymmetric hydrogenations using various combinations of phosphines, phosphites, phosphonites, and phosphoramidites. This 'mixed-ligand approach' may change the outcome of the reaction when at least two monodentate ligands are bound to the metal of the active catalyst in the transition state.

We have attempted to apply this mixed-ligand approach to the hydrogen-transfer reduction of methyl α-(acetamido)acrylate (**10b**), and the results are shown in *Table 7*. This substrate has been selected for a brief screening of two binary mixtures made up by the combination of **1** with one achiral or one chiral monodentate ligand, triphenylphosphine or (*R*)-**6**, respectively.

Table 7. *Transfer Hydrogenation of* **10b** *Using the 'Mixed-Ligand Approach'* (see text)

Entry	Catalyst system	Conditions[a])	Conversion [%]	ee [%]	Configuration
1	Rh/(*S*)-**1** 1:2	*A*	35	33	(*R*)
2	Rh/(*R*)-**6** 1:2	*B*	n.d.[b])	–	–
3	Rh/Ph_3P 1:2	*C*	>99	–	–
4	Rh/(*S*)-**1**/(*R*)-**6** 1:1:1	*D*	72	23	(*R*)
5	Rh/(*R*)-**1**/(*R*)-**6** 1:1:1	*D*	8	3	(*S*)
6	Rh/(*S*)-**1**/(*R*)-**6** 1:1:2	*D*	43	11	(*R*)
7	Rh/(*S*)-**1**/Ph_3P 1:1:1	*E*	>99	3	(*R*)
8	Rh/(*S*)-**1**/Ph_3P 1:2:1	*E*	>99	8	(*R*)

[a]) *A*: Preformed complex with $CF_3SO_3^-$, 22°, 4 h; *B*: complex formed *in situ*, 22°, 45.5 h. *C*: complex formed *in situ*, 22°, 2 h; *D*: complex formed *in situ*, 22°, 24 h; *E*: complex formed *in situ*, 22°, 4 h. [b]) Not detected.

For the ligand combination (*S*)-**1**/Ph_3P, the results of two runs at different ligand ratios are in keeping with the simultaneous presence of two catalysts containing two equivalents of the same ligand, each one contributing to the outcome of the reaction for its relative extent (*Table 7*, *Entries 7* and *8 vs. 1* and *3*). The situation is different in the case of the combination (*S*)-**1**/(*R*)-**6**. Here, the sharp difference in the rate of reduction observed for the matched pair (*S*)-**1**/(*R*)-**6** and for the mismatched one (*R*)-**1**/(*R*)-**6** (*Entries 4* and *5*) provides evidence that the complex featuring a 'heterotype combination' of ligands is the exclusive or the prevailing catalyst in solution. This species is, however, poorly stereoselective, and the ee values were, in all experiments, lower than that obtained with the complex made from (*S*)-**1** alone.

Conclusions. – We have demonstrated that the ligand Ph-binepine (**1**) is a powerful chiral inducer, even in asymmetric hydrogen-transfer reductions of C=C bonds, a reaction in which, so far, there has been no precedent for the use of chiral monodentate P-donor ligands. Stereoselectivities as high as 97% have been attained with the most appropriate substrate, itaconic acid (**2a**). This value is slightly higher than the best ones previously obtained in this reaction with bidentate chelating diphosphines, and supports further the view that axially chiral monodentate P-donor ligands can equal or even outperform the more-popular and long-standing bidentate counterparts.

The catalytic behavior of Rh/Ph-binepine cationic complexes towards itaconic acid derivatives stresses the importance of the presence of a free β-COOH group in the substrate. This structural feature not only dictates the configuration of the reduction product, but is as well mandatory for quantitative conversions and high stereoselectivities. This observation provides evidence that the β-carboxylate anion dictates the mode the substrate binds to Rh, and strongly supports the formation of a neutral adduct where the COO^- moiety provides for the bidentate chelate coordination of the substrate to the metal. The intermediacy of such a species has been invoked in asymmetric hydrogenations [20] and hydrogen-transfer reductions [3f] of these derivatives with Rh-based catalyst containing chiral diphosphine ligands. Our results are absolutely in keeping with this hypothesis.

