Nevertheless, density around Cl has to be interpreted with great care, because accuracy in density distribution near the atomic positions, especially of heavier atoms, decreases rapidly due to the uncertainty in scale factor and experimental errors in positional and thermal parameters.

Conclusion

As noted in the introduction, **1** and closely related chelated complexes exhibit dynamic behavior in solution, which results from the lability of coordinative bonding. Positional exchange of substituents at pentacoordinate Si is performed throughout a low-energy barrier by fission and re-formation of the coordinative bond together with the rotation of the intermediate four-coordinate silyl substituent around the "single bond" connection between the ligand skeleton and the silyl group (Scheme I).

The present density study shows that two effects have to be considered when the influence of bonding to silicon on the rotation barrier is discussed. It reveals the donor–acceptor bond as a lone pair on the pyridine-type nitrogen which is heavily polarized by silicon. An influence of this interaction on the barrier to rotation in solution seems likely. Furthermore, it shows that the lone pair on the amino-type nitrogen N1 of the higher saturated heterocycle is shifted into the Si–N bond. This anisotropic charge distribution between Si and N1 may possibly increase the rotation barrier, because N1 acts as a pivot during the rotation of the silyl group in the rearrangement in solution. This conclusion is supported by temperature-dependent NMR studies of the above-mentioned silaethylenes[26] which show in solution up to 60 °C no evidence of rotation about the central Si–C bond which is assumed to possess "multiple bonding character". This fact might be seen as an indication that this bond is kinetically stable against internal rotations, but any conclusions on the height of the barrier quoted as activation enthalpy can only be derived if dynamic NMR properties are observed and evaluated as a function of temperature.

Acknowledgment, We thank J. M. Savariault, M. S. Lehmann, and J. R. Allibon (ILL, Grenoble) for technical assistance with the neutron diffraction experiment. We gratefully acknowledge the help of the Institut für Kernphysik (Universität Frankfurt) for making the diffractometer available. This work has been supported by the Bundesministerium für Forschung und Technologie and by the Deutsche Forschungsgemeinschaft.

Registry No, **1**, 78271-96-2.

Supplementary Material Available: Listing of the observed and calculated structure factors of the three data sets (neutrons, 0.894 Å, 1.266 Å, X-rays, 0.71069 Å) (34 pages). Ordering information is given on any current masthead page.

Highly Enantioselective Isomerization of Prochiral Allylamines Catalyzed by Chiral Diphosphine Rhodium(I) Complexes. Preparation of Optically Active Enamines[1]

Kazuhide Tani,*[2a] Tsuneaki Yamagata,[2a] Susumu Akutagawa,[2b] Hidenori Kumobayashi,[2b] Takanao Taketomi,[2b] Hidemasa Takaya,[2c] Akira Miyashita,[2c] Ryoji Noyori,[2d] and Sei Otsuka*[2a]

Contribution from the Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan 560, Central Research Laboratory, Takasago Perfumery Co. Ltd., 31-36, 5-chome, Kamata, Ohta-ku, Tokyo, Japan 144, Chemical Materials Center, Institute for Molecular Science, Okazaki, Japan 444, and Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya, Japan 464. *Received December 19, 1983*

Abstract: Rh(I) complexes of types $[Rh(diphosphine)(diene)]ClO_4$ and $[Rh(diphosphine)(S)_n]ClO_4$ (diphosphine = cis-chelating tertiary diphosphine; diene = 1,5-cyclooctadiene or norbornadiene; S = solvent) were found to be effective catalysts for allylic hydrogen migration of tertiary and secondary allylamines to give the corresponding (*E*)-enamines and imines, respectively. Studies on diphosphine ligands with respect to the catalytic activity and product selectivity led to the discovery of a fully aryl-substituted diphosphine, BINAP [2,2′-bis(diphenylphosphino)-1,1′-binaphthyl], which produces very active Rh(I) complex catalysts. With $[Rh((\pm)\text{-BINAP})(COD)]ClO_4$ (COD = 1,5-cyclooctadiene) or $[Rh((\pm)\text{-BINAP})(S)_n]ClO_4$ as catalyst, (*Z*)-(diethylnerylamine, **1**) or (*E*)-*N*,*N*-diethyl-3,7-dimethyl-2,6-octadienylamine (diethylgeranylamine, **2**) was isomerized into the racemic (*E*)-enamine (*E*)-*N*,*N*-diethyl-3,7-dimethyl-1,6-octadienylamine (citronellenamine, **3**) with a chemical selectivity of over 95%, the 6-double bond being retained intact. A variety of substituted allylamines serves as the substrate, e.g., (*E*)-*N*,*N*-dimethyl-2-butenylamine, *N*,*N*-dimethyl-2-methyl-2-propenylamine, *N*,*N*-dimethyl-3-methyl-2-butenylamine, *N*,*N*-dimethyl-3-phenyl-2-butenylamine. Asymmetric isomerization of prochiral allylamines producing optically active enamines or imines can be effected with cationic Rh(I) complexes of various chiral diphosphine ligands such as (2*R*,3*R*)-DIOP and others. The ligand that gives the highest optical yield was (+)- or (−)-BINAP. Virtually perfect enantioselectivity (95–99% ee) was achieved with [Rh((+)- or (−)-BINAP)(COD)]$^+$ for the isomerization of **1** or **2** into the optically active (*E*)-enamine (**3**). A clear stereochemical correlation was established between the olefin geometry (*E* or *Z*) of substrates, the configuration of the chiral diphosphines (*R* or *S*), and the chiral carbon configuration of the product enamines (*R* or *S*). The present catalytic system thus provides a convenient and practical access to optically active aldehydes. For example, optically pure natural citronellal can be produced either from nerylamine with the Rh(I)–(+)-BINAP catalyst or from geranylamine with the Rh(I)–(−)-BINAP complex catalyst.

Olefin double-bond migration is one of the most extensively studied catalytic reactions. The isomerization is involved frequently in such transition-metal catalysis as hydroformylation, oligomerizations, and other reactions.[3,4] Although the catalysis

(1) Metal-Assisted Terpenoid Synthesis. 7. For part 6, see: ref 27.
(2) (a) Osaka University. (b) Takasago Perfumery Co. Ltd.. (c) Institute for Molecular Science. (d) Nagoya University.

(3) For some reviews, see: (a) Parshall, G. W. "Homogeneous Catalysis"; Wiley: New York, 1980; Chapter 33. (b) Rylander, P. N. "Organic Syntheses with Noble Metal Catalysts"; Academic Press: New York, 1973; Chapter 5.

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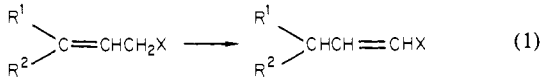
is a kinetic phenomena, the products obtained with active catalysts generally reflect thermodynamic control implying effective reversibility of the reaction steps involved. Migration of a multisubstituted inner double bond to the less substituted terminal one would not occur unless the latter gains relative stability. The inner to terminal double-bond migration observed in hydrozirconation[5] is presumably due to this product stabilization, the formation of a Zr(IV)–primary carbanion bond. Thus, the reaction remains stoichiometric. Catalytic inner to terminal double-bond migration reactions have been achieved with functionalized allylic systems (eq 1). Various complexes of Fe,[3,6-10] Ru,[4,6,11,12] Co,[3] Rh,[6,13-16]



(1)

Ir,[17] Ni,[4,18] Pd,[3,19] Pt,[20,21] and strong bases[22,23] have been proposed as catalysts for such allylic migrations. All of them, of course, lead to racemic products.

Several mechanisms have been proposed for transition-metal catalyzed isomerization of olefins.[3] Of these, two mechanisms have experimentally been recognized, the metal hydride addition–elimination (1,2-hydride shift) and π-allyl mechanism (1,3-shift). Regardless the mechanism, it appears to be a formidable task to achieve a stereospecific hydrogen migration in view of the microscopic reversibility. Only a few reports[24-26] describe asymmetric isomerization of prochiral olefins but with very low optical yields. We have also reported an asymmetric isomerization of prochiral allylamines, e.g., geranyl- or nerylamine derivatives, with chiral cobalt complex catalysts.[27] However, the optical yield obtained by the cobalt catalysts was too low ($\simeq$30% ee) to be of practical use. Recently we found an excellent rhodium catalyst which exhibits high catalytic activity and excellent enantioselectivity for the isomerization of prochiral allylamines.[28] We believe that the isomerization provides a new practical method for syntheses of optically pure aliphatic enamines and aldehydes. Here we describe full details of the preparative aspects.

