Asymmetric Hydrogenation of Prochiral Alkenes Catalysed by Ruthenium Complexes of (*R*)-(+)-2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl

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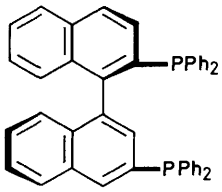
Two chiral ruthenium(II) complexes containing (*R*)-(+)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl [(*R*)-BINAP] were found to be effective catalysts for the asymmetric hydrogenation of 2-acylaminoacrylic and 2-acylaminocinnamic acids under mild conditions, to afford *N*-acyl-(*R*)-α-amino acids with 49—95% optical purity. The differences between the asymmetric hydrogenations effected by Ru^{II}- and Rh^{I}-(*R*)-BINAP systems are discussed. Asymmetric hydrogenation of methylenesuccinic acid and its derivatives with Ru-(*R*)-BINAP is also described.

Asymmetric hydrogenation of 2-acylaminocinnamic acids and their esters using rhodium complexes with chiral diphosphine ligands has been studied extensively in the last decade.[1] Sufficiently high asymmetric inductions (>90% e.e.) were achieved in the hydrogenations employing diphosphines such as (*R*,*R*)-(−)-DIOP,[2] (*S*,*S*)-CHIRAPHOS,[3] (*S*,*S*)-BPPM,[4] (*R*)-(*S*)-BPPFA,[5] and (*R*)- or (*S*)-BINAP.[6] There have, however, been relatively few reports on the successful asymmetric hydrogenation by such ruthenium complex catalysts.[7] In a recent communication[8] we demonstrated that a binuclear ruthenium complex of (*R*)-BINAP (**1**) having the formula $Ru_2Cl_4[(R)\text{-BINAP})]_2NEt_3$ (**2**) was an effective catalyst for hydrogenation of 2-acylaminocinnamic acids with satisfactory enantioselectivity. This finding stimulated recent studies on the Ru-BINAP catalysed asymmetric hydrogenation not only of the carbon-carbon double bond[9,10] but of the carbonyl group.[11,12]



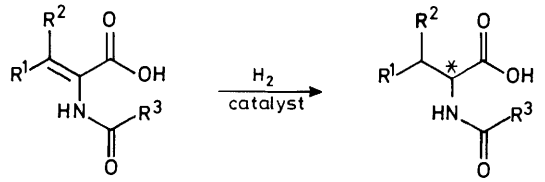
(R)-(+)-BINAP
(**1**)

Along with the binuclear complex (**2**), we prepared a mononuclear complex $RuHCl[(R)\text{-BINAP}]_2$ (**3**),[8] which was also found to catalyse the asymmetric hydrogenation of some olefins. This paper describes in some detail the results of asymmetric hydrogenation of 2-acylaminocinnamic and methylenesuccinic acids and their derivatives catalysed by complexes (**2**) and (**3**).

Results and Discussion

Asymmetric Hydrogenation of 2-Acylaminocinnamic and 2-Acetylaminoacrylic Acids.—With a view to evaluating the effectiveness of ruthenium-(*R*)-BINAP complexes (**2**) and (**3**) as asymmetric catalysts, studies on the hydrogenation of the title prochiral alkenes were carried out (Scheme 1). In most instances the hydrogenation proceeded completely within 24 h, and the expected *N*-acyl-α-amino acids were obtained almost quantitatively. The optical purities and preferred configuration of the products are summarized in Table 1, along with the results obtained using a Rh-(*R*)-BINAP catalyst.[6]

As was described in our preliminary report,[8] the binuclear complex (**2**) functioned as an effective catalyst for the hydrogenation of substrates (**4a**—**c**) under mild reaction conditions (35 °C; initial hydrogen pressure, 2 atm) in the presence of triethylamine. Each of the product mixtures contained the (*R*)-enantiomer in excess, and their optical purities (o.p.), in the



(**4**) (**5**)

a; $R^1 = R^2 = H, R^3 = Me$
b; $R^1 = Ph, R^2 = H, R^3 = Me$ } (**4**) and (**5**)
c; $R^1 = Ph, R^2 = H, R^3 = Ph$
d; $R^1 = H, R^2 = R^3 = Ph$ } (**4**)
e; $R^1 = H, R^2 = Ph, R^3 = Me$

