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Asymmetric isomerization of allylic compounds and the mechanism

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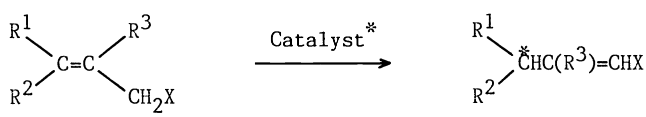
Abstract---Rhodium(I) complexes of the type [Rh(diphosphine)L_n]ClO_4 (L_n = n/2 molecules of solvent, diene, or diphosphine) are effective catalysts for 1,3-hydrogen migration of functionalized allylic compounds such as allylamines, allyl alcohols, allyl ethers, etc., and chiral diphosphine complexes cause asymmetric isomerizations. Per-aryldiphosphine with C_2 symmetry, binap, is the most effective ligand in all aspects and allylamine is the most suitable substrate; various kinds of allylamines are isomerized selectively to optically active (E)-enamines or imines with virtually perfect enantioselectivity (95-99 %ee) in high yields. Deuterium labeling experiments showed that this asymmetric isomerization of allylamines proceeds via highly stereospecific intramolecular 1,3-hydrogen migration. On the basis of the reaction intermediates detected by ^{31}P as well as ^{1}H NMR spectra and kinetic studies a plausible reaction mechanism is proposed for the catalysis. It is also concluded that the enantioselection is made at a stage of kinetically unimportance.

INTRODUCTION

Several transition metal complexes have been reported as effective catalysts for isomerization of functionalized allylic compounds (ref. 1). Almolst all of them, however, have only poor or no catalytic activity for the isomerization of allylic compounds having a trisubstituted olefin of the type 1 (R^1, $R^2 \neq$ H) (ref. 2), an essential substrate to achieve asymmetric isomerization and only a few examples of the asymmetric isomerization with very low optical inductions are available (ref. 3). Recently we have developed a highly efficient asymmetric

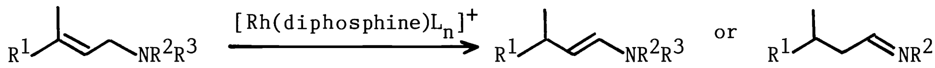


1   2   X = NR_2, OH, OR, etc.   (1)

isomerization of allylamine catalyzed by cationic rhodium(I) complexes of an optically active diphosphine (ref. 4). Here I want to describe the specific feature of the asymmetric catalysis, its extension to asymmetric isomerization of other allylic compounds, and the mechanistic aspects of the asymmetric isomerization of allylamines.

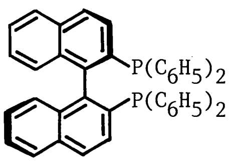
ASYMMETRIC ISOMERIZATION OF ALLYLAMINE

Cationic rhodium(I) complexes of the type [Rh(diphosphine)L_n]$^+$ (L_n = n/2 molecules of solvent or diene) are efficient isomerization catalysts for tert- and sec-allylamine to enamine or imine (ref. 4). In this isomerization only (E)-enamines were produced selectively. The catalytic activity is very sensitive to the property of a diphosphine ligand as well as to the kind

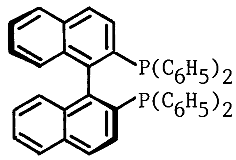


3 4 5(R^3 = H) (2)

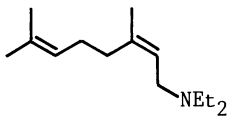
of ligand L_n. That decreases in the order significantly: per-aryldiphosphine > Ar_2P-X-PAr_2 (-X- = alkylene group) > per-alkyldiphosphine. A fully arylated diphosphine with C_2 chirality, binap (6) (ref. 5), was found to be the best ligand with respect to its activity and selectivity. For examples, the rhodium complex [Rh(binap)(cod)]ClO_4 (cod = 1,5-cyclooctadiene) isomerizes diethylnerylamine (7) or diethylgeranylamine (8) in THF to citronellal (E)-diethylenamine (9) in a yield over 96 % under fairly mild conditions (40 - 60 °C, 20 h), the double bond at C(6) being unaffected. The solvent complex $[Rh(binap)(S)_n]^+$ (S = solvent), which is prepared in situ from the diene complex by treating with hydrogen, is more active and the isomerization