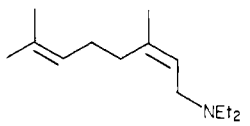
Table I. Effect of Phosphine Ligands on Isomerization of **1** to **3** with Rhodium(I) Phosphine Complexes[a]

catalyst[b]	conversion, %	selectivity, %
$[Rh((+)\text{-BINAP})]^+$	100	96
$[Rh((\pm)\text{-BINAP})(COD)]^+$	100	95
$[Rh(diphos)]^+$	92	96
$[Rh(diphos)(COD)]^+$	17	90
$[Rh(BDPF)]^{+c}$	83	94
$[Rh(DIPP)]^+$	53	87
$[Rh(BPPFA)(COD)]^+$	0	
$[Rh((\pm)\text{-BINAP})Cl]_2$[d]	0	
$[Rh(PPh_3)_2(H)_2(solvent)_2]^{+e}$	58	91
$[Rh(PPh_3)_2(COD)]^+$	30	88
$[Rh(diphos)_2]^+$	0	

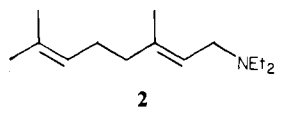
[a] [Substrate] = 0.4 M, [substrate]/[Rh] = 100, 40 °C, 23 h in THF unless otherwise noted. [b] A counteranion, ClO_4^-, is omitted for cationic complexes. $[Rh(diphosphine)]^+$ was prepared in situ by treating $[Rh(diphosphine)(COD)]ClO_4$ with H_2 (1 atm) at ambient temperature for 15 min and excess hydrogen was replaced by argon. BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl; BDPF = 1,1′-bis(diphenylphosphino)ferrocene; DIPP = 1,3-bis(diisopropylphosphino)propane; BPPFA = (*S*)-*N*,*N*-dimethyl-1-[(*R*)-1′,2-bis(diphenylphosphino)ferrocenyl]ethylamine. [c] [Substrate] = 0.8 M, [substrate]/[Rh] = 90. [d] Prepared in situ from $[Rh(C_2H_4)_2Cl]_2$ and 2 equiv of (±)-BINAP. [e] Prepared in situ from $[Rh(PPh_3)_2(COD)]ClO_4$ and H_2 (1 atm).

Results and Discussions

(A) Isomerization with Achiral Rhodium(I) Complexes, Active Catalysts. As representative (*Z*)- and (*E*)-allylamines, (*Z*)-*N*,*N*-diethyl-3,7-dimethyl-2,6-octadienylamine (diethylnerylamine) (**1**) and (*E*)-*N*,*N*-diethyl-3,7-dimethyl-2,6-octadienylamine (diethylgeranylamine) (**2**) were chosen, since the products are useful



1



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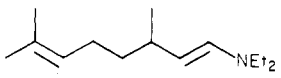

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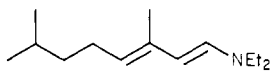

4

intermediates for terpene syntheses. The isomerization of **1** and **2** poses a problem of chemoselectivity regarding the two double bonds. Conventionally the allylic migration has been effected with various bases. Isomerization of **1** or **2** with strong base such as NaH–ethylene diamine or sodium naphthalene, however, produces mainly undesirable conjugated dienamine **4**.[23] The isomerization of **1** with the low-valent cobalt catalysts, as reported previously, produced (*E*)-*N*,*N*-diethyl-3,7-dimethyl-1,6-octadienylamine [(*E*)-diethylcitronellenamine] (**3**) accompanied with a considerable amount (15%) of **4**.[27] In order to find a more selective catalyst, several transition-metal compounds, which were reported to be active isomerization catalysts, were tested. Iron pentacarbonyl was totally inactive in toluene, ethanol, or acetic acid. This was also the case for coordinatively saturated hydride complexes

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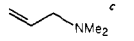
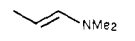
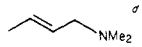
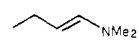
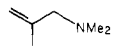
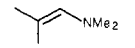
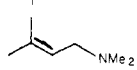
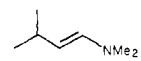
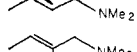
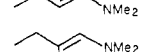
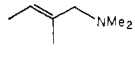
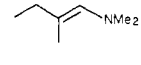
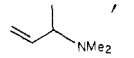
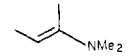
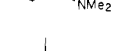
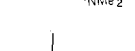
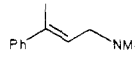
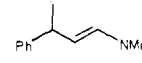
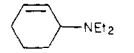
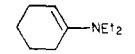
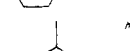
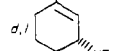
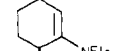
Table II. Scope of Substrate for Isomerization of Allylamine to Enamine with [Rh((±)-BINAP)]$^{+}$ [a]

substrate	product[b]	conversion, %	selectivity, %
 [c]		78	77
 [d]		52[e]	100
		97	100
		100	100
		trace[j]	
 [f]		100[g]	0[g]
 [h,i]		98	85
		94	95
 [h,i]		0[j]	
		100	96
 [h]		trace[j]	
 [h]		0[j]	

[a] [Rh((±)-BINAP)]$^{+}$ was prepared in situ from [Rh((±)-BINAP)(COD)]ClO_4 and H_2 (1 atm) in THF; [substrate] = 2.0 M, [substrate]/[Rh] = 100, 60 °C, 23 h, unless otherwise noted. The isomerizations, except for those of 2, (*E*)-*N*,*N*-dimethyl-3-phenyl-2-butenylamine, and (±)-*trans*-diethylpiperitylamine, were carried out in sealed NMR tubes using THF-d_8 as the solvent and monitored by ^{1}H NMR. [b] (*Z*)-Enamine could not be detected. [c] 17 °C, 23 h. The reaction mixture is heterogeneous, containing a considerable amount of yellow precipitates. The lower selectivity is partly due to the polymerization of the resulting isomerized product even at low temperature. [d] The substrate contains *N*,*N*-dimethyl-3-butenylamine (11.7%) and *N*,*N*-dimethyl-1-methyl-2-propenylamine (18.8%). The allylamine itself was isomerized smoothly to the enamine but the homoallylamine was recovered unchanged under the reaction conditions. [e] Based on (*E*)-*N*,*N*-dimethyl-2-butenylamine. [f] The allylamine contains 2.7% of *N*,*N*-dimethyl-3-butenylamine and 31.6% of (*E*)-*N*,*N*-dimethyl-2-butenylamine. [g] The products were a mixture of several unidentifiable high-boiling products, see text. [h] [Rh((±)-BINAP)(COD)]ClO_4 was used as catalyst; 40 °C, 23 h. [i] [Substrate] = 0.44 M, *E*:*Z* = 10.6:1. [j] Only the starting material was recovered.

$[NiHL_4]^+$, $CoHL_4$ [L = $P(OEt)_3$, $P(OPh)_3$], $CoH(diphos)_2$ [diphos = 1,2-bis(diphenylphosphino)ethane], and $FeH_2(diphos)_2$.

Cationic Rh(I) diphosphine complexes were very active. For example, [Rh(diphos)(COD)]ClO_4 (COD = 1,5-cyclooctadiene) showed activity, though not so high, and fairly high selectivity for the isomerization of **1** under very mild conditions (at 40 °C, in THF). The activity was further improved when the complex dissolved in THF was treated with hydrogen to remove the COD ligand. Removal of COD ligand and the absence of hydride ligand were confirmed by ^{1}H NMR spectroscopy. Without further characterization, the complex solution containing [Rh(diphos)$(S)_n$]$^+$ (S = solvent molecule, n = 2 or 3; for brevity we will designate this as [Rh(diphos)]$^+$)[29] was used as a mother liquor of the catalyst solution, and we obtained reasonably reproducible results. With a catalytic amount (1 mol %) of this compound prepared in situ, **1** was isomerized in THF (40 °C, 23 h) to give the racemic (*E*)-diethylcitronellenamine (**3**) in 92% conversion with 96% selectivity. The conjugated dienamine **4** was practically absent. Being encouraged by this finding a number of chelating diphosphines were then tested as the ligand with respect to the activity and selectivity for the isomerization of **1**. Some examples are shown in Table I.