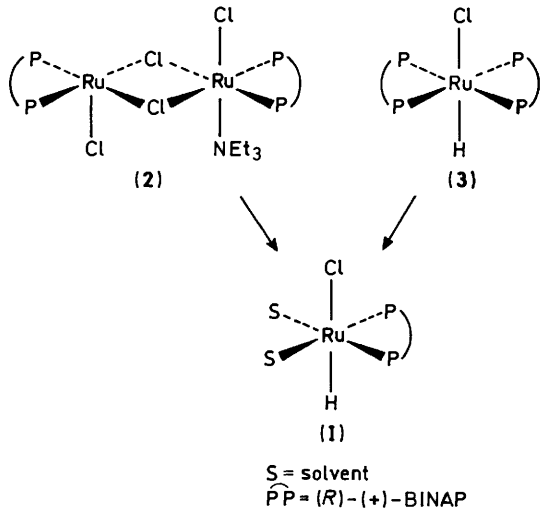
Scheme 1. 2-Acylaminoacrylic and 2-acylaminocinnamic acids and their hydrogenated products.

range 76—92%, were comparable with those of the products from the Rh-BINAP catalysed hydrogenation.[6] In the absence of triethylamine, however, (**2**) showed negligible catalytic activity. This suggests that complex (**2**) itself is not the real catalytically active species for the hydrogenation, but rather its precursor. The stereoselectivity of the catalyst depended on the hydrogen pressure with a lower optical yield being achieved at higher pressure. But, unfortunately, the complex (**2**) catalysed hydrogenation of (**4b**) under an atmospheric pressure of hydrogen proceeded very slowly and only 29 and 60% of the substrate was reduced after periods of 24 and 96 h, respectively. The temperature dependence of the catalysis was also seen in the hydrogenation of (**4c**) catalysed by (**2**). The best selectivity, achieved at 35 °C in 92% o.p., was reduced at both higher and

Table 1. Asymmetric hydrogenation of 2-acetylaminoacrylic acid and 2-acylaminocinnamic acids catalysed by Ru- and Rh-(*R*)-BINAP complexes[a,b]

	Complex (**2**)		Complex (**3**)		Rh-(*R*)-BINAP	
Substrate	O.p.[c]	(*R* or *S*)[d]	O.p.	(*R or S*)	O.p.	(*R or S*)
(**4a**)	76%	(*R*)	75%	(*R*)	67%	(*S*)
			95[e]	(*R*)		
(**4b**)	86	(*R*)	79	(*R*)	84	(*S*)
	58[f]	(*R*)	80[e]	(*R*)		
	49[g]	(*R*)				
(**4c**)	92	(*R*)	79	(*R*)	100	(*S*)
			49[e,h]	(*R*)		
(**4d**)	65	(*R*)			87	(*R*)

[a] Hydrogenation conditions using Ru-(*R*)-BINAP catalysts: substrate, 1.5 mmol; substrate/catalyst = 50 (catalyst as Ru atom); THF–EtOH (1:1; 30 cm^3); triethylamine, 1.8 mmol; H_2, 2 atm; 35 °C; 24 h. With regard to the conditions for Rh-(*R*)-BINAP system, see ref. 11. [b] Hydrogenations are 100% unless otherwise noted. [c] Optical purities are based on the reported maximum rotations: *N*-acetyl-(*R*)-alanine [(*R*)-(**5a**)], $[\alpha]_D^{26}$ +66.3° (*c* 2.0 in H_2O}: *N*-acetyl-(*S*)-phenylalanine [(*S*)-(**5b**)], $[\alpha]_D^{26}$ +46.0° (*c* 1.0 in EtOH); *N*-benzoyl-(*S*)-phenylalanine [(*S*)-(**5c**)]. $[\alpha]_D^{27}$ −40.3° (*c* 1.0 in MeOH), see ref. 3. [d] The enantiomer preferentially formed. [e] No triethylamine was added. [f] H_2, 10 atm. [g] H_2, 100 atm. [h] Conversion, 70%.



Scheme 2. A postulated structure of complex (**2**), the structure of complex (**3**), and a possible catalytically active species (**I**)

lower temperatures (74, 79, and 82% o.p. at 100, 65, and 0 °C, respectively).