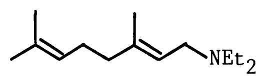
(R)-(+)-6



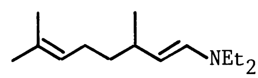
(S)-(-)-6



7



8

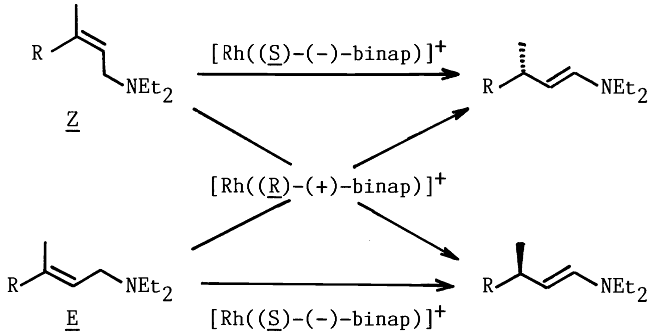


9

took place even at low temperature below -20 °C, though slowly (see below). When a diphosphine is used as L_n, the catalytic activity drops drastically and a bis(diphosphine) complex $[Rh(diphos)_2]ClO_4$ did not show any catalytic activity for the isomerization of 7 even at 120 °C, 18 h. If binap is employed as a diphosphine ligand, the bis(diphosphine) complex $[Rh(binap)_2]ClO_4$ showed also sufficiently high catalytic activity for the isomerization above 90 °C (ref. 6).

The first enantioselective hydrogen migration of tert-allylamine using cobalt complexes of a chiral diphosphine has been reported by Otsuka's group (ref. 7). The chemical and optical yields for the isomerization of 7 or 8, however, were at most 12 % and 30 %ee, respectively. A cationic rhodium complex of binap, [Rh(binap)(cod)]ClO_4 showed also excellent enantioselectivity for the isomerization of allylamines: 7 or 8 is convertible to an optically active (E)-enamine 9 in 95 to 99 %ee. A beautiful stereochemical correlation between the substrate geometry, chirality of binap, and the product configuration is present as shown in Scheme 1. Besides the diene complex, both $[Rh(binap)(S)_n]^+$ and $[Rh(binap)_2]^+$ gave equally high enantioselectivity in the same direction for the isomerization as the diene complex, though the catalytic activity varies considerably according to the catalyst precursors. As is obvious from the mirror image correlation, in order to obtain maximum optical yields it is essential to use isomerically pure substrates and enantiomerically pure binap. With highly purified reagents the optical yields of the isomerization of 8 by the (-)-binap-rhodium catalyst exceeded 99.0 % for a wide range of temperature (below 80 °C), the 3R configuration being produced. The temperature invariability of the chiral recognition is amazing. Above 100 °C, the optical yield starts to decrease slowly (98 %ee at 100 °C, 95 %ee at 140 °C). The present asymmetric isomerization of 8 is employed as a key step of the industrial production of

SCHEME 1

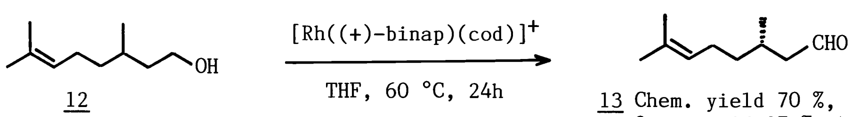


R = $(CH_3)_2C{=}CHCH_2CH_2$, simple alkyl, C_6H_5, etc.

l-menthol (ref. 8). Several representative results are summarized in Table 1. A secondary allylamine (10) was also isomerized by the present catalyst to give the corresponding optically active imine (11) in very high chemical and optical yields. As for the substrate allylamine (3), simple alkyl, phenyl, or hydroxyalkyl group besides prenylmethyl group can be employed as the substituent R^1. N-Phenyl- and N,N-diphenylallylamine, however, do not undergo the isomerization with the cationic rhodium(I) complexes. These results suggest the importance of nitrogen basicity in the substrate for effective catalysis.

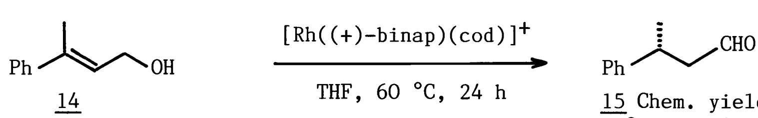
ISOMERIZATION OF OTHER ALLYLIC COMPOUNDS

The cationic rhodium(I) complex $[Rh(diphosphine)L_n]^+$ serves as an active catalyst also for isomerization of allylic compounds other than allylamines; e.g., allyl alcohol, allyl ether, or N-allylamide. In these isomerization also, binap is the best choice as a diphosphine ligand and several representative results are summarized in Table 2. Primary and secondary allylic alcohols isomerize smoothly to aldehydes and ketones respectively, though the yields of aldehydes are not so high due to further transformation of the product aldehydes in the presence of rhodium complexes. With a rhodium complex $[Rh((+)\text{-binap})(cod)]ClO_4$ allyl alcohols of the type 1 (R^1, $R^2 \neq H$, X = OH) can be smoothly isomerized to optically active aldehydes (eq.