The catalytic activity varies considerably depending on the nature of the diphosphine ligands. A fully aryl-substituted diphosphine, 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP),[30] forms the best catalyst in terms of the chemoselectivity and activity, while fully alkyl-substituted diphosphine, e.g., 1,3-bis(diisopropylphosphino)propane (DIPP), give catalysts of lower activity. A diphosphine having a tertiary amine substituent, (*S*)-*N*,*N*-dimethyl-1-[(*R*)-1′2-bis(diphenylphosphino)-ferrocenyl]ethylamine (BPPFA),[31] was totally inactive at 40 °C. This is probably due to the tridentate chelation preventing the substrate coordination or hindering formation of the transition state. Such N–P chelate coordination to Rh(I) is known for (*R*)-*N*,*N*-dimethyl-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]-ethylamine.[32] The presence of a diene ligand in the (diphos)Rh^I complex reduces the catalytic activity. However, the retarding effect of COD ligand is not significant in case of the (BINAP)Rh^I complex-catalyzed isomerization (quantitative aspects will be described in a future paper). The presence of excess diphosphine ligands markedly reduces the catalytic activity; i.e., [Rh(diphos)$_2$]ClO_4[33] does not catalyze the isomerization at all under similar conditions (40–60 °C).

(29) Throughout this paper we use the formulation of [Rh(diphosphine)]$^+$ instead of [Rh(diphosphine)(solvent)$_n$]$^+$.

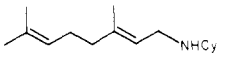
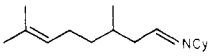
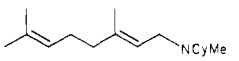
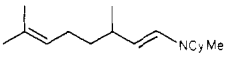
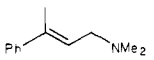
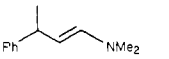
(30) (a) Miyashita, A.; Takaya, H.; Toriumi, K.; Ito, T.; Souchi, T.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 7932. (b) Noyori, R.; Takaya, H. *Jpn. Kokai Tokkyo Koho* **1978**, 53–13605.

(31) (a) Hayashi, T.; Yamamoto, K.; Kumada, M. *Tetrahedron Lett.* **1974**, 4905. (b) Hayashi, T.; Mise, T.; Fukushima, M.; Kagotani, M.; Nagashima, N.; Hamada, Y.; Matsumoto, A.; Kawakami, S.; Konishi, M.; Yamamoto, K.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1138.

(32) Cutten, W. R.; Einstein, R. W. B.; Husung, C. H.; Willis, A. C.; Shan, Y. *J. Am. Chem. Soc.* **1980**, *102*, 988.

(33) (a) Sacco, A.; Ugo, R. *J. Chem. Soc.* **1964**, 3274. (b) Maureen, C. H.; Kilbourn, B. T.; Taylor, K. A. *J. Chem. Soc. A* **1970**, 2539.

Table III. Asymmetric Isomerization of Prochiral Allylamine to Optically Active (*E*)-Enamine with Cationic Rh(I) Chiral Diphosphine Complexes[a]

substrate[b]	catalyst[c]	product	conversion, %	selectivity, %	optical yield, % ee (abs config)
1	[Rh((+)-BINAP)]$^+$	**3**	99	96	93 (*R*)
	[Rh((+)-BINAP)(COD)]$^+$		97	97	95 (*R*)
	[Rh((−)-BINAP)(COD)]$^+$		97	100	92 (*S*)
	[Rh((−)-DIOP)]$^+$		76	96	26 (*S*)
	[Rh((−)-CyDIOP)]$^+$		18	80	77 (*S*)
	[Rh((−)-*i*-PrDIOP)]$^+$		9	63	41 (*S*)
	[Rh((−)-EtDIOP)]$^+$		31	81	38 (*R*)
	[Rh(BPPM)]$^+$		69	91	14 (*R*)
2	[Rh((+)-BINAP)(COD)]$^+$	**3**	100	94	96 (*S*)
	[Rh((−)-BINAP)(COD)]$^+$		100	99	93 (*R*)
	[Rh((−)-DIOP)]$^+$		100	93	22 (*R*)
	[Rh((−)-CyDIOP)]$^+$		13	53	51 (*R*)
	[Rh((−)-*i*-PrDIOP)]$^+$		16	64	43 (*R*)
	[Rh((−)-EtDIOP)]$^+$		22	73	37 (*S*)
	[Rh((+)-BINAP)(COD)]$^+$		100	100	96 (*S*)
	[Rh((−)-DIOP)]$^+$		14	99	12 (*R*)
	[Rh((−)-CyDIOP)]$^+$		100	95	11 (*S*)
	[Rh((−)-*i*-PrDIOP)]$^+$		52	95	2 (*S*)
	[Rh((−)-EtDIOP)]$^+$		40	93	16 (*S*)
	[Rh((+)-BINAP)]$^+$		100	100	91 (*S*)
	[Rh((+)-BINAP)(COD)]$^+$		94	88	90 (*R*)

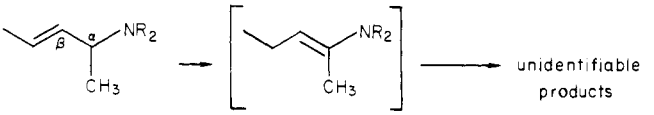
[a] [Substrate] = 0.44 M, [substrate]/[Rh] = 100, 40 °C, 23 h, in THF. [b] Purity: **1** = 94.9%, free from **2**; **2** = 93.6%, including ca. 1.0% of **1**; Cyclohexylgeranylamine = 100%; Cyclohexylmethylgeranylamine = 98.2%; (E)-*N*,*N*-Dimethyl-3-phenyl-2-butenylamine = 99.5%, containing ca. 0.5% of the *Z* isomer. [c] The counteranion omitted is ClO_4. [Rh(diphosphine)]$^+$ was prepared in situ by reducing [Rh(diphosphine)(diene)]ClO_4 with molecular hydrogen. Perhaps two or three solvent molecules coordinate to the Rh(I) center. [d] 60 °C, 48 h.

Cationic complexes of a monodentate tertiary phosphine, PPh_3, exhibit catalytic activity. For example, a diene rhodium(I) complex, $[Rh(PPh_3)_2(COD)]ClO_4$,[34] or a (hydrido)rhodium(III) complex, $[Rh(PPh_3)_2(H)_2(solvent)_2]^+$,[34] formed in situ by treating the diene complex with molecular hydrogen, is active but the activity is definitely lower compared to the (BINAP)Rh[I] complex. Notably, neutral Rh(I)–diphosphine complexes, e.g., [Rh((±)-BINAP)Cl]$_2$, prepared in situ by the reaction of $[Rh(C_2H_4)_2Cl]_2$ with 2 equiv of (±)-BINAP, were totally inactive under comparable conditions (40 °C, THF solvent).

Substrate Scope. Structural variation of the allylamine was examined for this isomerization (60 °C, THF) employing [Rh((±)-BINAP)]$^+$[29] as the catalyst. The isomerization of *N*,*N*-dimethylallylamine derivatives of low molecular weight was carried out in THF-d_8 in a sealed NMR tube, the reaction being monitored by ^{1}H NMR. Table II summarizes the results.

Several features are worth noting. First of all, the isomerization always produces exclusively (*E*)-enamines regardless of the double-bond geometry of starting olefins. The *E* configuration was confirmed from a large coupling constant (~14 Hz) between the olefinic protons in the trans position found in the ^{1}H NMR and a fairly strong absorption band around 985–935 cm^{-1} in the IR spectra. This is true for a considerable range of structural variation in allylamine molecules (Table II, also Table III) we tested. The selectivity for this product stereochemistry was always perfect as far as we could detect by means of gas chromatography and/or ^{1}H NMR spectroscopy. Thus, an isomeric mixture of *N*,*N*-dimethyl-3-phenyl-2-butenylamine (*E*:*Z* = 10.6:1) gave only the (*E*)-enamine, This geometrical selectivity is notable in view of the poor stereoselectivity observed for the $Fe(CO)_5$ *hν*-catalyzed isomerization of allylic amides, urea, and carbamate derivatives[35] and also for the $RuHCl(PPh_3)_3$- or $RhH(PPh_3)_4$-catalyzed isomerization of allylamides.[6] The perfect stereoselectivity of the present catalysis may imply preferential formation of a syn-η^3-allyl complex as the intermediate or transient species since the syn configuration accounts better for the *E* geometry. At this moment, however, the possibility of a thermodynamic control cannot be excluded.

