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Asymmetric hydrogenation of prochiral carboxylic acids catalyzed by the five-coordinate ruthenium(II)-hydride complex $[RuH(binap)_2]PF_6$ (binap = (*R*)- or (*S*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) *

Masahiko Saburi [a], Hiroshi Takeuchi [a], Masamichi Ogasawara [a], Touru Tsukahara [a], Youichi Ishii [b], Takao Ikariya [b], Tamotsu Takahashi [a] and Yasuzo Uchida [a]

[a] *Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113 (Japan)*
[b] *Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113 (Japan)*

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Abstract

The five-coordinate complex $[RuH(binap)_2]PF_6$ (I, binap = (*R*)- or (*S*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) has been found to have sufficient catalytic activity for asymmetric hydrogenation of itaconic acid and other prochiral carboxylic acids under mild conditions. The catalytic hydrogenation of itaconic acid by I was examined under a variety of conditions, and the addition of triethylamine was found to effect high enantioselectivities (> 90% ee). ^1H and ^{31}P NMR examinations of reaction mixtures of I and itaconic acid under conditions similar to the hydrogenation suggested the formation of ruthenium species containing one binap chelate.

Introduction

Previously [1] the preparation and some reactions have been reported of a five-coordinate ruthenium(II) complex $[RuH(binap)_2]PF_6$ (I, binap = (*R*)- or (*S*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl [2]). I forms a mixture of two isomers in solution, and both stereoisomers of the $[RuH(binap)_2]^+$ cation assume square-pyramidal geometry (*trans* and *cis* form, Fig. 1a, b). I is readily converted into a molecular hydrogen complex $[RuH(\eta^2\text{-}H_2)(binap)_2]PF_6$ on contact with H_2 gas (Fig. 1c).

Correspondence to: Dr. M. Saburi, Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan.

* Dedicated to Professor Akio Yamamoto upon his retirement from Tokyo Institute of Technology and in honor of his contribution to organometallic chemistry.

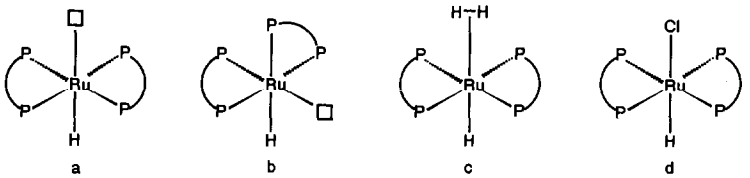
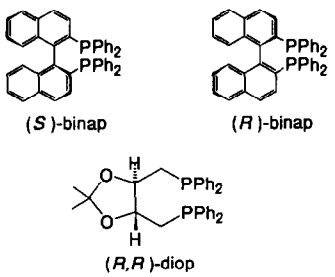


Fig. 1. Structures of Ru–binap complexes: a, *trans* form of $[RuH(binap)_2]^+$; b, *cis* form of $[RuH(binap)_2]^+$; c, *trans*-$[RuH(\eta^2\text{-}H_2)(binap)_2]^+$; and d, *trans*-$RuHCl(binap)_2$; a small square represents a vacant coordination site in a and b.



The excellent catalytic activity of Ru–binap systems for asymmetric hydrogenation of a variety of substrates has attracted considerable attention in recent years [3–5]. Among the Ru^{II}–binap complexes investigated in this context such as $Ru_2Cl_4(binap)_2(NEt_3)$ [4] and $Ru(RCOO)_2(binap)$ (R = CH_3–, CF_3–, *etc.*) [5], *trans*-$RuHCl(binap)_2$ II [6] provides a unique example that contains two binap ligands per Ru atom. We have proposed [4] that the five-coordinate $[RuH(binap)_2]^+$ cation could be an activated form of the coordinatively saturated complex II. Thus, the dissociation of a Cl^- from II should lead to the formation of the *trans* isomer of the five-coordinate species (Fig. 1a, d). Asymmetric catalytic hydrogenation of several prochiral carboxylic acids with I and II were therefore carried out to compare their catalytic properties.