(3)

12 → 13 Chem. yield 70 %, Opt. yield 37 %ee

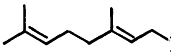
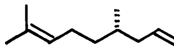
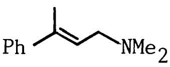
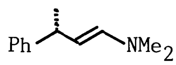
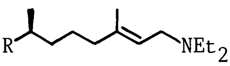
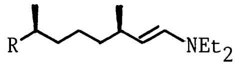
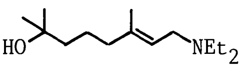
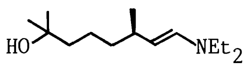


(4)

14 → 15 Chem. yield 47 %, Opt. yield 53 %ee

3,4). The optical yields, however, are very low compared with those realized in the isomerization of prochiral allylamines, though much higher than the hitherto reported examples of the asymmetric isomerization of allyl alcohols (ref. 3). Noteworthy is the fact that even an alcohol having a styrene-type conjugation can be isomerized (eq. 4). The stereochemical correlations were the same with those observed for the isomerization of allylamine. Isomerization of allyl phenyl ether and allylacetyl amide, however, produced E/Z mixtures of an enol ether and an enamide.

TABLE 1. Asymmetric isomerization of allylamines catalyzed by $[Rh(binap)L_n]ClO_4$ [a]

Substrate	Catalyst [b]	Product	Chemical yield(%)	Optical yield(%ee)
7	$[Rh((-)\text{-binap})(S)_n]^+$	(S)-9	95	93
"	$[Rh((+)\text{-binap})(cod)]^+$	(R)-9	94	95
"	$[Rh((+)\text{-binap})_2]^+$ [c]	"	13	96
"	$[Rh((-)\text{-binap})(cod)]^+$	(S)-9	97	92
8	$[Rh((+)\text{-binap})(cod)]^+$	"	94	96
"	$[Rh((-)\text{-binap})(cod)]^+$ [d]	(R)-9	99	99
"	$[Rh((-)\text{-binap})_2]^+$ [e]	"	100	98
 NHCy(10)	$[Rh((+)\text{-binap})(cod)]^+$	 NCy(11)	100	96
	$[Rh((+)\text{-binap})(cod)]^+$ [f]		83	90
	$[Rh((-)\text{-binap})_2]^+$ [g]		95	97 [h]
	$[Rh((-)\text{-binap})(nbd)]^+$ [g]		98	(+12°) [i]

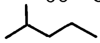
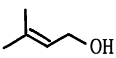
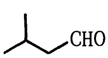
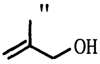
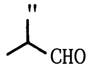
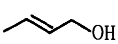
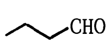
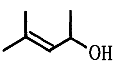
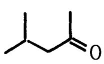
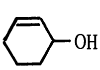
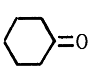
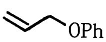
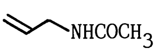
[a] [Substrate] = 0.44 M, [substrate]/[Rh] = 100, 40 °C, 23 h, in THF unless otherwise noted. [b] S = solvent; nbd = norbornadiene. [c] [Substrate]/[Rh] = 176. [d] [Substrate] = 2.5 M, [substrate]/[Rh] = 8,000, 80 °C, 4 h. [e] [Substrate] = 2.3 M, [substrate]/[Rh] = 8,000, 100 °C, 15 h. [f] 60 °C, 48 h. [g] [Substrate] = 2.3 M, [substrate]/[Rh] = 2,000, 100 °C, 15 h. [h] R =  (ref. 9). [i] $[\alpha]_D^{23}$ of the hydrolyzed aldehyde. The reported maximum rotation is +14.9° (ref. 10).

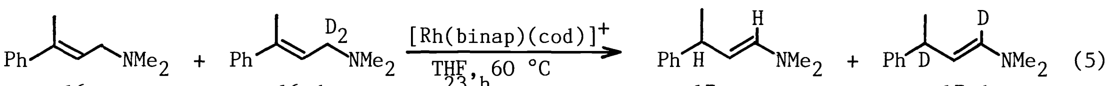
TABLE 2. Isomerization of allylic compounds catalyzed by $[Rh(diphosphine)L_n]ClO_4$ [a]

Substrate	Product	Catalyst [b]	Conversion (%)	Selectivity (%)	Remarks
		$[Rh(binap)(cod)]^+$	64	80	
"	"	$[Rh(binap)(S)_n]^+$	88	61	
"	"	$[Rh(dppb)(S)_n]^+$	50	24	
"	"	$[Rh(dipb)(S)_n]^+$	42	20	
		$[Rh(binap)(S)_n]^+$	99	90	
		"	87	93	
		"	88	34	
		"	82	98	
		"	100	97	E/Z = 87/13
		"	42	89	E,Z mixture

[a] [Substrate] = 0.2M, [substrate]/[Rh] = 200, 60 °C, 24 h, in THF. [b] dppb = $Ph_2P(CH_2)_4PPh_2$; dipb = $(i\text{-}Pr)_2P(CH_2)_4P(i\text{-}Pr)_2$; S = solvent.