The good performance of Ph-binepine (**1**) in the hydrogen transfer reduction of α,β-unsaturated acid derivatives expands further the scope of this ligand to a new process, which adds to the previous ones, where this ligand has already shown its efficiency. It is worth to stress that, by now, the list of reactions where this chiral inducer has led to ee values $>90\%$ (or where it has outperformed by far any other competitor) is fairly long, covering a wide variety of organic reactions catalyzed by different transition-metal complexes of Rh [10a–c], Ru [10d,e], Pt [12b], and Pd [12a]. The results of this work emphasize further the versatility of Ph-binepine (**1**) as a chiral inducer of general utility, and confirm the comparably wider scope of this ligand in respect to all the other binaphthalene-core monodentate P-donor ligands of similar design.

Experimental Part

1. *General.* All reactions were carried out under anh. N_2 using standard *Schlenk* techniques, unless otherwise specified. Solvents were dried by standard procedures, distilled, and stored under N_2. Purchased chemicals (*Aldrich*, *Lancaster*, *Strem*) were used without further purification. Ligand **1** and its oxide, **1(O)** [10c], $[Na\{[3,5\text{-}(CF_3)_2C_6H_3]_4\}B]$ [23a,b], $[Rh(nbd)_2]^+[BF_4]^-$, and $[Rh(nbd)_2]^+[CF_3SO_3]^-$ [24], (*E*)- and (*Z*)-**12** as well as (*E*)- and (*Z*)-**13** [25] were all prepared according to literature procedures. Acids obtained from transfer hydrogenation of the corresponding unsaturated substrates were converted to the corresponding esters with (trimethylsilyl)diazomethane before analysis by chiral GC [26]. NMR spectra were recorded on a *Varian Mercury Plus* spectrometer operating at 400 MHz (^1H), 100 MHz (^{13}C), and 162 MHz (^{31}P) at r.t. Chemical shifts δ are reported in ppm rel. to Me_4Si (^1H, ^{13}C) or 85% H_3PO_4 (^{31}P) as external standard. The enantiomeric excess (ee) was determined by chiral GC (see below).

2. *Determination of Enantiomeric Excess.* The ee values of the following products were determined by chiral GC or optical rotation. GC Retention times (t_R) are given in min.

2.1. *2-Methylsuccinic Acid Dimethyl Ester* (=*Dimethyl 2-Methylbutanedioate)*. Column, *DACTBS-GAMMA-OV 1701* (25 m, i.d. 0.25 mm, ft 0.25 μm); temp. 50°, 2°/min, 170°, 20 min; *PTV* injector (0–400°), detection at 250°, N_2 carrier gas (15 psi, 2 ml/min); t_R 17.39 (*S*), 18.29 (*R*).

2.2. N-*Acetylalanine Methyl Ester* (=*Methyl 2-(Acetamido)propanoate*). Column, *Chirasil-Val-L* (50 m, i.d. 0.32 mm, ft 0.25 μm); temp. 80°, 10 min, 1°/min, 110°, 20 min, 2°/min, 200°, 30 min; *PTV* injector (0–400°), detection at 250°, N_2 carrier gas (20 psi, 2 ml/min); t_R 10.68 (*R*), 12.10 (*S*).

2.3. N-*Acetylphenylalanine Methyl Ester* (=*Methyl 2-(Acetamido)-3-phenylpropanoate*). Column, *Chirasil-Val-L* (50 m, i.d. 0.32 mm, ft 0.25 μm); temp. 110°, 5 min, 1.5°/min, 180°, 1 min, 2°/min, 200°, 30 min; *PTV* injector (0–400°), detection at 250°, N_2 carrier gas (20 psi, 2 ml/min); t_R 36.49 (*R*), 36.96 (*S*).

2.4. *3-Acetamidobutyrate Ethyl Ester* (=*Ethyl 3-(Acetamido)butanoate*). Column, *Mega DEttBuSi-BETACDX* (25 m, i.d. 0.25 mm, ft 0.25 μm); temp. 120°, *PTV* injector (0–400°), detection at 250°, N_2 carrier gas (17 psi, 1 ml/min); t_R 2.82 (*S*), 3.89 (*R*).

2.5. *3-Acetamido-3-phenylpropionate Ethyl Ester* (= *Ethyl 3-(Acetamido)-3-phenylpropanoate*). The ee and the configuration of the prevailing enantiomer were assigned based on reported optical-rotation data [27].