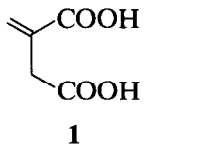
In order to find factors that affect enantioselectivity in hydrogenation catalyzed by I, the effects of reaction temperature, hydrogen pressure, and the addition of triethylamine (NEt_3) on the enantiomeric purities of the products were examined with regard to the catalytic hydrogenation by I of itaconic acid. Asymmetric hydrogenation, catalyzed by transition metal complexes, of this dicarboxylic acid has been extensively investigated. The observation that its hydrogenation proceeds more selectively in the presence of NEt_3 than in its absence prompted us to investigate the reactions of complex I with itaconic acid in the presence or absence of NEt_3 under conditions similar to those of the hydrogenation.

The ^1H and ^{31}P NMR measurements of a mixture involving I, itaconic acid, and NEt_3 indicated the liberation of a binap from I, which resulted in the formation of a new ruthenium species containing only one binap chelate. Another type of binap dissociation was also detected in the absence of NEt_3, although most of the I remained unchanged. We will discuss the differences in NMR behavior among Ru–binap species in reaction mixtures, which should be related not only to the features of truly catalytically active species, but also to the asymmetric inductions effected under the corresponding conditions.

Results and discussion

Asymmetric hydrogenation of itaconic acid catalyzed by [RuH((R)-binap)$_2$]PF$_6$ (R–I)

We previously reported [4b] that RuHCl((*S*)-binap)$_2$ (S–II) effects asymmetric hydrogenation of itaconic acid to afford (*R*)-methylsuccinic acid of high optical purity. In order to compare the catalytic activity and selectivity of the five-coordinate complex [RuH(binap)$_2$]PF$_6$ I with II, we first tested the hydrogenation of itaconic acid (**1**) using I as the catalyst. The complexes I and II containing (*R*)- and (*S*)-binap as the ligands will be referred to hereafter as *R*–I and *R*–II, and *S*–I and *S*–II, respectively.



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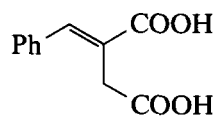

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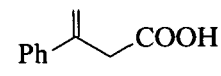

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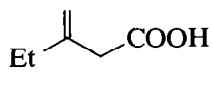

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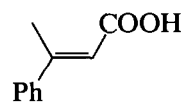

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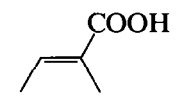

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As expected, complex *R*–I displayed sufficient catalytic activity to hydrogenate **1** under mild conditions. Thus, under an initial H_2 pressure of 3 atm at 50°C (substrate/catalyst (S/C) = 100, no NEt_3 added), **1** was hydrogenated completely within 24 h to give the product (*S*)-methylsuccinic acid (*S*–**2**) with a selectivity (76% ee) comparable to that obtained [7*] using *R*–II under the same conditions (see Table 1, entries 1 and 16). As will be described later, I and II displayed comparable enantioselectivities in the asymmetric hydrogenation of other prochiral carboxylic acids.

With a view to attain sufficient selectivity for the complex I-catalyzed asymmetric hydrogenation of **1**, the effects of temperature, H_2 pressure, and addition of NEt_3 on the enantiomeric purities of the products were investigated, and the results are listed in Table 1. Under low H_2 pressure (1–3 atm), the hydrogenation products always showed moderate to high enantiomeric excess, while the selectivity was markedly reduced under higher initial H_2 pressure (50 atm, entries 5 and 10). The enantioselectivity of hydrogenation catalyzed by Ru(CH_3COO)$_2$(binap) is known [5b] to be significantly affected by H_2 pressure, depending on the substrate. The pressure dependence of the enantioselectivity in the hydrogenation of **1** with complex I is similar to that in the hydrogenation of *E*-2-methyl-2-butenoic acid with the acetato complex.

The addition of NEt_3 had a striking effect on the asymmetric induction. When the molar ratio of amine *vs.* substrate (N/S) equals or exceeds unity, selectivities higher than 90% ee were achieved under low H_2 pressure in the temperature range 25–50°C (entries 6–9 and 12–15). Under these conditions, temperature had no significant effect on selectivity (see entries 6–9). In the absence of NEt_3, the

* Reference number with asterisk indicates a note in the list of references.