As shown in Table II, several linear allylamine derivatives undergo smooth isomerization under mild conditions in the presence of the cationic rhodium(I) BINAP complex catalyst, producing the corresponding (*E*)-enamines with excellent selectivity. It is noteworthy that while the trisubstituted allylamine, *N*,*N*-dimethyl-3-methyl-2-butenylamine, is readily isomerized, the Rh(I) complexes were not effective for the isomerization of (*E*)-*N*,*N*-dimethyl-2-methyl-2-butenylamine (Table II). The reason is not clear at the moment. Another limitation we became aware of is the requirement of having no alkyl substituent at the α-position. Thus the reaction of *N*,*N*-dimethyl-1-methyl-2-propenylamine produced only an intractable oil, although the conversion of the starting allylamine was fairly fast as detected by ^{1}H NMR and gas chromatography. This may be due to the instability of the ketone–enamine initially formed, which results in secondary condensation or isomerizationr eactions. Such high reactivity of the enamines derived from acyclic methyl ketones has been reported.[36]



Interestingly, even *N*,*N*-dimethyl-3-phenyl-2-butenylamine, having a styrene-type conjugated olefin, was also effectively isomerized to the corresponding enamine, which no longer has the conjugation. This effective catalysis even for trisubstituted

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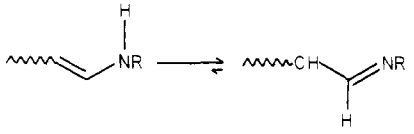
(35) Hubert, A. J.; Moniotte, P.; Goebbels, G.; Warin, R.; Teyssie, P. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1954.
(36) (a) Madsen, P.; Lawesson, S.-O. *Recl. Trav. Chim. Pays-Bas* **1966**, *85*, 753. (b) Bianchetti, G.; Croce, P. D.; Pocar, D. *Tetrahedron Lett.* **1965**, 2039. (c) Biachetti, G.; Pocar, D.; Croce, P. D.; Vigevani, A. *Chem. Ber.* **1965**, *98*, 2715.

allylic systems contrasts with the very low activity of $Fe(CO)_5$,[6] $[Ir(COD)(PMePh_2)_2]PF_6$,[17] $H_2Ru(PPh_3)_4$,[11] or $Pd(PhCN)_2Cl_2$[19] for such multisubstituted allylic systems.

Cyclic allylamine, 3-dimethylaminocyclohexane, was also isomerized easily to give the corresponding enamine. The inertness of the cyclic allylamine (±)-*trans*-3-(diethylamino)-4-isopropyl-1-methylcyclohexene is apparently due to steric hindrance caused by the 4-trans isopropyl group.

A secondary amine, (*E*)-*N*-cyclohexyl-3,7-dimethyl-2,6-octadienylamine (cyclohexylgeranylamine), was also isomerized with $[Rh((\pm)\text{-BINAP})]^+$ smoothly to the corresponding *N*-alkyl imine,



a more stable valence isomer of a secondary enamine (see Table III). The isomerization rate was faster than that of **2**, as assessed qualitatively from the preparative runs.

The effect of N-substituents was also studied. Aryl substituents retard the reaction drastically as evidenced by the inertness of (*E*)-*N*-phenyl- and (*E*)-*N*,*N*-diphenyl-3,7-dimethyl-2,6-octadienylamine (40 °C, for 23 h). This implies the importance of the basicity of the amine nitrogen which participates in the substrate coordination.

Homoallylamine, such as *N*,*N*-dimethyl-3-butenylamine or 2-(2-(diethylamino)ethyl)-6-methyl-1,5-heptadiene, which is involved as an impurity in the sample of **1** and **2** (see Experimental Section), was not isomerized with the present catalyst systems under ordinary conditions (40–60 °C, in THF).

(B) Asymmetric Isomerization. The finding of active cationic Rh(I)–diphosphine complex catalysts for the allylic isomerization has prompted us to challenge asymmetric isomerization. As a representative prochiral allylamine, we chose the neryl- and geranylamine derivatives; The isomerization was carried out in THF at 40 °C for 23 h employing 1 mol % of a cationic rhodium(I) complex. As expected, the diphosphine ligand plays a key role in this catalysis.

As shown in Table III Rh(I) complexes with popular chiral diphosphines, (−)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane [(−)-DIOP][37] and (2*S*,4*S*)-*N*-(*tert*-butoxycarbonyl)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine (BPPM),[38] both of which are excellent ligands for asymmetric hydrogenation of dehydroamino acid derivatives, showed moderate activity with high chemoselectivity for isomerization of **1** but with disappointing optical yields. Rhodium(I) complexes with tetralkyl analogues of (−)-DIOP [(−)-*i*-PrDIOP and (−)-EtDIOP][39] showed low catalitic activities and poor optical yields. With (−)-CyDIOP ligand,[39] however, a fairly high optical yield (~77% ee) was attained. The highest optical yield and fastest rate were achieved with (+)- or (−)-BINAP. This was also the case for isomerization of **2**.

The chiral carbon configuration of the (*E*)-enamine **3**, obtained from the geranylamine **2**, was opposite to that obtained from the nerylamine **1**. Also the isomerization of **2** with the ((+)-BINAP)Rh^I catalyst gave the enamine (3*S*)-**3** with 96% ee whereas the isomerization with the (−)-BINAP catatlyst produced (3*R*)-**3** with 93% ee. Thus, a clear sterochemical correlation between the geometry of the double bond in the starting allylamine, the configuration of the diphosphine ligands, and those of the products was established (Figure 1). This contrasts to the case of chiral diphosphine Rh(I) complex catalyzed hydrogenation of some prochiral olefins such as (*E*)- or (*Z*)-α-(acetylamino)cinnamic acid.[40] Although a similar correlation has been observed for the cobalt-catalyzed isomerization of **1** and **2**, the correlation is based on relatively low optical yields.[27]

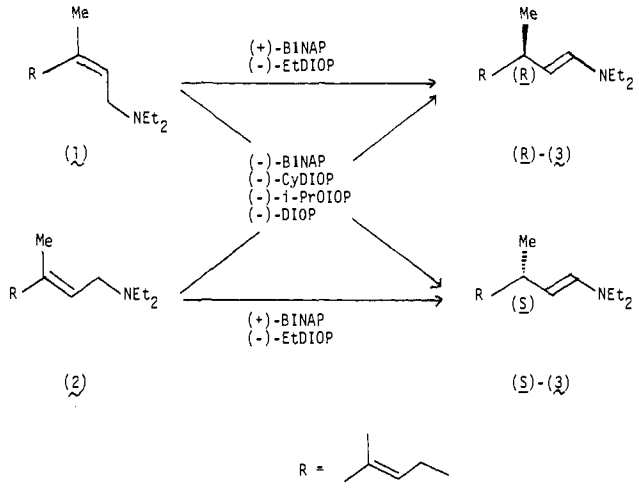


Figure 1. Correlation between substrate geometry, configuration of diphosphines, and chirality of (*E*)-enamine produced.

It is evident that in order to obtain high optical yields, the starting allylamine should be free from the geometrical isomer. As described in the Experimental Section, diethylneryl- (**1**) and diethylgeranylamine (**2**) were synthesized by the telomerization of isoprene[41,42] and myrcene,[43,44] respectively, with diethylamine, and the purity of the allylamines used in this experiment was estimated to be 94.9% for **1** and 93.6% for **2** by GLC analysis, the impurity being isomeric olefinic amines (see Table VI). The presence of these isomeric amines except for the opposite geometric isomer in the starting allylamine should not seriously affect assessment of the optical yield (vide infra), because all of these isomers are achiral, and their isomerized products, if any, will produce only achiral enamines. As the geranylamine derivative, **2**, used in this experiment was contaminated with a small amount of the opposite geometric isomer, **1**, a higher optical yield than that recorded in Table III was expected to be achieved with a more pure starting amine. After a careful distillation using a high-efficiency column of a hundred theoretical plates, a sample of **2**, whose purity was 99.7% and practically free from the geometrical isomer, was obtained. The sample was isomerized with an optical yield no less than 99% (see Table V), a virtually perfect optical induction.