MECHANISTIC ASPECTS ON THE ASYMMETRIC ISOMERIZATION OF ALLYLAMINE

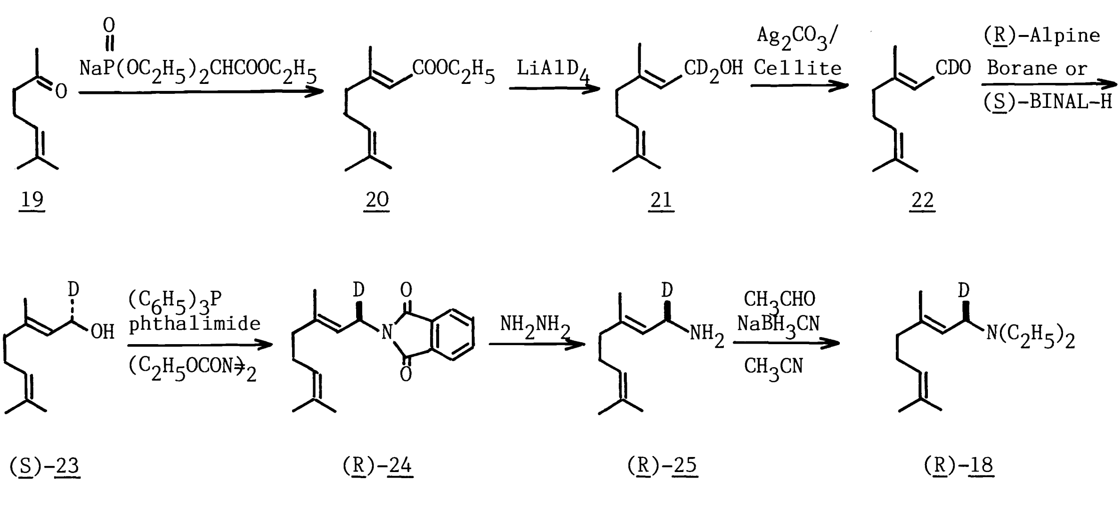
Labeling experiments. It is generally recognized that the transition metal catalyzed olefin isomerizations proceed via one of two distinct seqences; the reversible addition-elimination of M-H to the double bond, leading to 1,2-hydrogen shift and the π-allyl mechanism, resulting in 1,3-hydrogen shift (ref. 1b). Isomerization of 1,1-dideuterated allylamine (16-d_2) catalyzed by $[Rh(binap)(cod)]ClO_4$ gave exclusively 1,3-dideuterated enamine (17-d_2). In addition, the isomerization in the presence of an equal amonunt of the parent nondeuterated allylamine (16) produced only a mixture of an enamine 17 and its dideuterated compound 17-d_2. Careful investigation of the reaction products by ^1H NMR and GC-MS analyses showed the absence of mono-deuterated products (eq. 5). Therefore it is concluded that the present isomerization proceeds exclusively via intramolecular 1,3-hydrogen shift. These results strongly favor the



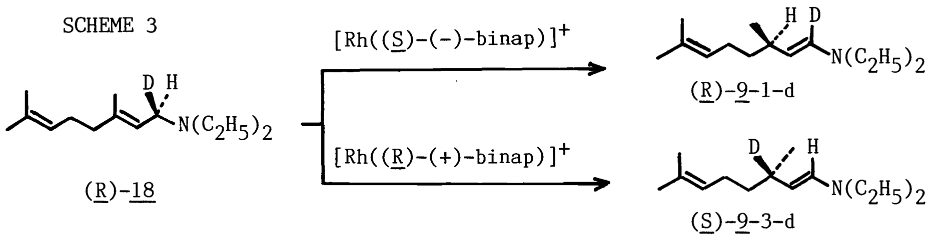
16   16-d_2 17   17-d_2 (5)

π-allyl mechanism. Next we performed the isomerization of an enantiomerically labeled allylamine in order to see "Which enantiotopic hydrogen at C(1) does migrate to C(3)?" An isotopically labeled compound, (R)-diethylgeranyl-1-d-amine ((R)-18) was prepared from prenylacetone (19) in seven steps by the sequence outlined in Scheme 2 and the optical purity was assessed to be ca. 93 % based on the optical purity of the parent primary geranyl-1-d-amine ((R)-25) determined by 400 MHz NMR analysis of its (R)-α-methyoxy-α-(trifluoromethyl)phenylacetyl amide using a triple resonance technique. The isomerization of (R)-18 catalyzed by $[Rh((-)\text{-binap})(S)_n]^+$ in THF (40 °C, 40 h) showed that the C(1) proton moved selectively to C(3) to give (R,E)-citronellal enamine, (R)-9-1-d. The reaction catalyzed by the (+)-binap-rhodium complex resulted likewise in the formation of (S)-9-3-d via deuterium migration. The ^1H and ^2H NMR analyses of these products revealed that the enantiospecificity of the 1,3-hydrogen migration was more than 97 %. No deuterium isotope effect was detected within the limit of accuracy of the present NMR analyses. The formal stereorelationship of the geranylamine substrate and the E enamine is illustrated in Scheme 3. If one assumes a hypothetical, cannonical s-trans conformation for the geranylamine (with respect to the C(2)--C(3) double bond and the diethylamino group), the 1,3-hydrogen shift is viewed to be occurring in a suprafacial manner.