Table 1

Asymmetric hydrogenation of itaconic acid catalyzed by $[RuH((R)\text{-binap})_2]PF_6$ and related complexes

Entry	Catalyst [a]	H_2 (atm)	Temperature (°C)	N/C [b]	N/S [c]	Conversion (%)	ee (%) [d]
1	*R*–I	3	50	0	0	100	76
2		3	25	0	0	100	57
3		1	50	0	0	100	81
4		1	25	0	0	75	83
5		50	25	0	0	100	1
6		3	25	200	2	100	91
7		3	50	200	2	100	90
8		1	25	200	2	83	94
9		1	50	200	2	100	89
10		50	25	200	2	100	19
11		3	25	50	0.5	100	71
12		3	25	100	1	100	90
13		3	25	400	4	100	93
14		3	25	200	1	100	93
15		3	25	50	2	100	94
16	*R*–II	3	50	0	0	100	82
17		3	25	200	2	100	93
18	III	3	50	0	0	100	31
19		3	50	50	0.5	100	23

[a] Catalysts: *R*–I $[RuH((R)\text{-binap})_2]PF_6$; *R*–II, $RuHCl((R)\text{-binap})_2$; III, $[RuH(diop)_2]PF_6$. [b] Molar ratio of triethylamine to catalyst. [c] Molar ratio of triethylamine to itaconic acid. [d] The (*S*) enantiomer was preferentially formed.

asymmetric induction of complex I-catalyzed hydrogenation of **1** showed an unusual temperature dependency. The product obtained at 50°C has a higher ee value (76%) than that obtained at 25°C (57%) under an initial H_2 pressure of 3 atm (Table 1, entries 1 and 2). The fact that the ee of the product at an elevated temperature is higher than that obtained at a lower temperature is opposite to the general tendency of asymmetric induction encountered in most asymmetric reactions. Under an H_2 pressure of 1 atm, the selectivities at 25°C and at 50°C were almost equal.

We conclude that there are at least two reaction paths for the complex I-catalyzed hydrogenation under amine-free conditions, and that the dominant active species generated from I at 50°C is different from that formed at 25°C. It was also anticipated that these active species formed in the absence of NEt_3 are very distinct from those formed in the presence of amine. Evidence for formation of different active species or their precursors from complex I under respective conditions will be presented later.

Asymmetric hydrogenation of prochiral carboxylic acids

Complex I-catalyzed asymmetric hydrogenations of several prochiral carboxylic acids **3**–**7** were carried out under two sets of representative conditions employed for the hydrogenation of itaconic acid; *i.e.*, (i) at 50°C without NEt_3, and (ii) at 25°C in the presence of NEt_3. The results of hydrogenation are summarized in Table 2.

Table 2

Asymmetric hydrogenation of prochiral carboxylic acids [a]

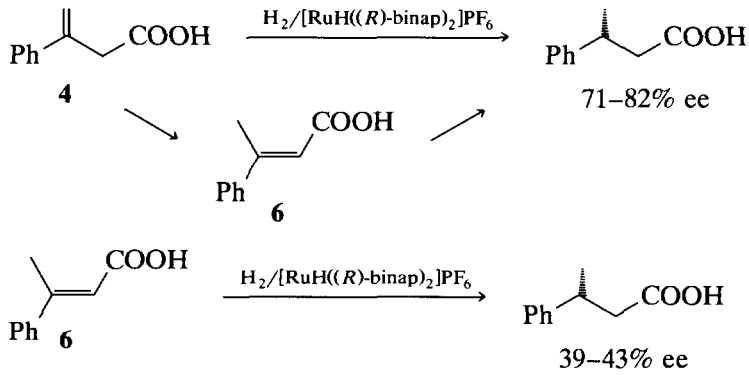
Substrate	Catalyst [b]	N/S	Temperature (°C)	Conversion (%)	ee (%)	Configuration
3	*R*-I	0	50	100	82	(*S*)
	R-I	1	25	100	72	(*S*)
	R-I	2	25	100	75	(*S*)
	R-II	0	50	100	80	(*S*)
4	*R*-I	0	50	100	71	(*R*)
	R-I	1	25	100 [c]	82	(*R*)
	S-II	0	50	100	71	(*S*)
	III	0	50	100	32	(*R*)
5	*R*-I	0	50	100	69	(*S*)
	R-I	1	25	100	60	(*S*)
	S-II	0	50	100	73	(*R*)
	III	0	50	100	23	(*S*)
6	*R*-I	0	50	100	39	(*R*)
	R-I	1	50	100	43	(*R*)
	S-II	0	50	93	46	(*S*)
7	*R*-I	0	50	100	77	(*R*)
	R-I	1	25	100	88	(*R*)
	R-II	0	50	100	79	(*R*)

[a] Reaction conditions: H_2, 3 atm; substrate/catalyst = 100; time, 24 h; solvent, THF–EtOH (1:1). [b] Catalysts: I, $[RuH(binap)_2]PF_6$; II, $RuHCl(binap)_2$; III, $[RuH((R,R)diop)_2]PF_6$. [c] 3-phenylbutanoic acid (84%) + 3-phenyl-2-butenoic acid (14%).