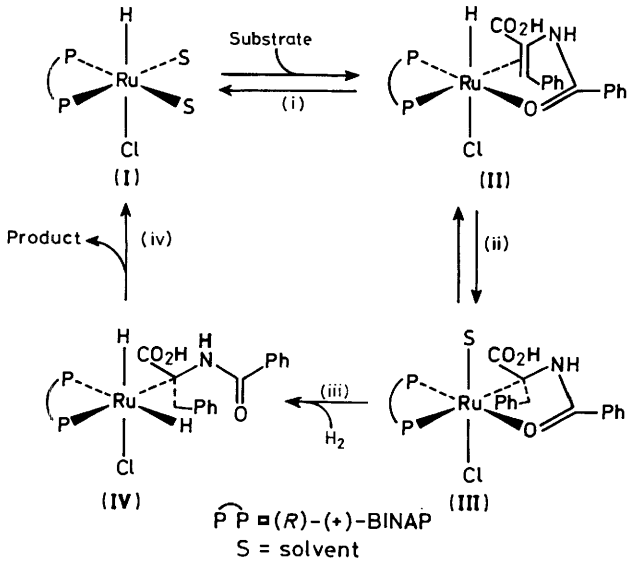
Under similar reaction conditions to those mentioned above, complex (**3**) was also an active catalyst for the hydrogenation of (**4a**—**c**). The optical purities of the products were comparable with those obtained by employing complex (**2**) as the catalyst (Table 1). This suggests that the catalytically active species generated from (**2**) and (**3**) under the hydrogenation conditions may be identical or at least closely similar to each other. It should be noted that the colour of the reaction mixtures involving either (**2**) or (**3**) as the catalyst precursor were both deep orange–brown.

One of the plausible structures for the catalytically active species, commonly generated from both (**2**) and (**3**), could be a co-ordinatively unsaturated (or solvent co-ordinated) complex such as (**I**) (see Scheme 2). The *X*-ray structure study[13] confirmed that complex (**3**), containing two BINAP ligands, assumes octahedral geometry with the *trans* configuration (Scheme 2). It is possible that the dissociation of one of the two BINAP ligands from (**3**) leads to the formation of the solvent-co-ordinated active species (**I**) in Scheme 2. James has postulated the formation of a similar unsaturated ruthenium species RuHCl(DIOP) in the catalytic hydrogenation of acrylamide with *trans*-$RuHCl(DIOP)_2$.[14]

^1H- and ^{31}P-N.m.r. data provide supporting evidence that complex (**2**) may adopt the binuclear structure depicted in Scheme 2, although the exact structure has yet to be determined by *X*-ray crystallography. If complex (**2**) gives rise to the species (**I**), it may do so by obtaining a hydride ligand from a solvent molecule in the presence of triethylamine; this would be accompanied by a structural change from a binuclear to a mononuclear unit. It has been recognized that $[RuCl_2(PPh_3)_3]$ is converted into $[RuHCl(PPh_3)_3]$ in the presence of triethylamine and/or ethanol.[15] Therefore, the transformation from (**2**) to (**I**) is likely to occur in an ethanol–THF mixture containing triethylamine.

In addition, it was found that complex (**3**) functioned as an active catalyst for the hydrogenation of substrates (**4a**—**c**) in the absence of triethylamine. The optical purities of the products obtained under these conditions were apparently different from those recorded in the presence of the amine (see Table 1). It seems that the enantioselection achieved in the reactions of 2-acylaminoacrylic and 2-acylaminocinnamic acids in the absence of triethylamine are significantly affected by the bulkiness of the substituents. Thus, (**4c**), the substrate with sterically bulkier substituents, gave the product with lowest optical purity, while the least hindered substrate (**4a**) was hydrogenated with the highest selectivity. In contrast, in the presence of the amine the effects of the substrate bulk on the enantioselection were not obvious. Furthermore the colour of the reaction mixture was light yellow in the absence of triethylamine in contrast to deep orange–brown in the presence of triethylamine. These observations suggest that depending on whether or not amine is present during the generation from complex (**3**) of the active species, the latter will differ considerably from each other. The exact nature of the active species derived from (**3**) under amine-free conditions is at present difficult to predict.