Thus with the cationic rhodium(I) complex of (+)- or (−)-BINAP ligand, all prochiral allylamines listed in Table III, including the secondary amine, were isomerized to the corresponding optically active (*E*)-enamine or imine with high optical yields. (*E*)-*N*,*N*-Dimethyl-3-phenyl-2-butenylamine is a slow-reacting substrate, presumably due to its styrene-type conjugation. Its isomerization with the ((+)-BINAP)Rh^I catalyst gave the 3*R* (*E*)-enamine in 83% yield with 90% ee, which has the same stereochemistry around the asymmetric carbon atom as that of (3*S*)-**3** produced from the (*E*)-allylamine **2** with the same catalyst.

The presence of a hydroxyl group in allylamine also does not affect the present isomerization. Thus, (*Z*)-*N*,*N*-diethyl-7-hydroxy-3,7-dimethyl-2-octenylamine (diethyl-7-hydroxy-6,7-dihydronerylamine) was isomerized with $[Rh((+)\text{-BINAP})(NBD)]ClO_4$ (NBD = norbornadiene) similarly in THF (100 °C, 15 h) to give the optically active (*E*)-*N*,*N*-diethyl-7-hydroxy-3,7-dimethyl-1-octenylamine [(*E*)-diethyl-7-hydroxydihydrocitronellenamine], which, on hydrolysis with dilute sulfuric acid, gave (+)-7-hydroxydihydrocitronellal with optical rotation, $[\alpha]^{23}_D$ + 11° (benzene), higher than the reported value, $[\alpha]^{20}_D$ +10°.[45]

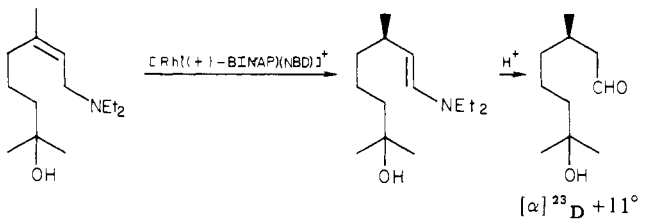
(37) (a) Dang, T. P.; Kagan, H. B. *Chem. Commun.* **1971**, 481. (b) Kagan, H. B.; Dang, T. P. *J. Am. Chem. Soc.* **1972**, *94*, 6429.
(38) (a) Achiwa, K. *J. Am. Chem. Soc.* **1976**, *98*, 8265. (b) Baker, G. L.; Fritschel, S. J.; Stille, J. R.; Stille, J. K. *J. Org. Chem.* **1981**, *46*, 2954.
(39) Tani, K.; Suwa, K.; Yamagata, T.; Otsuka, S. *Chem. Lett.* **1981**, 265.
(40) Vineyard, B. D.; Knowles, W. S.; Sabacky, M. J.; Bachman, G. L.; Weinkauff, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 5946.
(41) Takabe, K.; Katagiri, T.; Tanaka, J. *Tetrahedron Lett.* **1972**, 4009.
(42) Takabe, K.; Katagiri, T.; Tanaka, J. *Chem. Lett.* **1977**, 1025.
(43) Takabe, K.; Katagiri, T.; Tanaka, J. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 222.
(44) Fujita, T.; Suga, K.; Watanabe, S. *Chem. Ind. (London)* **1973**, 231.
(45) Skorianetz, W.; Giger, H.; Ohloff, G. *Helv. Chim. Acta* **1971**, *54*, 1797.

Table IV. Effect of Additives on Asymmetric Isomerization of **1** with $[Rh((+)\text{-BINAP})]^+$[a]

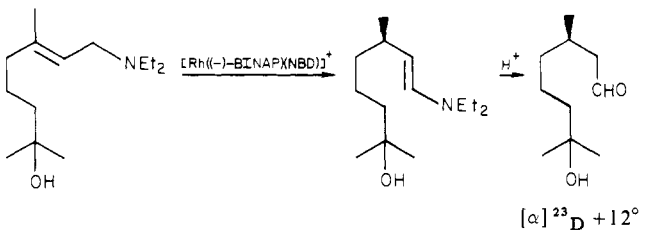
additive to $[Rh((+)\text{-BINAP})]^+$	selectivity for **3**, %	optical yield,[b] % ee
	96	93
$4NEt_3$	92	92
COD[c]	97	95
COD + $4NEt_3$	96	96
3COD	99	99

[a] $[Rh((+)\text{-BINAP})]^+$ was prepared in situ by treating $[Rh((+)\text{-BINAP})(COD)]ClO_4$ with H_2 (1 atm) in THF, [substrate] = 0.44 M, [substrate]/[Rh] = 100, 40 °C, 23 h. Conversion, 94–100%. [b] Absolute configuration, *R*. [c] $[Rh((+)\text{-BINAP})(COD)]ClO_4$ was used as a catalyst without treating with H_2.

Similarly with $[Rh((-)\text{-BINAP})(NBD)]ClO_4$ catalyst, (*E*)-*N*,*N*-diethyl-7-hydroxy-3,7-dimethyl-2-octenylamine was also isomerized to the same enamine and subsequently converted to (+)-7-hydroxydihydrocitronellal of $[\alpha]^{23}_D$ +12°. This hydroxy-



$[\alpha]^{23}_D$ +11°



$[\alpha]^{23}_D$ +12°

dihydrocitronellal is known as a perfumery with specific olfactory properties, namely, the odor of lily of the valley.[45]

The effect of additives such as COD, NEt_3, etc. on the selectivity for enamine formation and optical yield in the $[Rh((+)\text{-BINAP})]^+$-catalyzed isomerization of **1** (THF, 40 °C, 23 h) was examine (Table IV); their effect on the catalytic rate will be reported separately. It appears that an addition of triethylamine up to 4 equiv of the Rh(I) complex does not affect the optical yield seriously, while the presence of free COD slightly improves the selectivity and optical yield. Dienamine **4** was found to be a strong inhibitor; 2 mol of **4** completely suppressed the reaction.

As for the solvent, tetrahydrofuran, methanol, and acetone can be used. In dioxane the reaction was very slow and in dichloromethane, acetonitrile, or 1,2-dimethyoxyethane the isomerization did not take place at 40 °C.

Temperature dependence of the optical yields for the isomerization of diethylgeranylamine (**2**) using extra pure (99.7%) sample was examined employing a very low catalyst concentration ([substrate]/[Rh] = 8000). As shown in Table V, an amazing feature of the present catalyst is the invariant optical yield (92.2% ee) for a wide range of reaction temperature 0–80 °C. The temperature dependence is not linear, however. Above 100 °C the optical yield starts to decrease, the carbon stereochemical integrity remaining the same for the whole temperature range (0–140 °C). The constant optical yield observed for the limited temperature range (0–80 °C) may be explained assuming $\Delta\Delta S^{\ddagger} \simeq 0$ in the Curtin–Hammet principle.[46] Apparently the principle breaks for a wide range of temperature.

Estimation of the Optical Yields. Since the main body of the present experiments is concerned with the optical purity of the citronellalenamine **3**, it is indispensable to have a reliable reference for the estimate. We are aware of the recent NMR techniques[47]

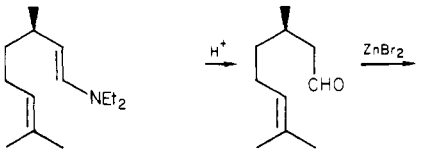
Table V. Temperature Effect on the Optical Yield for the Isomerization of **2** with $[Rh((-)\text{-BINAP})(COD)]ClO_4$[a]

temp, °C	conversion, %	optical yield of **3**,[b] % ee	temp, °C	conversion, %	optical yield of **3**,[b] % ee
60	55	99.2	100	99	97.6
70	74	99.2	120	98	96.7
80	88	99.3	140	99	94.8

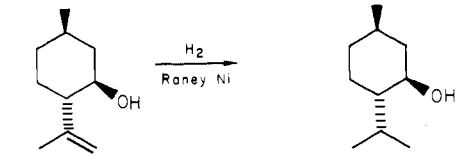
[a] [Substrate] = 2.56 M; [Rh] = 0.32 mM in THF. Reaction period: = 7 h for the reaction at 60–100 °C, 2 h for the reaction at 120 °C, and 1.5 h for the reaction at 140 °C. Purity of **2** = 99.7%. [b] The absolute configuration is *R*.

and gas chromatographic[48] or liquid chromatographic methods[49] employing a chiral stationary phase for *absolute* optical yield determinations. Our attempts using such a technique, e.g., ^1H NMR method using chiral lanthanide shift reagents or liquid chromatographic method using optically active poly(triphenylmethyl methacryrate) as a stationary phase,[50] were unsuccessful. We therefore resorted to a rather classical method and took pure *l*-menthol as a reliable base for judicious estimate of the optical purity of the citronellalenamine **3**.