SCHEME 2



SCHEME 3



^{1}H and ^{31}P NMR Studies. Both ^{31}P and ^{1}H NMR measured at -80 °C to 40 °C of a mixture of a catalyst [Rh(binap)(cod)]ClO_4 and 7 in THF-d_8 did not give any useful information concerning the reaction intermediates. A doublet signal of the COD complex in the ^{31}P NMR spectrum was not affected appreciably by addition of the substrate 7 during the whole temperature range. A ^{1}H NMR stectrum of a 1:2 mixture of the COD complex and 7 was essentially the same as a sum of the individual sepctra below 0 °C except for slight down-field-shifts ($\Delta\delta \sim 0.15$) of signals due to α-methylene protons of neryl and N-ethyl groups of 7. This suggests weak interaction of 7 with the rhodium complex through the nitrogen lone pair. Above 0 °C, isomerization took place and the signals due to the product enamine 9 appeared gradually. In order to get more detailed information about the reaction intermediates a more labile solvent complex was employed. Thus a 1:1 mixture of [Rh((+)-binap)$(MeOH)_2$]ClO_4 and 8 in acetone-d_6 (0.01 M each) was prepared at -90 °C (Note 1). The ^{31}P NMR spectra (161 MHz) measured at -80 °C indicated only a doublet signal at δ 53.25 (J_{Rh-P} = 199.5 Hz) due to the bis(acetone) complex [Rh((+)-binap)(acetone-d_6)$_2$]ClO_4 (Note 2). The ^{1}H NMR spectrum showed signals quite similar to those of the free allylamine 8 except for broadening of the signals at δ 3.00, 2.45, and 0.95 due to C(1) methylene and N-ethyl protons. These phenomena suggest the presence of a rapid equilibrium between the bis(acetone) complex and an N-coordinated substrate complex, e.g. [Rh((+)-binap)(acetone-d_6)(8)]$^+$ (designated as [Rh(binap)(N-A)(S)]$^+$) (Note 3). At -60 °C, a set of two double doublets centered at δ 30.42 (J_{Rh-P} = 193.7 Hz, J_{P-P} = 58.7 Hz) and 49.87 (J_{Rh-P} = 193.7 Hz) gradually appeared on consumption of the doublet signal due to the bis-(acetone) complex. This signal set was also observed when (S)-9 was added to the complex [Rh((+)-binap)$(MeOH)_2$]ClO_4 at -40 °C, indicating that these signals are due to an enamine-Rh^+ complex, which may contain a chelate-coordinated enamine (designated as [Rh(binap)(N-π-E]$^+$) (ref. 11). At this stage a new doublet appeared at δ 51.22 (J_{Rh-P} = 195.6 Hz) which was tentatively assigned to bis(enamine) complex (designated as [Rh(binap)(N-E)$_2$]$^+$). At higher temperature, the change in NMR spectra proceeded more smoothly. The ^{31}P NMR spectrum taken after complete consumption of the starting allylamine at 0 °C was shown in Fig. 1a in which there observed an intense eight-line signal and a weak doublet at δ 51.22 (J_{Rh-P} = 195.6 Hz)

Note 1. Acetone-d_6 was used as a solvent instead of THF-d_8, because the bis(methanol) complex, when dissolved in THF without substrate, gave sparingly soluble solids and acetone can also be used as an effective solvent for the catalysis.

Note 2. Chemical shifts were recorded relative to external 85% phosphoric acid. The spectra of the standard were taken before and after each measurement of the spectra of samples. When the ^{31}P NMR spectra (40.25 MHz) were run using a 3-5% methanol-d_4 solution of phosphoric acid in a coaxial sealed capillary as an external standard each signal appeared at ca. 2.84 ppm higher-field position.

Note 3. The ^{1}H NMR spectrum (100 MHz, measured at -40 °C immediately after sample preparation) of a more concentrated sample (ca. 0.1 M of [Rh((+)-binap)$(MeOH)_2$]ClO_4 and 0.1M of 8) showed slight down-field-shifts of the α-methylene protons of geranyl and N-ethyl groups ($\Delta\delta \sim 0.3$), which suggest weak coordination of 8 through nitrogen lone pair. For an N-coordinated substrate complex, a five-coordinated complex [Rh(binap)(N-A)(S)$_2$]$^+$ is also possible.