Comparison of Hydrogenations with Ru- *and* Rh-(R)-*BINAP Catalyst Systems.*—We have recognized two significant facts suggesting intrinsic differences between the Ru- and Rh-(*R*)-BINAP catalysed hydrogenations. The first is that the direction of asymmetric induction effected by the Rh-(*R*)-BINAP catalyst, affording the *S*-enantiomers in excess for the hydrogenations of (**4a**—**c**),[6] is the reverse of that with the Ru-(*R*)-BINAP catalysts (**2**) and (**3**) described above (see Table 1). This inversion of the enantioselection is also found in other chiral diphosphine ligand systems such as (*S,S*)-CHIRAPHOS.[3,7d] However, in contrast to this, there is a reported example where both the Rh- and Ru-catalysts, bearing the ligand [(*S,S*)-DIOP], produce the same dominant enantiomer.[7c] The



Scheme 3. A plausible pathway for asymmetric hydrogenation of (*Z*)-2-benzoylaminocinnamic acid (**4c**) with Ru^{II}-(*R*)-BINAP catalyst

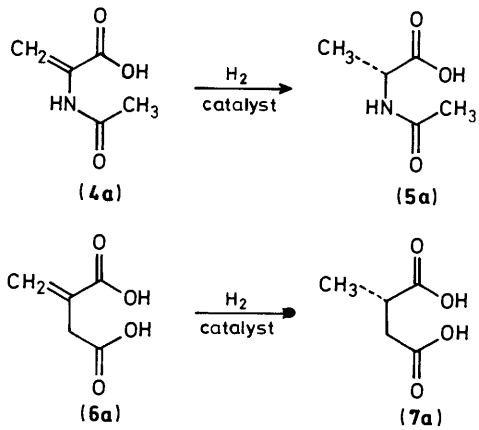
second distinct difference is found among Ru- and Rh-(*R*)-BINAP catalysed hydrogenations of (*Z*)- and (*E*)-2-benzoylaminocinnamic acid, (**4c**) and (**4d**). The hydrogenation with Rh-(*R*)-BINAP catalyst gave the enantiomeric *N*-benzoyl-(*S*)- and (*R*)-phenylalanine from (**4c**) and (**4d**), respectively. In contrast, the *R* products were preferentially formed from both (**4c**) and (**4d**) in the hydrogenations catalysed by complex (**2**) (Table 1).

The detailed mechanism of asymmetric hydrogenation of *N*-acyldehydroamino acids by chiral diphosphinerhodium(I) complexes, including the rate- and enantioselectivity-determining steps, has been elucidated by Brown and Halpern.[16] But hydrogenations of alkenes catalysed by a d^6-Ru^{II} centre, with preferred octahedral co-ordination, have been considered more complicated than those at a square-planar d^8-Rh^I centre.[7c] It was supposed that hydrogenations of simple alkenes with $[RuHCl(PPh_3)_3]$ involved the bis-phosphine species,[17] but as for an asymmetric hydrogenation of prochiral olefins including ruthenium-diphosphine species,[14] a reasonable reaction pathway and the origin of stereoselectivity for overall catalysis have not yet been completely clarified. As described previously, we postulate the solvated Ru^{II} species (**I**), which is regarded as a bis-phosphine analogue, as the catalytically active species. Taking into consideration some discussions[7c,14,15,17] on the mechanism of Ru complex catalysed hydrogenations, as well as the results obtained in this study, a tentative sketch for a part of the catalytic cycle of asymmetric hydrogenations mediated by (**I**) is given in Scheme 3. One of the biggest differences between the Ru and Rh complex catalysed cycle is the octahedral structure of the alkene ligating complex in the Ru cycle. In the Rh system, the Rh^I-alkene complex was isolated and identified as having a four-co-ordinate square-planar structure.[18] Since the configuration of the hydrogenated product is fixed when an olefinic group of the substrate is co-ordinated to the metal atom, this structural difference may play an important roll in the enantiofacial differentiation in these two types of catalysis.

It should also be noted that the proposed Ru-(*R*)-BINAP catalysed cycle step (ii), in which a Ru^{II}-alkyl species (**III**) is produced by an intramolecular hydride shift reaction of a Ru^{II}-alkene complex (**II**), is, to a substantial degree, reversible. This presents a sharp contrast to that of the corresponding step in the Rh^I-diphosphine catalysed process which is virtually irreversible.[16]