Benzylidenesuccinic acid (**3**), a phenyl-substituted derivative of **1**, was hydrogenated under the above conditions to give (*S*)-benzylsuccinic acid (72–82% ee). Under conditions (i), the asymmetric induction for **3** is almost equal to that for **1**, suggesting that there is no significant difference at the stereocenter-determining stage in this catalytic cycle. Under conditions (ii), the selectivity for **3** is considerably lower than that for **1**. This may be due to the substituent effects of the phenyl group in **3**.

The hydrogenation of 3-phenyl-3-butenoic acid (**4**) and 3-ethyl-3-butenoic acid (**5**), both of which contain a vinylidene group and a carboxyl function at the β-position as in **1**, proceeded smoothly under the same conditions. The enantiomeric purities of the products were somewhat lower than those of **1**, especially in the case of **5**. It was observed, further, that the hydrogenation product of **4** in the presence of NEt_3 was contaminated with 3-phenyl-2-butenoic acid (**6**), which should be formed through the isomerization of **4** promoted by some ruthenium species (see Scheme 1).

As the hydrogenation product of **6** is same as that of **4**, the asymmetric hydrogenation of **6** was also carried out. It turned out that 3-phenylbutanoic acid obtained by the hydrogenation of **6** has only moderate enantiomeric purities (39–43% ee), in spite of the fact that it assumes the identical configuration (*R*) as that from **4**. This suggests that the hydrogenation products of **4** should include those arising from the preceding isomerization into **6** and successive hydrogenation (Scheme 1), and that the by-pass route is responsible, at least in part, to the lower



Scheme 1. Hydrogenation of **4** and **6** catalyzed by complex I.

selectivity for **4** in comparison with **1**. Although none of the corresponding unsaturated acid, 3-methyl-2-pentenoic acid, which can be formed by double bond migration, was detected in crude hydrogenation products of **5**, the insufficient enantioselectivity for this substrate would be ascribed to the influence of a similar two step process concomitant taking place with the ordinary hydrogenation.

The asymmetric hydrogenation of (*E*)-2-methyl-2-butenoic acid (tiglic acid, **7**) was performed under the same conditions. The selectivities (77–88% ee), are considerably higher than those for **6**. While both **6** and **7** are substituted acrylic acids, the pattern of substitution differs: the phenyl and methyl groups at C_3 for **6** and the methyl groups at C_2 and C_3 for **7**. These results suggest that differences of substitutions in analogous substrates lead to significant differences of selectivity in asymmetric hydrogenation.

Catalyst effects

As we postulated in the Introduction complex I could be an activated form of complex II. The five-coordinate species generated by the dissociation of Cl^- from II is identical with the complex cation of I. Indeed, II was found to be effective for the asymmetric hydrogenation of itaconic acid under the same conditions employed for I-catalyzed reactions (Table 1). Further, the II-catalyzed hydrogenation of other unsaturated carboxylic acids in the absence of NEt_3 proceeded to give the expected products having enantiomeric purities almost equal to those obtained with complex I (Table 2). These facts strongly suggest that the change of II into the five-coordinate species $[RuH(binap)_2]^+$ should be the initial process for the generation of catalytically active species from II under NEt_3-free conditions.

Another chiral five-coordinate complex $[RuH(diop)_2]PF_6$ (III, diop = (*R*,*R*)-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane) was recently prepared by essentially the same procedure as that for I [8]. Asymmetric hydrogenations of typical unsaturated carboxylic acids catalyzed by III were also carried out under the same conditions (Tables 1 and 2).