Thus the optical yield of isomerization of *N*,*N*-diethylneryl- (**1**) and *N*,*N*-diethylgeranylamine (**2**) was mainly assessed on the estimated maximum rotation of the product enamine, (*E*)-*N*,*N*-diethylcitronellenamine (**3**), $[\alpha]^{21}_D \pm 77.6°$ (*n*-hexane), which was determined after converting the enamine into *l*-menthol via the reaction route shown below (see Experimental Section), a ste-



3, $[\alpha]^{21}_D$ −73.1° (*n*-hexane)



$[\alpha]^{21}_D$ −47.1° (EtOH), *l*-menthol

reoselective cyclization of (+)-citronellal into isopulegol being reported.[51] The optical rotation optically pure *l*-menthol has long been established to be $[\alpha]^{20}_D$ −50.0° (EtOH).[52] Although great care against moisture must be taken during the measurement of the rotation of **3** due to the moisture sensitivity of the enamine, the fairly large rotation and the opposite smaller optical rotation of the hydrolyzed product, citronellal, minimize the experimental error in the estimation of the optical yields and prevent the overestimate. The estimated optical yield based on the optical rotation of the enamine product was repeatedly compared with that based on the optical rotation of citronellal derived from the

(46) Eliel, E. L. "Stereochemistry of Carbon Compounds"; McGraw-Hill: New York, 1962; Chapters 6 and 8.

(47) (a) Sullivan, G. R. *Top. Stereochem.* **1976**, *10*, 287. (b) Pirkle, W. H.; Hoover, D. J. *Ibid.* **1982**, *13*, 263. (c) Yamaguchi, S. "Asymmetric Synthesis"; Morrison, J. D. Ed.; Academic Press: New York, 1983; Vol. I, Chapter 9. (d) Weismann, G. R. "Asymmetric Synthesis"; Morrison, J. D., Ed.; Academic Press: New York, 1983; Vol. I, Chapter 10. (e) Fraser, R. R. "Asymmetric Synthesis"; Morrison, J. D., Ed.; Academic Press: New York, 1983; Vol. I, Chapter 11.

(48) Schurig, G. C. V. "Asymmetric Synthesis"; Morrison, J. D., Ed.; Academic Press: New Yor, 1983; Vol. I, Chapter 7.

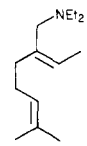
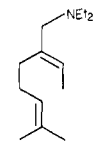
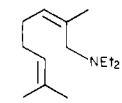
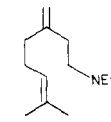
(49) (a) Pirkle, W. H.; Finn, J. M. "Asymmetric Synthesis"; Morrison, J. D., Ed.; Academic Press: New York, 1983; Vol. I, Chapter 8. (b) Pirkle, W. H.; Finn, J. M.; Hamper, B. C.; Schreiner, J.; Pribish, J. R. "Asymmetric Reactions and Processes in Chemistry"; Eliel, E. L., Otsuka, S., Eds.; American Chemical Society: Washington, DC, 1982; ACS Symp. Ser. No. 185, p 245. (c) Blaschke, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 13.

(50) Yuki, H.; Okamoto, Y.; Okamoto, I. *J. Am. Chem. Soc.* **1980**, *102*, 6356.

(51) Nakatani, Y.; Kawashima, K. *Synthesis* **1978**, 147.

(52) Huggett, W. E. *J. Soc. Chem. Ind.* **1941**, *60*, 67.

Table VI, Components of the Samples for **1** and **2**

	components, %						
	1	**2**					unidentified products
sample for **1**	94.9	0	0.1	0.1	1.5	2.1	1.3
sample for **2**	1.0	93.6	0.6	1.3		2.3	1.2

enamine. The statistics indicated that the estimates based on enamine were at least not greater than those based on the citronellal (the systematic error was less than 1–2%). When the product quantity is ample, the enamines were hydrolyzed to isolate citronellal and the optical yields assessed, employing the neat sample, against the reported maximum rotation, $[\alpha]^{20}_D$ + 16.50° (neat).[53,54] The optical yield for the isomerization of *N*-cyclohexylgeranylamine was assessed on the basis of the estimated maximum optical rotation of the product cyclohexylcitronellal imine, $[\alpha]^{20}_D$ +6.3° (*n*-hexane) (see Experimental Section). The optical yield for the isomerization of (*E*)-*N*,*N*-dimethyl-3-phenyl-2-butenylamine was determined after converting the product enamine, (−)-(*E*)-*N*,*N*-dimethyl-3-phenyl-1-butenylamine, into (−)-3-phenylbutanoic acid (see Experimental Section).

Conclusion

The present catalyst system, cationic (BINAP) Rh^I complexes, enables us to produce almost optically pure terpene enamines or aldehydes with a desired carbon-3 configuration in excellent chemical yields. This is exemplified by production of citronellal in both 3*R* and 3*S* configurations; the optical purity of (3*R*)-citronellal exceeds that (75–80% ee) of citronellal naturally available.[53,54,56] The complex catalyst is remarkably stable, optical yields higher than 99% being maintained throughout many turnovers (>7000/mol catalyst) for a wide range of reaction temperature (0–80 °C).

The substituents on the double-bond carbon atom, which constitute the enantiofaces of prochiral allylamine substrates, are in general two alkyl groups (one is methyl and the other a longer alkyl moiety). Although excellent enantioface selection can be seen in some chiral Rh(I) complex catalyzed hydrogenation of a few olefins, their prochiral double-bond carbon atoms carry generally two substituents of quite different polarity. In addition to the double-bond coordination, auxiliary interaction of substrates, e.g., carbonyl oxygen atom coordination to the metal atom, appears to assist the enantioface selection in the hydrogenation catalysis. The present virtually perfect enantioface selection in asymmetric catalysis is quite amazing when one looks at the structure of the allylamine substrates. One would then suspect that coordination of the nitrogen lone pair to the metal may also play an important role in the chiral recognition. Labeling experiments clearly established an exclusive intramolecular 1,3-hydrogen shift in the isomerization of (*E*)-*N*,*N*-dimethyl-3-phenyl-2-butenylamine suggesting involvement of an η-allylic intermediate.[28a] The geometry of the syn-η-allylic coordination, however, does not allow a simultaneous nitrogen coordination! A question then arises as to whether the nitrogen coordination participates in the enantioface selection or not. This issue deserves scrutiny indeed. The mechanistic aspects will be a subject of future publication.

Experimental Section

^{1}H NMR spectra were recorded on JEOL JNM FX 100, JEOL JNM MH 100, and/or JEOL PMX 60 spectrometers. IR spectra were obtained by using a Hitachi Infrared Spectrometer 295 instrument. Gas liquid chromatograms were obtained with Yanagimoto G-80, Shimazu GC-6A, GC-2C, and/or Hitachi 163 instruments using Triton X 305 and/or OV-101 packed in a glass column (3 m × 5 mm ϕ or 30 m × 0.2 mm ϕ from Gaskuro Kogyo Co. Ltd.). GC-mass spectra were measured on Hitachi 063 and Hitachi RMU-6MG using OV-101 in fused silica, 25 m × 0.2 mm ϕ column. Preparative gas chromatographies were run on a Shimazu GC-2C using Triton X 305 packed in a glass column (2.25 m × 1 cm ϕ). Optical rotations were measured on a JASCO DIP-SL Automatic Polarimeter. Melting points were determined on a Yamato Scientific Co. Ltd. Melting Points Apparatus. Air-sensitive reagents and products were manipulated under nitrogen or argon atmosphere.