Two facts support the reversibility of steps (i) and (ii) in the reactions of (*E*)-2-acetylaminocinnamic acid (**4e**). The catalytic hydrogenation of (**4e**) with (**2**) was incomplete after 24 h, a ^1H n.m.r. spectrum of the reaction mixture indicating that it contained a substantial amount of the (*Z*)-isomer (**4b**), in addition to unchanged (**4e**) and the hydrogenated product. Furthermore, it was found that upon treatment with a catalytic amount of complex (**3**) under an argon atmosphere (**4d**) was almost completely isomerized into (**4c**). In such a case where isomerization proceeds faster than the hydrogenation, the hydrogenation products from these isomeric substrates would have identical configuration and enantiomeric purity. However, in the Rh-(*R*)-BINAP catalysed hydrogenation, the (*E*)-substrate (**4d**) is assumed to be chelated to rhodium through a carboxylate group[19] and the *Si*-face of the olefin functionality [while the (*Z*)-substrate (**4c**) ligates through an amide carbonyl and the *Re*-face] and to be converted into an (*R*)-product without any isomerization. The appreciable differences which emerged from the hydrogenation results of these substrates with (**2**) and (**3**) as catalysts (Table 1), suggested an incomplete isomerization of (**4d**) to (**4c**). At present, not all the data have been rationalized and the origin of enantioselection brought about by the Ru-(*R*)-BINAP catalysts still remains unspecified.

Asymmetric Hydrogenation of Methylenesuccinic Acid and Its Derivatives.—In the foregoing section we established the efficient catalytic activity of complexes (**2**) and (**3**) for the asymmetric hydrogenation of 2-acylaminoacrylic and 2-acylaminocinnamic acids. Encouraged by these results we investigated the ability of (**2**) and (**3**) to catalyse the asymmetric hydrogenation of methylenesuccinic acid (**6a**), where the steric arrangement of the C=C double bond and the carboxyl group at C-4 is the same as that of C=C and C=O of the acylamino function in (**4a**) (see Scheme 4). Such an arrangement of two



Scheme 4. Asymmetric hydrogenation of (**4a**) and (**6a**)

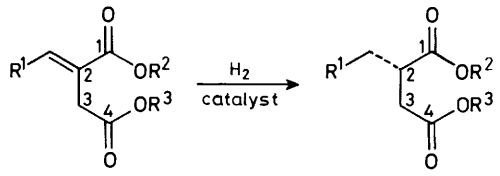
functional groups in a molecule has been suggested as an essential prerequisite to the Rh^I-diphosphine complex catalysed asymmetric hydrogenation.[1b] Nevertheless most Rh^I complexes of chiral diphosphines so far examined have been reported to be poor catalysts for effecting the hydrogenation of (**6a**) with high e.e., behaviour which contrasts with that of the Rh^I complexes of BPPM[20] and its analogues.[21,22] Several Ru^{II} catalysts containing DIOP were also found to be poor catalysts for the asymmetric hydrogenation of (**6a**) in terms of activity and enantioselectivity.

Since complex (**3**) effected the highest selectivity in the asymmetric hydrogenation of (**4a**), (**6a**) was first hydrogenated under mild conditions with (**3**) as the catalyst to give, in high yield, (*S*)-methylsuccinic acid (**7a**) having 86% o.p. (see Table 2). It is notable that the direction of asymmetric induction in this conversion is regarded as intrinsically identical with that found

Table 2. Asymmetric hydrogenation of methylenesuccinic acid and related compounds[a]

Substrate	Catalyst	Time (h)	Conversion (%)	O.p. (%)[b]
(6a)	**(2)**	24	100	88
	(3)	24	100	86
(6b)	**(2)**	24	100	79
(6c)	**(2)**	24	100	60
	(3)	24	100	54
(6d)	**(2)**	24	96	68
	(3)	24	71	54
(6e)	**(2)**	24	94	90
	(3)	24	56	88
(6f)	**(2)**	48	100	72
	(3)	48	17	48
(6g)	**(2)**	48	20	0
	(3)	48	10	0
(8)	**(3)**	24	39	34[c]
(9)	**(3)**	24	0	—

[a] Reaction conditions: substrate, 1.5 mmol; substrate/catalyst = 50 (catalyst as Ru atom); THF–EtOH (1:1; 30 cm^3); triethylamine, 1.8 mmol [added to catalyst (**2**) system]; H_2, 2 atm; 35 °C. [b] Optical purities are determined on the basis of the reported maximum rotations: (*R*)-methylsuccinic acid [(*R*)-(**7a**)], $[\alpha]_D^{20}$ +16.88° (*c* 2.2 in EtOH) (E. Berner and R. Leonardsen, *Liebigs Ann. Chem.*, 1939, **538**, 1); (*S*)-benzylsuccinic acid [(*S*)-(**7e**)], $[\alpha]_D^{25}$ −27° (*c* 2 in AcOEt) (S. G. Cohen and A. Milovanovic, *J. Am. Chem. Soc.*, 1968, **90**, 3495). [c] Product contains the (*R*)-isomer in excess.