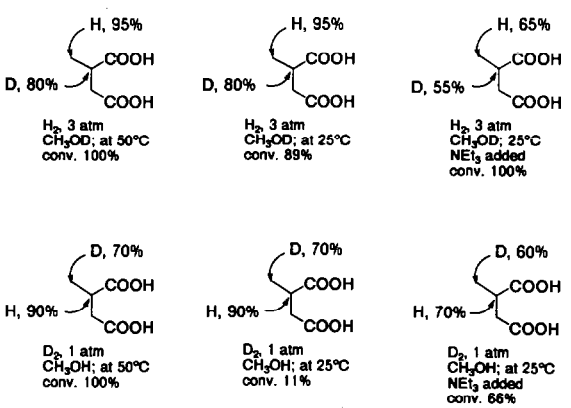
Although the hydrogenations with complex III went to completion for three substrates examined (**1**, **4** and **5**), the products showed distinctly lower enantiomeric purities (< 40% ee) compared with those from the corresponding I-catalyzed reactions. Evidently the effectiveness of binap as the ligand for Ru^{II} complex catalysts is greatly superior to that of diop.

Deuterium distribution in hydrogenation products using D_2 or CH_3OD as deuterium sources

Recent mechanistic investigations [9,10] on the asymmetric hydrogenation of unsaturated acids employing $Ru(CH_3COO)_2$(binap) as a catalyst have shown that one of the two hydrogens incorporated into the products originates from a solvent methanol, and the other from a gaseous hydrogen molecule. Deuterium incorporation study [9] using D_2 or CH_3OD as sources indicated that the proton from hydrogen gas and that from methanol are introduced, respectively, to the β and α positions of α,β-unsaturated acids, but to the γ and β positions for a β,γ-unsaturated acid.

Itaconic acid **1** has two carboxyl groups and possesses structural features of both the α,β- and the β,γ-unsaturated acids. In order to clarify which partial structure actually works in the catalytic cycle, the pattern and extent of deuterium incorporation were examined by ^1H NMR analysis of methylsuccinic acid obtained under a D_2 atmosphere or in CH_3OD solvent. The results of hydrogen isotope incorporation are shown in Scheme 2, with the reaction conditions.

It is evident that the hydrogen from gaseous H_2 is dominantly introduced to the methyl group and the proton from a methanol OH group to the methine part. This indicates that itaconic acid interacts as a β,γ-unsaturated acid with the Ru–binap species in the course of hydrogenation. In addition, solvent methanol commonly participates in the catalytic cycle promoted by Ru–binap catalysts, even if the truly active Ru–binap species, generated from such independent precursors as complex I and $Ru(CH_3COO)_2$(binap), may be fairly different from each other. Further, the addition of NEt_3 causes a more significant disorder for the deuterium incorporation, presumably due to an enhanced exchange of hydrogen isotope between gaseous hydrogen and solvent, promoted by the Ru species. We consider that such a difference in deuterium incorporation accords with the observation that the enantioselectivity obtained in the presence of NEt_3 is greater than that in its absence.



Scheme 2. Hydrogen incorporation to methyl and methine positions of methylsuccinic acid formed by hydrogenation of itaconic acid catalyzed by complex I.

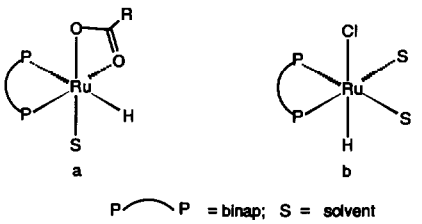


Fig. 2. Proposed structures of catalytically active species derived from $Ru(CH_3COO)_2$(binap) (a), and from *trans*-RuHCl(binap)$_2$ (b).

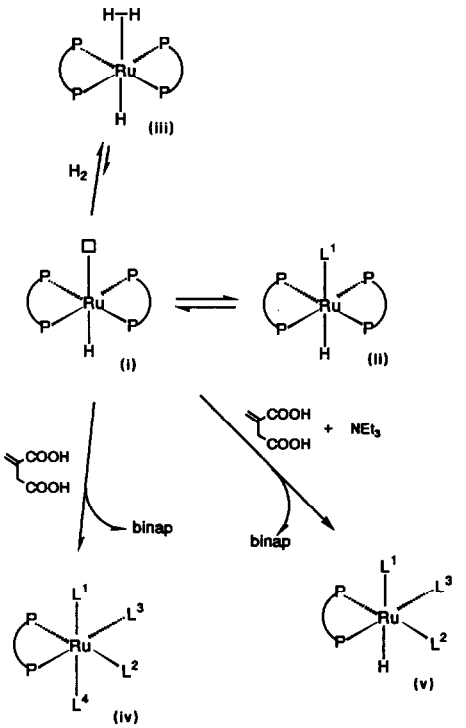
^1H and ^{31}P NMR examinations of interactions of complex I with itaconic acid and triethylamine