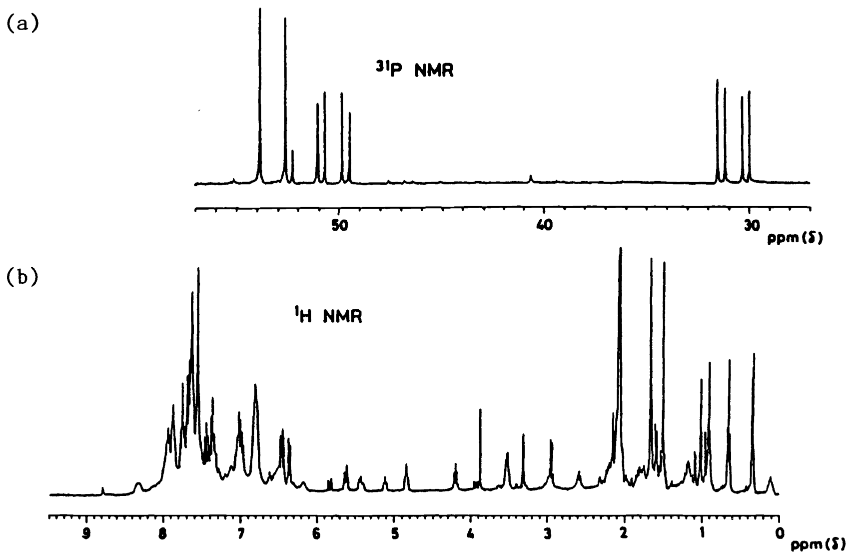


Fig. 1 ^{31}P(161 MHz) (a) and ^{1}H NMR(400 MHz) (b) of a mixture of 8 (0.01M) and [Rh((+)-binap)$(MeOH)_2$]ClO_4 (0.01M) in acetone-d_6 after reaction at 0 °C, 2h.

in addition to a doublet at δ 53.25 (J_{Rh-P} = 199.5 Hz) due to the starting bis(acetone) complex. If an excess of substrate was employed, the spectrum resulted in only a doublet signal of the bis(enamine) complex. Even at -80 °C, the doublet signal of the starting bis(acetone) complex changed slowly and after 900 h converged completely to a set of the eight-line signals but no further change was observed at this temperature (Note 4). The ^{1}H NMR spectrum (400 MHz) of this sample (Fig. 1b), though complex, exhibited a doublet at δ 0.33 (J = 6.4 Hz), two triplets at δ 0.64 (J = 7.3 Hz) and 0.90 (J = 7.0 Hz), which supports the formation of an enamine-Rh^+ complex. Despite careful search, no ^{1}H signal assignable to the metal-hydride was detected, implying that a hydride π-allyl complex, if formed, would not be stable enough for NMR detection. These observations suggest that in the methanol complex-catalyzed reaction transformation of $[Rh(binap)(N\text{-}\pi\text{-}E)]^+$ to an active catalyst, e.g., $[Rh(binap)(S)_2]^+$ (S = solvent or allylamine) producing enamine should be the rate-determining.

Kinetic studies

The rates of isomerization of 7 using [Rh((±)-binap)(cod)]ClO_4 in THF-d_8 and [Rh(+)-binap)$(MeOH)_2$]ClO_4 in acetone-d_6 as catalysts were measured by monitoring the ^{1}H NMR signals of the substrate and product, because the reaction proceeds very cleanly and gave only 9 as the sole detectable product. The two reactions follow different rate laws. The initial rate dependence on the catalyst concentration was 1st order for both cases. For the COD complex catalyzed isomerization the initial rate dependence on the initial substrate concentration was as shown in Fig. 2 and the rate follows equation 6, where R_0, $[A]_0$, and [C] are the initial rate, initial substrate and catalyst concentration respectively (k and K are constants).

$$R_0 = k[C][A]_0/(1 + K[A]_0) \qquad (6)$$
$$[A]_0 = 0.05 - 0.55\ \text{M};\ [C] = 0.82 - 4.05\ \text{mM}$$

For the bis(methanol) complex catalyzed isomerization, however, the initial rate dependence was rather peculiar as shown in Fig. 3. The rate can be described in terms of a composite equation (eq. 7), where [S] is the solvent concentration (k'and k" are constants).

Note 4. ^{31}P NMR of a mixture of [Rh((+)-binap)$(MeOH)_2$]ClO_4 and 7 in acetone showed also a similar spectral change and gave a set of similar eight-line signals at slightly lower field (Δδ 0.6-0.4) due to a diastereomer of the enamine complex obtained from 8.

$$R_0 = k'[C][S] + k''[C][A]_0 \qquad (7)$$
$$[A]_0 = 0.05 - 1.25\ M;\ [C] = 3.2 - 58\ mM$$

In addition , product inhibition was observed; the reciprocal of the initial rate varies linearly as the initial concentration of the added enamine.