(6) (7)

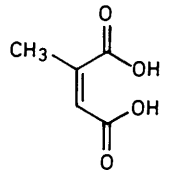
a; $R^1 = R^2 = R^3 = H$
b; $R^1 = H, R^2 = Me, R^3 = H$
c; $R^1 = R^2 = H, R^3 = Me$
d; $R^1 = H, R^2 = R^3 = Me$
e; $R^1 = Ph, R^2 = R^3 = H$
f; $R^1 = Ph, R^2 = H, R^3 = Me$
g; $R^1 = Ph, R^2 = R^3 = Me$

Scheme 5. Asymmetric hydrogenation of methylenesuccinic acid and its derivatives

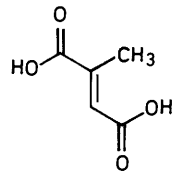
in the reaction of (**4a**) to *N*-acetyl-(*R*)-alanine (see Scheme 4). The successful result with (**6a**) prompted us to conduct asymmetric hydrogenations of substrates (**6b**—**g**) under mild conditions (Scheme 5). The results thus obtained were summarized in Table 2.

The hydrogenation of (**6a**) was catalysed by complex (**2**) in the presence of triethylamine, to afford (*S*)-methylsuccinic acid (**7a**) with a high o.p. (88%). In the presence of (**2**) or (**3**) as the catalyst, (**6b** and **c**), the monomethyl esters of (**6a**), were also completely converted into the saturated products within 24 h, but the optical purities of the products were reduced in comparison with those from (**6a**). Especially significant was the drop in optical purity of the product derived from C-4 methyl ester (**6c**) compared with that from the C-1 methyl ester (**6b**). Further, it was found that reduction of the diester (**6d**) was incomplete after 24 h, an indication that esterification lowered the catalytic reactivity. In contrast it was reported[23] that the effects of esterification on the hydrogenations of (**6a**, **c**, **d**) using Rh^I-DIPAMP catalyst were markedly different from those exhibited by the Ru-(*R*)-BINAP catalysts described above. Thus, in terms of reactivity and enantioselectivity the diester (**6d**) was a better substrate for the Rh catalyst than the diacid (**6a**).

The hydrogenated product from citraconic and mesaconic acids, (**8**) and (**9**), are methylsuccinic acid, similarly obtained from (**6a**). In order to elucidate the influences arising from different orientations of functional groups in these substrates, the hydrogenations of (**8**) and (**9**) were examined employing complex (**3**) as the catalyst. Hydrogenation of (**8**) was in-



(8)



(9)

complete within 24 h, giving, interestingly, the (*R*)-isomer in excess (34% o.p.); no hydrogenation of (**9**) was observed. These results suggest that in a substrate the steric arrangement exemplified in (**6a**) of a C=C double bond and a carboxy group, is essential to ensure catalytic activity towards alkene hydrogenation by complexes (**2**) and (**3**).

A further difference between (**6a**) and (**8**) or (**9**) which may affect the results is that the last two alkenes are trisubstituted, while the first is disubstituted. Although benzylidenesuccinic acid (**6e**) is a trisubstituted alkene, its stereochemical array of C=C and carboxy functions is the same as that in (**6a**). Hence the hydrogenation of (**6e**) was carried out to see the effects of trisubstitution. Table 2 reveals that the reaction rate for (**6e**), in comparison with that for (**6a**), was markedly decreased, particularly where complex (**3**) was used as catalyst. However, the optical purities of the products from (**6e**) (88—90%) were approximately the same as the corresponding values for the reactions of (**6a**). It is evident, therefore, that the arrangement of functional groups is an important factor in ensuring efficient asymmetric hydrogenation with the catalysts (**2**) and (**3**).