It had been expected that a coordinatively saturated six-coordinate ruthenium(II) complex employed to catalyse hydrogenation or other reactions would be ineffective unless it were converted into a coordinatively unsaturated (or solvent coordinated) species. For instance, a Ru–binap species having a hydride ligand (Fig. 2a) was postulated [9] as the active form derived from $Ru(CH_3COO)_2$(binap). We have proposed [4b] the transformation of six-coordinate complex II into a Ru species with a binap and a hydride (Fig. 2b) in the presence of NEt_3 under hydrogen atmosphere. In these cases, however, NMR examinations of reaction mixtures provided no direct evidence for the presence of such coordinatively unsaturated mono-hydride complexes.

It is noteworthy that the five-coordinate cation $[RuH(binap)_2]^+$ is by itself coordinatively unsaturated (see Scheme 3, (**i**)). It is probable that a solvent molecule occupies the vacant site of the five-coordinate cation **i** to afford a solvent coordinated species (**ii**; L^1 = solvent) in solution (Scheme 3). Under a hydrogen atmosphere, however, it is readily converted [1] into the molecular hydrogen complex $[RuH(\eta^2\text{-}H_2)(binap)_2]^+$ (**iii**) as shown in Scheme 3. We examined the conversion of **i** into other coordinatively unsaturated or solvent coordinated species under conditions similar to hydrogenation, by following ^1H and ^{31}P NMR spectral changes of a mixture of complex I and itaconic acid **1** under various conditions.

The ^{31}P NMR spectra of complex I alone in a mixture of THF and methanol (1 : 1) and of a mixture of I and **1** (molar ratio, 1 : 50) in the same mixed solvent are shown in Fig. 3a, b. Importantly, we observed a singlet at δ −15.5 in Fig. 3b which is assignable to the non-coordinating binap. Further, two small signals at δ 29.5 and 63.8 appeared, in addition to the original signals due to the five-coordinate **i**. This indicates that a small portion of **i** loses one of two binap ligands to give rise to a coordinatively unsaturated mono-binap Ru species, although it is uncertain which of these signals should be ascribed to the latter. The mono-binap Ru^{II} species derived from **i** upon contact with **1** is given as **iv** in Scheme 3 (the ligands L^1–L^4 are not specified). However, the ^1H NMR spectrum revealed no apparent difference before and after the addition of **1**. We would not expect to detect the hydride signal of such a mono-binap species, because it would be expected to be very weak.

When H_2 gas was introduced into a solution containing I and **1** (1 : 50), the ^{31}P NMR signals of I disappeared completely and those of the molecular hydrogen



Scheme 3. Transformation of complex I under various conditions (see text).

complex $[RuH(\eta^2\text{-}H_2)(binap)_2]^+$ emerged (Fig. 3c). It should be noted that the signals of non-coordinating binap and of the new species **iv** were observed unchanged. This suggests that some highly unsaturated species such as **iv** exist in small concentrations under the hydrogenation conditions (without NEt_3, at 25–30°C).

To investigate further the unusual temperature dependence of enantioselectivity in the absence of NEt_3, the above sample solution was heated to 50°C for 1 h. However, no noteworthy change was seen in the ^{31}P NMR spectrum, both the signals of the H_2 complex **iii** and of the mono-binap species **iv** remaining practically unchanged.