Diphosphine Ligands. The following diphosphines were prepared according to the literature methods: (*R*)-(+)-{$[\alpha]^{25}_D$ + 299° (C_6H_6)}, (*S*)-(−)- {$[\alpha]^{25}_D$ −229° (C_6H_6)}, and (±)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl [(+)-, (−)-, and (±)-BINAP],[30] (−)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane [(−)-DIOP] {$[\alpha]^{24}_D$ −11.9° (C_6H_6)},[37] (−)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(dicyclohexylphosphino)butane [(−)-CyDIOP] {$[\alpha]^{20}_D$ −24.1° (C_6H_6)},[39] (−)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diisopropylphosphino)butane [(−)-*i*-PrDIOP] {$[\alpha]^{20}_D$ −31.0° (C_6H_6)},[39] (−)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diethylphosphino)butane [(−)-Et-DIOP] {$[\alpha]^{20}_D$ −25.5° ($CHCl_3$)},[39] (2*S*,4*S*)-*N*-(*tert*-butoxycarbonyl)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine (BPPM) {$[\alpha]^{20}_D$ −37.0° (C_6H_6)},[38] (*S*)-*N*,*N*-dimethyl-1-[(*R*)-1′,2-bis(diphenylphosphino)ferrocenyl]ethylamine [(*S*)-(*R*)-BPPFA] {$[\alpha]^{25}_D$ +337° ($CHCl_3$)},[31] 1,2-bis(diphenylphosphino)ethane(diphos),[57] 1,3-bis(diisopropylphosphino)propane (DIPP),[58] and 1,1′-bis(diphenylphosphino)-ferrocene (BDPF).[59]

Allylamine Derivatives. (*Z*)-*N*,*N*-Diethyl-3,7-dimethyl-2,6-octadienylamine (diethylnerylamine (**1**) purity 94.9%)[41,42] and (*E*)-*N*,*N*-diethyl-3,7-dimethyl-2,6-octadienylamine (diethylgeranylamine (**2**), purity 93.6% and 99.7%)[43,44] were prepared from the reaction of isoprene and myrcene, respectively, with diethylamine by the known method. The purity of **1** and **2** used for usual experiments were determined by GLC and the components of these samples were carefully analyzed by using GC-mass technique and the results are shown in Table VI. In order to eliminate the geometrical isomer, which affects the optical yield seriously, the above sample of **2** was subjected to an efficient fractional distillation thorough a column with 100 theoretical plates (bp 70 °C (2 mm)) to give a sample of 99.7% purity containing less than 0.04% of **1**. (*E*)-*N*-Cyclohexyl-3,7-dimethyl-2,6-octadienylamine (cyclohexylgeranylamine, purity 100%),[60] (*E*)-*N*,*N*-diethyl-7-hydroxy-3,7-dimethyl-2-octenylamine (purity 98.5%),[61] and (*Z*)-*N*,*N*-diethyl-7-hydroxy-3,7-dimethyl-2-octenylamine (purity 98.5%)[61] were prepared by the known methods. *N*,*N*-Dimethylallylamine was a commercial product from Tokyo Kasei Co. Ltd. Preparations of other allylamines are given below.

(*E*)-*N*-Cyclohexyl-*N*-methyl-3,7-dimethyl-2,6-octadienylamine (**cyclohexylmethylgeranylamine**) was prepared from myrcene and methylcyclohexylamine according to a similar method as for the preparation of **2**[43] in 38% yield after fractional distillation of the initial crude product

(53) Sully, B. D.; Williams, P. L. *Perfum. Essent. Oil Rec.* **1968**, *59*, 365.
(54) A referee suggested an absolute method to determine percent ee by ^{1}H NMR or HPLC measurement after converting citronellal into citronellic acid derivatives.[55] The ^{1}H NMR method, albeit convenient, does not provide very accurate percent ee values. Although the HPLC method using citronellic acid amide may provide more accurate results, it requires much work involving chemical conversions of several steps. Thus it is not simpler than the present method. The optical purity, assessed by the above absolute method using HPLC, of a citronellal sample which shows a rotation $[\alpha]^{25}_D$ +12.00° (neat) is 80.4% ee. If this relation is employed, our reference rotation $[\alpha]^{20}_D$ +16.50° (neat) for optically pure citronellal corresponds to 110.6% ee, indicating that no overestimation is involved in our method.
(55) Valentine, Jr., D.; Chan, K. K.; Scott, C. G.; Johnson, K. K.; Toth, K.; Saucy, G. *J. Org. Chem.* **1976**, *41*, 62.
(56) (a) O'Donnell, G. W.; Sutherland, M. D. *Aust. J. Chem.* **1966**, *19*, 525. (b) Ciardelli, F.; Pino, P. *Ric. Sci.*, Paste 2: *Sez. A* **1964**, *4*, 694.
(57) Chatt, J.; Hart, F. A. *J. Chem. Soc.* **1960**, 1378.
(58) Issleib, K.; Müller, D.-W. *Chem. Ber.* **1959**, *92*, 3175.
(59) Rausch, M. D.; Ciappenlli, D. J. *J. Organomet. Chem.* **1967**, *10*, 127.
(60) Kumobayashi, H.; Taketomi, T.; Akutagawa, S.; Nakayama, T.; Yoshida, T. *Jpn. Kokai Tokkyo Koho* **1979**, 54–5907.
(61) Takabe, K.; Katagiri, T.; Tanaka, J. *Tetrahedron Lett.* **1975**, 3005.

containing ca. 15% of the *Z* amine: bp 125 °C (1 mm); purity 98.2%; ^{1}H NMR ($CDCl_3$) δ 1.0–2.6 (m, 11 H, C_6H_{11}), 1.60 (s, 3 H, CH_3), 1.63 (s, 3 H, CH_3), 1.67 (s, 3 H, CH_3), 2.05 (br s, 4 H, CH_2CH_2), 2.20 (s, 3 H, NCH_3), 3.80 (d, J = 7.1 Hz, 2 H, CH_2N), 5.07 (m, 1 H, CH=), 5.25 (t of m, J = 7.1 Hz, 1 H, CH=); IR (neat film) 1670 (m) cm^{-1} ($\nu_{C=C}$); Anal. ($C_{17}H_{30}N$) C, H, N.

(*E*)-*N*,*N*-Diphenyl-3,7-dimethyl-2,6-octadienylamine (diphenylgeranylamine) was prepared from the reaction (50 °C for 0.5 h and then at ambient temperature for further 15 h) of geranyl chloride[62] (3.5 g, 0.02 mol) with lithium diphenylamide, prepared in situ from diphenylamine (3.4 g, 0.02 mol) and *n*-butyl lithium. After usual workup and purification through column chromatography on silica gel (Merk 70-230 mesh, *n*-hexane–ethyl acetate (95:5) as eluant) followed by vacuum distillation, the allylamine was obtained as a colorless liquid (3.9 g, 64%): bp 162–4 °C (10^{-3} mm); purity >99%; ^{1}H NMR ($CDCl_3$) δ 1.57 (s, 3 H, CH_3), 1.60 (s, 3 H, CH_3), 1.65 (s, 3 H, CH_3), ~2.0 (br s, 4 H, CH_2CH_2), 4.28 (d, J = 7.1 Hz, 2 H, CH_2N), 4.90–5.10 (m, 1 H, =CH), 5.34 (t, J = 7.1 Hz, 1 H, =CH), 6.76–7.00 (m, 6 H, Ar), 7.10–7.28 (m, 4 H, Ar); IR (neat film) 1670 ($\nu_{C=C}$), 1585 ($\nu_{C=C}$), 745, 690 (Ph) cm^{-1}; Anal. ($C_{22}H_{27}N$) C, H, N.