The esterification of carboxy groups in the diacids (**6a**) and (**6e**) also resulted in a decrease in the reactivity and/or selectivity for the hydrogenation with Ru-(*R*)-BINAP catalysts (Table 2). Indeed, the diester (**6g**) was barely reduced with complexes (**2**) and (**3**) even after a longer reaction period (48 h), and the products showed no detectable optical activities. Thus we conclude that the best way to achieve effective asymmetric hydrogenation of (**6e**) or its analogues is to employ the diacid form of the substrates and to perform the hydrogenations in the presence of triethylamine using complex (**2**) as the catalyst.

Experimental

Optical rotations were measured with a JASCO DIP-360 digital polarimeter. ^1H N.m.r. spectra were obtained with a JEOL GX-400 or Hitachi R-40 spectrometer.

All solvents used (tetrahydrofuran, ethanol, and toluene) were dried, distilled, and stored under a nitrogen atmosphere. Commercially available 2-acetylaminoacrylic acid (**4a**), methylenesuccinic acid (**6a**), dimethyl methylenesuccinate (**6d**), and 4-methyl hydrogen methylenesuccinate (**6c**) were used as received. 2-Acetylaminocinnamic and 2-benzoylaminocinnamic acids (**4b**) and (**4c**) were prepared by literature methods.[24] 1-Methyl hydrogen methylenesuccinate (**6b**) was also prepared by the reported method.[23] Benzylidenesuccinic acid and its esters (**6e**—**g**) were obtained by the Stobbe reaction.

Preparation of $Ru_2Cl_4[(R)\text{-BINAP})_2NEt_3$ (**2**).—A mixture of $[RuCl_2(COD)]_n$[25] (333 mg, 1.19 mmol), BINAP (849 mg, 1.36 mmol), and triethylamine (1 ml) in toluene (20 ml) was refluxed for 3 h. The toluene was then removed under reduced pressure and the resulting solid was washed with toluene (3 ml) and ether (3 ml × 3). The orange-red precipitate was dissolved in

methylene dichloride (4 ml), the solution filtered to remove insoluble solid, and the filtrate diluted with ether to give the crystalline complex. The orange-red powder was filtered off, washed with ether (×3), and dried *in vacuo* (79% yield, 796 mg).

Preparation of $RuHCl[(R)\text{-}BINAP]_2$ (**3**).—To a suspension of $[RuCl_2(COD)]_n$ (146 mg, 0.521 mmol) in ethanol (15 ml) were added (*R*)-BINAP (650 mg, 1.04 mmol) and triethylamine (1 ml), and the mixture was refluxed for 3 h under a nitrogen atmosphere to give a yellow precipitate. This was filtered off, washed successively with ethanol (5 ml) and ether (5 ml ×3), and dried *in vacuo*. The resulting yellow powder was dissolved in methylene dichloride, and the solution filtered and diluted with ether to give a yellow powder which was collected, washed with ether, and dried *in vacuo* (51%, 369 mg).

Hydrogenation Procedure.—All the hydrogenations were carried out in a 50 ml glass tube reactor except for the reaction under 100 kg/cm^3 of H_2 for which a 100 ml stainless steel autoclave was used.

Under an argon atmosphere, catalyst (0.030 mmol), substrate (1.50 mmol), and, as required, triethylamine (1.8—2.0 mmol), were introduced into the reactor, and the solvent THF–ethanol (1:1; 30 cm^3) was added. The atmosphere was then replaced with hydrogen and the solution was allowed to react under the prescribed conditions. On completion of the reaction, the solvent was removed under reduced pressure. The products from 2-acetylaminoacrylic acid (**4a**) and 2-acetylaminocinnamic acid (**4b**) were then recovered by the following procedure. The residue was extracted with boiling water, and the extract was treated with cation exchange resin (Dowex 50W-X8, H^+ form) and filtered. The filtrate was evaporated to dryness to give the product.

The residues from other substrates in the form of free acid were dissolved in aqueous sodium hydroxide (0.5M), and washed three times with diethyl ether. The aqueous layer was acidified with hydrochloric acid (1M), and extracted three times with diethyl ether. The extracts were combined, dried ($MgSO_4$), and evaporated to give the products.

The residues from the ester substrates were stirred in aqueous sodium hydroxide (1M) overnight, after which the solutions were treated as those from the acidic substrates.

The conversion for each hydrogenation was determined from the ^1H n.m.r. spectrum of the reaction mixture. The optical purities of the products were determined by the optical rotation values of the mixtures.

Acknowledgements

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