We then directed our efforts toward elucidating the significant effects of NEt_3 on the selectivity. We observed that successive additions of 1 and NEt_3 to I (1 : 50 : 100 molar ratio) at ambient temperature resulted in a remarkable change in the NMR spectra in a short period. Thus, in the ^{31}P NMR spectrum, two doublets (δ 48.0 and 68.3, $J_{P,P} = 42.3$ Hz) and the singlet (δ −15.9) assignable to the free binap appeared as a result of the above treatments, while the signals of complex I disappeared (Fig. 4a). In accordance with the changes observed by ^{31}P NMR, the signals due to the Ru–H resonances of I were no longer apparent, but a doublet of doublets (δ −15.9, J(H,P) = 23.2 and 35.4 Hz) emerged in the hydride region of the ^1H NMR spectrum (Fig. 4b). These NMR features are consistent with the assumption that a new ruthenium(II) species coordinating both a binap and a hydride, in such a manner as **v** in Scheme 3, is produced almost quantitatively from **i** (or **ii**) without heating or introduction of H_2 gas.

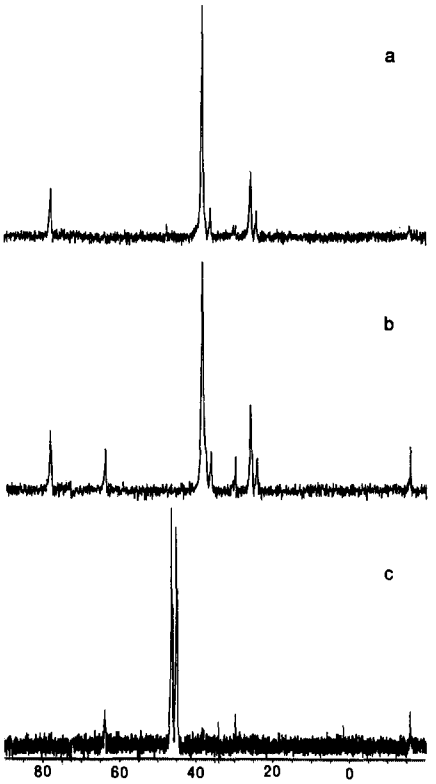


Fig. 3. ^{31}P NMR spectra in THF–CH_3OH (1:1): a, an isomeric mixture of complex I; b, a mixture of complex I and itaconic acid (1:50); and c, a mixture of I and itaconic acid (1:50) after introducing H_2 gas.

It is noteworthy that the structural characteristics of **v**, having only one binap chelate and a hydride, are the same as those of the proposed activated form of the diacetate complex (Fig. 2b) [9], although the remaining ligands in **v**, L^1–L^3, have not yet been determined. We consider that a mono-binap complex such as **v** should be the catalytically active species by itself or a catalytic precursor under the hydrogenation conditions in the presence of NEt_3. It is reasonable, therefore, that the results of complex I-catalyzed hydrogenation under these conditions are considerably different from those in the absence of NEt_3 (Tables 1 and 2).

In conclusion, we have detected by NMR two novel Ru^{II} species with only one binap ligand, **iv** and **v**, derived from the five-coordinate cation **i** under different conditions. The species **iv** is formed by a reaction of **i** with itaconic acid in the absence of NEt_3. The other (**v**) is readily generated by simultaneous additions of itaconic acid and NEt_3 to a solution of I. These species are expected to act as or to be converted into the principal active species under the respective reaction conditions.

Experimental

All the solvents used and triethylamine were dried and distilled by conventional methods, and stored under nitrogen. (*R*)- and (*S*)-binap were presented by

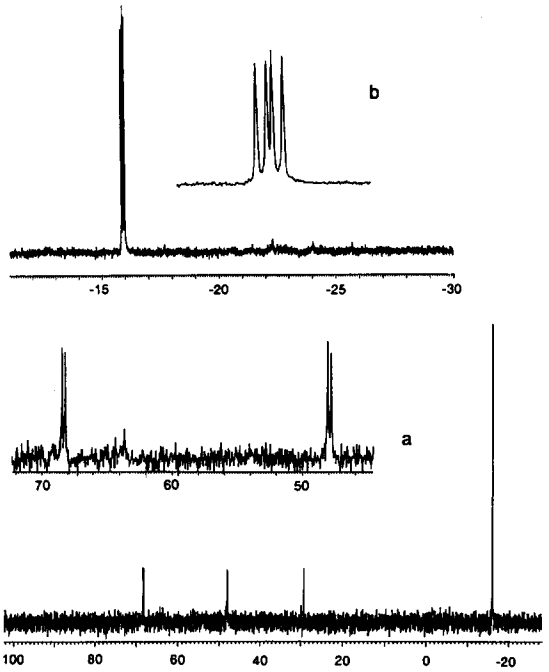


Fig. 4. NMR spectra of a mixture of complex I, itaconic acid, and NEt_3 (1:50:100): a, ^{31}P NMR spectrum in THF–CH_3OH; and b, ^1H NMR spectrum in THF-d_8-CD_3OD.