3. *Syntheses of the Complexes* **3**. 3.1. *[Rh(nbd){(*S*)-***1***}$_2$]$^+$ BF_4^-* (**3a**). To a soln. of $[Rh(nbd)_2]^+$ $[BF_4]^-$ (41 mg, 0.11 mmol) in MeOH/CH_2Cl_2 1:1 (10 ml) was added (*S*)-**1** (100 mg, 0.257 mmol), and the mixture was stirred at r.t. for 1 h. The solvent was removed at reduced pressure, and the residue was dissolved in CH_2Cl_2 (2 ml). Addition of Et_2O brought about precipitation of the complex, which was filtered off, washed with Et_2O, dried *in vacuo*, and recrystallized from CH_2Cl_2/Et_2O. Yield: 89 mg (77%). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.39 (*s*, 2 H, nbd); 1.87 (*d*, *J* = 12.4, CH_2); 2.30–2.37 (*m*, CH_2); 2.51 (*d*, *J* = 14.0, CH_2); 3.10 (*d*, *J* = 13.6, CH_2); 3.60 (br. *s*, 2 H, nbd); 3.95 (br. *s*, 2 H, nbd); 5.53 (br. *s*, 2 H, nbd); 6.70 (*d*, *J* = 8.4, 2 arom H); 7.12 (*d*, *J* = 8.4, 2 arom. H); 7.17–7.21 (*m*, 4 arom. H); 7.35–7.39 (*m*, 2 arom. H); 7.42–7.48 (*m*, 4 arom. H); 7.50–7.53 (*m*, 12 arom. H); 7.76 (*d*, *J* = 8.8, 2 arom. H); 7.97 (*d*, *J* = 8.4, 2 arom. H); 8.04 (*d*, *J* = 8.4, 2 arom. H); 8.30 (*d*, *J* = 8.0, 2 arom. H). ^{31}P-NMR (162 MHz, $CDCl_3$): 35.74 (*d*, *J*(P,Rh) = 153.2). Anal. calc. for $C_{63}H_{50}BF_4P_2Rh$ (1058.76): C 71.47, H 4.76; found: C 71.68, H 4.51.

3.2. *[Rh(nbd){(*S*)-***1***}$_2$]$^+$ $CF_3SO_3^-$* (**3b**). To a soln. of $[Rh(nbd)_2]^+[CF_3SO_3]^-$ (56 mg, 0.128 mmol) in MeOH/CH_2Cl_2 1:1 (10 ml) was added (*S*)-**1** (100 mg, 0.257 mmol), and the mixture was stirred at r.t. for 1 h. The solvent was removed at reduced pressure, and the residue was dissolved in CH_2Cl_2 (2 ml). Addition of Et_2O brought about precipitation of the complex, which was filtered off, washed with Et_2O, dried *in vacuo*, and recrystallized from CH_2Cl_2/Et_2O. Yield: 104 mg (72%). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.33 (*s*, 2 H, nbd); 1.90 (*d*, *J* = 12.1, CH_2); 2.32–2.35 (*m*, CH_2); 2.51 (*d*, *J* = 14.0, CH_2), 3.18 (*d*, *J* = 14.0, CH_2); 3.60 (br. *s*, 2 H, nbd); 3.91 (br. *s*, 2 H, nbd); 5.58 (br. *s*, 2 H, nbd); 6.71 (*d*, *J* = 8.6, 2 arom. H); 7.11 (*d*, *J* = 8.2, 2 arom. H); 7.15–7.20 (*m*, 4 arom. H); 7.22–7.28 (*m*, 2 arom. H); 7.34–7.38 (*m*, 4 arom. H); 7.42–7.53 (*m*, 12 arom. H); 7.74 (*d*, *J* = 8.2, 2 arom. H); 7.96 (*d*, *J* = 8.2, 2 arom. H); 8.00 (*d*, *J* = 8.2, 2 arom. H); 8.28 (*d*, *J* = 8.6, 2 arom. H). ^{31}P-NMR (162 MHz, $CDCl_3$): 35.79 (*d*, *J*(P, Rh) = 155.1). Anal. calc. for $C_{64}H_{50}F_3O_3P_2SRh$ (1121.02): C 68.57, H 4.54; found: C 68.34, H 4.65.