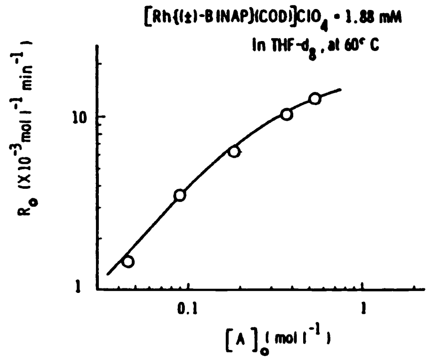


Fig. 2 Dependence of initial rates on substrate concentrations for isomerization of 7 catalyzed by $[Rh((\pm)\text{-binap})(cod)]^+$ in THF-d_8 at 60 °C.

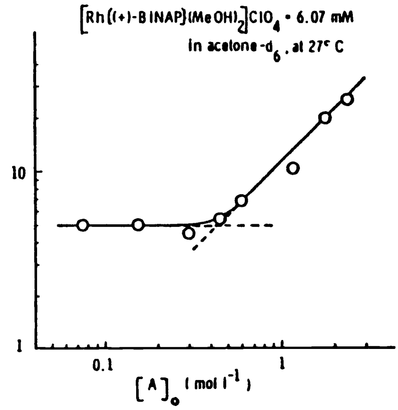
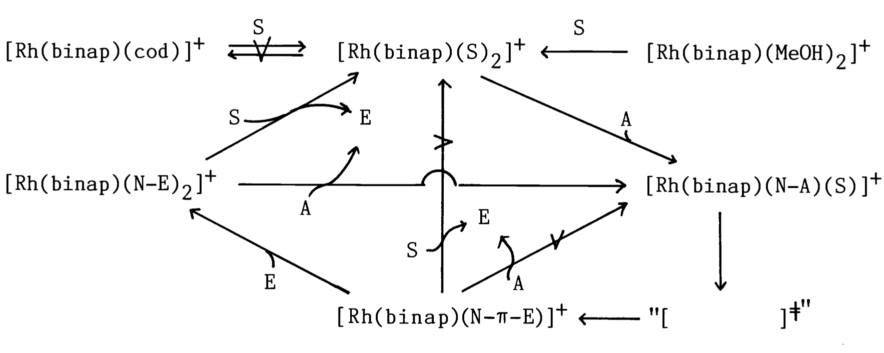


Fig. 3 Dependence of initial rates on substrate concentrations for isomerization of 7 catalyzed by $[Rh((+)\text{-binap})(MeOH)_2]^+$ in acetone-d_6 at 27 °C.

Possible reaction mechanisms of the asymmetric 1,3-hydrogen migration and the reaction pathways

The observation that despite the different kinetic laws both the COD and methanol complex catalyzed isomerization gave comparable degrees of enantioselection with the same product stereochemistry suggests an identical stereochemical discrimination step. On the basis of the kinetic and NMR studies the isomerization may be accounted for by the reaction cycle described in Scheme 4. For the COD complex catalyzed isomerization dissociation of COD ligand would be the rate-determining step, whereas for the methanol complex catalyzed reaction release of the product from an enamine-rhodium complex $[Rh(binap)(N\text{-}\pi\text{-}E)]^+$ (two parallel reactions, a solvent-assisted apparent unimolecular reaction and a second-order reaction, are possible) would be the rate-determining one. When the amount of the product increases, a path via bis(enamine) complex would become important. Neither of the reactions may be responsible for the enantio-discrimination. Enantioselection would be made at a stage somewhere in the course of transfromation of $[Rh(binap)(S)_n]^+$ to $[Rh(binap)(N\text{-}\pi\text{-}E)]^+$, which is not kinetically important. This feature may be consistent with the observed unusual non-linear temperature dependence of the enantioselection.