Takasago Research Institute Inc. 3-Phenyl-2-butenoic acid (**4**) and 3-methylenepentanoic acid (**5**) were prepared by reported methods [11,12].

Gas chromatographic (GC) analysis was performed with a Shimadzu GC-14A instrument equipped with a fused silica capillary column (Shimadzu CBP10, 25 m) and a flame ionization detector. High performance liquid chromatography (HPLC) was carried out with a Jasco VIP-2 apparatus equipped with a Shimadzu SPC-7A UV spectrometric detector and a Shimadzu Chromatopac CR-5A, employing chiral stationary columns Daicel CHIRALCEL-OB or -OD. ^1H NMR (400 MHz) and ^{31}P NMR (162 MHz) spectra were measured with a JEOL JNM-GX 400 spectrometer.

Hydridobis[(R)- or (S)-2,2'-bis(diphenylphosphino)-1,1',binaphthyl]ruthenium(II) hexafluorophosphate [RuH((R)- or (S)-binap)$_2$]PF_6 (I)

These complexes were prepared according to the reported method [13] with slight modifications. A mixture of $[RuH(cod)(NH_2NMe_2)_3]PF_6$ (IV) (0.242 g, 0.45 mmol) [14] and (*R*)- or (*S*)-binap (0.566 g, 0.91 mmol) in ethanol (10 ml) was heated under reflux for 2 h under a nitrogen atmosphere. The resultant mixture containing deep red precipitates was evaporated under reduced pressure, and the solid thus obtained was dissolved in THF. The solution was filtered and diethyl ether was added to the filtrate. Red fine-needle crystals were collected, washed three times with diethyl ether, and dried under reduced pressure (0.483 g, 72%). Anal. Found: C, 69.4; H, 4.5%. Calc. for $C_{88}H_{65}F_6P_5Ru$: C, 69.8; H, 4.4%.

Hydridobis[(R,R)-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane]ruthenium(II) hexafluorophosphate [RuH(diop)$_2$]PF$_6$ (III)

A mixture of IV (0.100 g, 0.187 mmol) and diop (0.195 g, 0.392 mmol) in ethanol (10 ml) was stirred at room temperature for 3 h. The deep-red solution was evaporated under reduced pressure to dryness at room temperature, and the residue was dissolved in dichloromethane. Hexane was added to afford an oily product, which solidified on standing for several days at room temperature. Anal. Found: C, 59.5; H, 5.5%. Calc. for $C_{62}H_{65}F_6O_4P_5Ru$: C, 59.9; H, 5.4%.

Asymmetric hydrogenation of prochiral carboxylic acids

A mixture of carboxylic acid (**1**, **3**–**7**) (1.0 mmol), catalyst (I, II, or III) (0.01 mmol) and triethylamine (as required) in a mixture of THF (5 ml) and ethanol (5 ml) was stirred under hydrogen for 24 h. The detailed reaction conditions are given in Tables 1 and 2. The solvent was removed under reduced pressure, and 1 M aqueous NaOH (10 ml) was added. After filtration, the aqueous layer was washed with chloroform, and then acidified with 2 M HCl to pH 1. The acidic aqueous solution was extracted three times with chloroform, and the dried chloroform solution was evaporated to give the crude product. An aliquot of the product was dissolved in THF and then treated with diazomethane to determine the conversion of hydrogenation by GC analysis.

Enantiomeric excesses of the products were determined as follows. Another aliquot of the product (*ca.* 0.1 mmol) was dissolved in THF (2 ml) and aniline (1.1 mol/carboxyl group), *N*,*N*′-dicyclohexylcarbodiimide (1.1 mol/carboxyl group), and 4-dimethylaminopyridine (2 mg) were added. The mixture was stirred at room temperature for 20 h, the precipitate was filtered off, and the filtrate was evaporated. The residue was purified by short column chromatography on silica gel with diethyl ether as an eluent. The enantiomeric purities of the amides thus obtained were determined by chiral HPLC analysis [15].

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