3.3. *[Rh(nbd){(*S*)-***1***}$_2$]$^+$ {[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$B}$^-$* (**3c**) [23c]. To a soln. of $[Rh(nbd)Cl]_2$ (29.5 mg, 0.064mmol) in CH_2Cl_2 was added a soln. of $[Na\{[3,5\text{-}(CF_3)_2C_6H_3]_4\}B]$ (113.4 mg, 0.128 mmol) in CH_2Cl_2 (2 ml). The clear yellow soln. became rapidly cloudy due to precipitation of NaCl. The mixture was stirred for 45 min, and then filtered over a pad of Na_2SO_4. To the resulting clear filtrate, (*S*)-**1** (100 mg, 0.257 mmol) was added, which resulted in an orange color. The soln. was stirred at r.t. for 2 h. Addition of hexane brought about precipitation of the product as a micro-crystalline red powder, which was filtered off and recrystallized from CH_2Cl_2/Et_2O. Yield: 59 mg (50%). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.34 (*s*, 2 H, nbd); 1.83 (*d*, *J* = 12.0, CH_2); 2.38–2.44 (*m*, CH_2); 2.54 (*d*, *J* = 14.4, CH_2); 2.79 (*d*, *J* = 14.0, CH_2); 3.69 (br. *s*, 2 H, nbd); 3.82 (br. *s*, 2 H, nbd); 5.19 (br. *s*, 2 H, nbd), 6.56 (*d*, *J* = 8.8, 2 arom. H); 7.09 (*d*, *J* = 8.0, 2 arom. H); 7.14–7.35 (*m*, 12 arom. H); 7.39–7.56 (*m*, 10 arom. H); 7.12 (*s*, 4 arom. H); 7.70 (*d*, 2 arom. H); 7.72 (*s*, 8 arom. H); 7.78 (*d*, *J* = 8.4, 2 arom. H); 8.01 (*d*, *J* = 8.4, 2 arom. H); 8.12 (*d*, *J* = 8.0, 2 arom. H). ^{31}P-NMR (162 MHz, $CDCl_3$): 35.53 (*d*, *J*(P,Rh) = 155.1). Anal. calc. for $C_{95}H_{62}BF_{24}P_2Rh$ (1834.31): C 62.18, H 3.41; found: C 62.31, H 3.30.

4. *General Procedure for the Transfer Hydrogenation of Butenedioic Acids* [3c]. The substrate (2 mmol) and the preformed Rh complex (0.030 mmol) were dissolved in DMSO (4 ml) under N_2. In the case of the *in situ* generated catalyst, the soln. was first stirred for 30 min. Then, HCOOH/Et_3N 5:2 (10 mmol HCOOH, 4 mmol Et_3N) was added, whereupon the color of the soln. changed from orange to yellow under evolution of gas. After stirring the mixture at the given temp. for the required time (see *Tables*), 10% aq. HCl (10 ml) was added. The mixture was filtered, the product was extracted with AcOEt (4 × 50 ml), and the combined org. layers were dried (Na_2SO_4). The solvent was removed *in vacuo* to afford the crude product, whose identity was checked by NMR. Conversions and ee values were determined by GC, as reported above.

5. *General Procedure for the Transfer Hydrogenation of Precursors of α- and β-Amino Acids* [3b]. The substrate (2 mmol) and the preformed Rh complex (0.030 mmol) were dissolved in DMSO (4 ml) under N_2. In the case of the *in situ* catalyst, the soln. was first stirred for 30 min. Then, HCOOH/Et_3N 5:2 (10 mmol HCOOH, 4 mmol Et_3N) was added, whereupon the color of the soln. changed from orange to yellow under evolution of gas. After stirring the mixture at the given temp. for the required time, the

mixture was made alkaline with 2N aq. NaOH (5 ml), and then filtered. The filtrate was washed with Et_2O (4×15 ml), acidified with 10% aq. HCl (3 ml), and extracted with Et_2O (4×15 ml). The combined org. layers were dried (Na_2SO_4), and the solvent was removed *in vacuo*. The identity of the crude product was checked by NMR. Conversions and ee values were determined by GC, as reported above.

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