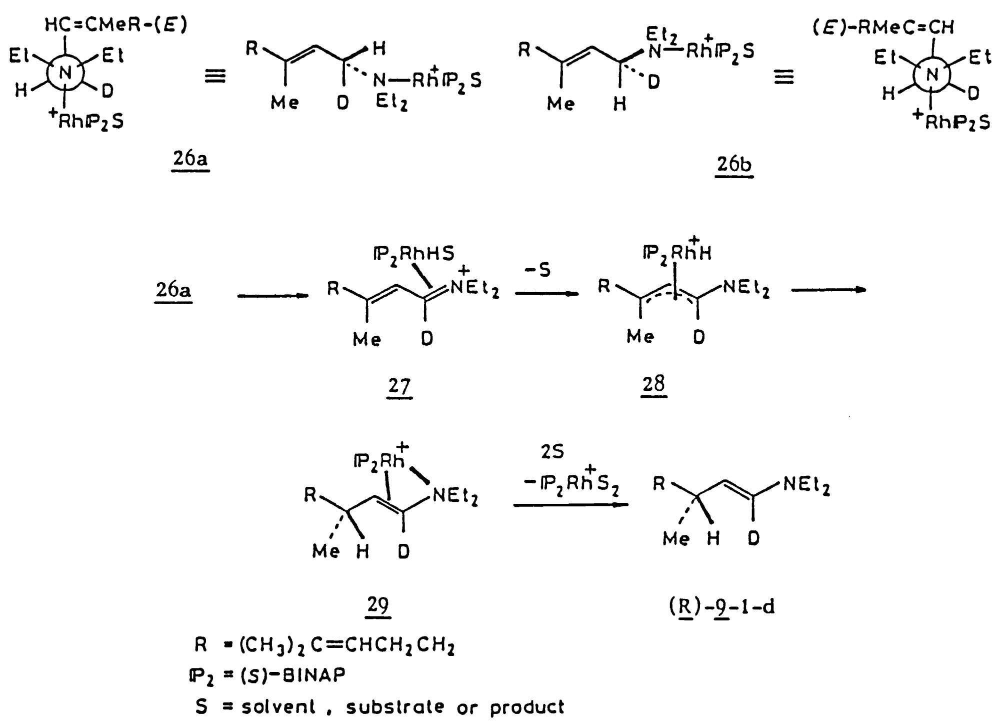
SCHEME 4



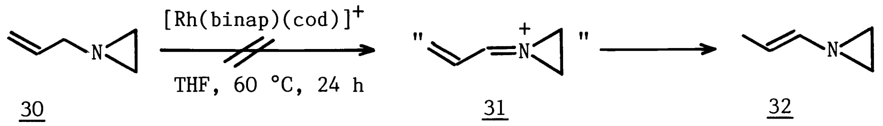
A: allylamine; E: enamine; S: solvent

As one of the most plausibe mechanisms for the observed stereospecific 1,3-hydrogen migration we consider the one described in Scheme 5. The rhodium-catalyzed isomerization starts with the formation of simple nitrogen coordinated rhodium complex [Rh(binap)(N-A)(S)]$^+$ as shown in Scheme 4. Among possible several conformers of such N-allylamine rhodium complexes involved in the reaction of (R)-18 with binap rhodium complexes, the most stable one would be 26, where the allylamine has a conformation with the C(2)-C(3) double bond plane being gauche with NEt_2 directing N lone-pair trans to C(2) and eclipsing one of the C(1) hydrogens (deuterium or protium) as expected from the theoretical calculation about simple allylamine (ref. 12) and the Rh-N bond is anti-periplanar to the C(2)-C(3) bond on steric ground. Although the two enantiomeric conformers of free geranylamine leading to 26a and 26b should be present in an equal population, the two complexes 26a and 26b, formed by coordination of a chiral rhodium complex, become diastereomeric. In the complex 26 the deuterium and protium at C(1) can be differentiated (cf. the Newman projection of 26a or 26b) and the non-eclipsed, out-of-plane protium in case of 26a is favorable for the metal hydride elimination by least motion leading to a rhodium-immonium complex 27 via a four-center transition state. Then the metal hydride species delivers the hydrogen atom to the C(3) position possibly via a π-allyl intermediate 28 to form the (E)-enamine complex 29 possessing an aza-allyl type structure responsible for the eight-line signals in ^{31}P NMR spectra, which ultimately give the free (E,R)-enamine (R)-9-1-d and the active rhodium catalyst. The transformation of 26 to 29 is facile as confirmed from ^{31}P NMR and when (S)-(-)-binap complex is used, the course starting from the diastereomer 26a would have the eminent preference.

SCHEME 5



N-Allylaziridine 30, where an immonium structure 31 is unfavorable (ref. 13), did not isomerize at all by [Rh(binap)(cod)]$^+$ in THF at 60 °C (eq. 8). This observation may be consistent with intermediacy of an immonium-rhodium complex in the catalytic cycle.



(8)

CONCLUSION

A few salient features of the asymmetric isomerization of functionalized allylic compounds are summarized as follows: (1) excellent catalytic activity and selectivity of cationic rhodium complexes of the type [Rh(diphosphine)L_n]$^+$, (2) per-aryldiphosphine, binap which has a C_2 symmetry, is the best diphosphine ligand and allylamines are the best substrate; i) 100 % (E)-enamine formation, ii) >96 %ee, iii) the clear stereochemical correlation between the ligand, substrate, and product, (3) mechanistic aspects of the asymmetric isomerization of allylamine; i) 100 % stereospecific intramolecular 1,3-hydrogen migration probably via π-allyl mechanism, ii) a composite rate equation, iii) the enantioselection may be achieved at a step of kinetically unimportance, which contrasts with the catalytic asymmetric hydrogenation of acetaminocinnamate by rhodium(I) diphosphine complexes (ref. 14).

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