(*E*)-*N*-Phenyl-3,7-dimethyl-2,6-octadienylamine (phenylgeranylamine) was similarly prepared from the reaction of geranyl chloride (4.3 g, 0.025 mol) with an excess of lithium anilide (5 g, 0.05 mol) obtained from *n*-butyllithium and aniline in *n*-hexane. After usual workup, crude phenylgeranylamine was obtained as an orange liquid. The crude allylamine was purified on silica gel column (Merk 70–230 mesh, *n*-hexane–ethyl acetate (21:1) as eluant) and subsequently by vacuum distillation to give a pure product as a pale yellow oil (3.5 g, 61%): bp 115–117 °C (1 mm); purity >99%; ^{1}H NMR ($CDCl_3$) δ 1.60 (s, 3 H, CH_3), 1.69 (s, 6 H, CH_3), ~2.1 (br s, 4 H, CH_2CH_2), 3.45 (br, 1 H, NH), 3.66 (d, J = 6.6 Hz, 2 H, CH_2N), 4.9–5.1 (m, 1 H, =CH), 5.30 (t of m, ^3J = 6.6 Hz, 1 H, =CH), 6.50–6.75 (m, 3 H, Ar), 7.05–7.20 (m, 2 H, Ar); IR (neat film) 3410 (ν_{NH}), 1670 ($\nu_{C=C}$), 1600 ($\nu_{C=C}$), 745, 690 cm^{-1} (Ph); Anal. ($C_{16}H_{23}N$) C, H, N.

***N*,*N*-Dimethyl-3-methyl-2-butenylamine**, 3-Methyl-2-buten-1-ol was converted to 1-chloro-3-methyl-2-butene (bp 108–118 °C, 61% yield) by treatment with thionyl chloride at 50 °C for 2.5 h in chloroform. The chloride (14.1 g, 0.14 mol) was slowly added to 50% aqueous dimethylamine (40 g, 0.27 mol) at 0 °C under vigorous stirring. The reaction mixture was stirred at ambient temperature further for 2 days and to the resulting mixture was slowly added an excess of 50% potassium hydroxide solution at ambient temperature with stirring. The separated organic layer was washed with water, dried over anhydrous magnesium sulfate, and distilled to give the allylamine as a colorless oil (7 g, 46%): bp 120–121 °C; purity 95%; ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 3 H, CH_3), 1.42 (br s, 3 H, CH_3), 1.90 (s, 6 H, $N(CH_3)_2$), 2.55 (d, J = 6.9 Hz, 2 H, NCH_2), 4.94 (t of m, ^3J = 6.9 Hz, 1 H, CH=); IR (neat film) 1680 cm^{-1} ($\nu_{C=C}$).

(*E*)-*N*,*N*-Dimethyl-2-methyl-2-butenylamine, Methyl (*E*)-2-methyl-2-butenoate (37.4 g, 0.33 mol) was converted to (*E*)-1-chloro-2methyl-2-butene (13.6 g, 58% yield, bp 110–112 °C) by reduction with lithium aluminum hydride and subsequent chlorination with triphenylphosphine–carbon tetrachloride. The chloride (13.6 g, 0.13 mol) was slowly added to a large excess of 50% aqueous dimethylamine (117 g, 1.3 mol) at ambient temperature under vigorous stirring. The resulting reaction mixture was stirred further for 15 h at that temperature. After treatment with an excess of 5 N sodium hydroxide solution, the organic layer was extracted with ether, washed with water, dried over anhydrous magnesium sulfate, and distilled to give 10.6 g (72%) of the allylamine: bp 115–117 °C; purity 98.4%; ^{1}H NMR ($CDCl_3$) δ 1.60 (d of m, ^3J = 7 Hz, 3 H, CH_3), 1.62 (s, 3 H, CH_3), 2.14 (s, 6 H, $N(CH_3)_2$), 2.73 (br s, 2 H, CH_2N), 5.15–5.35 (m, 1 H, CH=); IR (neat film) 1678 cm^{-1} ($\nu_{C=C}$); Anal. ($C_7H_{15}N$) H, N. C: calcd 74.30; found 73.21.

(*E*)-*N*,*N*-Dimethyl-3-phenyl-2-butenylamine was prepared from ethyl (*E*)-3-phenyl-2-butenoate.[63] The ester was reduced with lithium aluminum hydride, chlorinated with thionyl chloride in chloroform, and finally aminated with 50% aqueous dimethylamine solution as described above to give the allylamine (E/Z = 10.6/1) in 52% yield, bp 156 °C (3 mm). The more purified (*E*)-allylamine (E/Z = 195/1) was isolated from the above E–Z mixture by preparative gas chromatography. ^{1}H NMR ($CDCl_3$) δ 1.98 (br s, 3 H, CH_3), 2.20 (s, 6 H, $N(CH_3)_2$), 2.96 (d, J = 6.8 Hz, 2 H, CH_2), 5.81 (t of q, ^3J = 6.8, ^4J = 1.2 Hz, 1 H, =CH), 6.97–7.40 (m, 5 H, Ph); IR (neat film) 1645 ($\nu_{C=C}$), 756, 695 cm^{-1} (Ph); Anal. ($C_{12}H_{17}N$) C, H, N.

(*E*)-*N*,*N*-Dimethyl-2-butenylamine was prepared from the reaction of (*E*)-1-chloro-2-butene (9.5 g, 0.1 mol) with an excess of 50% aqueous dimethylamine (0.75 mol) at ambient temperature for 24 h as a colorless liquid containing *N*,*N*-dimethyl-1-methyl-2-propenylamine (18.8%) and *N*,*N*-dimethyl-3-butenylamine (11.7%) (7.0 g, 70%), bp 93 °C. The purity and the compsotion were determined by ^{1}H NMR and GLC. The mixture was used for the isomerization experiments without further purification. (*E*)-*N*,*N*-Dimethyl-2-butenylamine: ^{1}H NMR ($CDCl_3$) δ 1.70 (m, 3 H, CH_3), 2.23 (s, 6 H, $N(CH_3)_2$), 2.87 (m, 2 H, CH_2), 5.47–5.70 (m, 2 H, CH=CH); IR (neat film) 1680 ($\nu_{C=C}$), 960 cm^{-1} (*trans*-CH=CH).

***N*,*N*-Dimethyl-2-methyl-2-propenylamine**[64] was similarly prepared from 3-chloro-1-methyl-1-propene (9.1 g, 0.1 mol) with an excess of 50% aqueous dimethylamine (0.75 mol) in 25% yield (2.5 g): bp 93 °C; purity 98%; ^{1}H NMR ($CDCl_3$) δ 1.75 (s, 3 H, CH_3), 2.18 (s, 6 H, $N(CH_3)_2$), 2.79 (s, 2H, CH_2), 4.84 (m, 2 H, $=CH_2$); IR (neat film) 1655 ($\nu_{C=C}$), 893 cm^{-1} ($=CH_2$).

***N*,*N*-Dimethyl-1-methyl-2-propenylamine** was similarly prepared from 3-chloro-1-butene (10.8 g, 0.12 mol) with an excess of 50% aqueous dimethylamine (0.75 mol) as a colorless oil (5.0 g, bp 75 °C) containing (*E*)-*N*,*N*-dimethyl-2-butenylamine (31.1%) and *N*,*N*-dimethyl-3-butenylamine (12.7%) as impurities. The mixture was used for the isomerization experiments without further purification. *N*,*N*-Dimethyl-1-methyl-2-propenylamine: ^{1}H NMR ($CDCl_3$) δ 1.07 (d, J = 6.6 Hz, 3 H, CH_3), 2.50 (s, 6 H, $N(CH_3)_2$), 2.67–3.00 (m, 1 H, CH), 4.83–5.23 (m, 2 H, $=CH_2$), 5.63–6.17 (m, 1 H, =CH); IR (neat film) 1645 cm^{-1} ($\nu_{C=C}$).

(±)-3-(Diethylamino)cyclohexene, 3-Hydroxycyclohexene (7 g, 0.071 mol) was chlorinated with a mixture of carbon tetrachloride (64 mL) and triphenylphosphine (24.2 g, 0.074 mol) to give 5.2 g (56% yield) of 3-chlorocyclohexene as a colorless liquid, bp 142–146 °C. The chloride was dropwise added at ambient temperature to a suspension of lithium diethylamide in ether (50 mL), prepared from diethylamine (6.6 g, 0.09 mol) and *n*-butyl lithium (0.09 mol), and the resulting mixture was stirred overnight at that temperature. The volatile materials were collected in vacuo (<100 °C (1 mm)). Fractional distillation of the distillate gave the crude allylamine, bp 105–108 °C (52 mm), 2.2 g (18% yield). Further purification by preparative gas chromatography gave the purified allylamine (purity >99%). ^{1}H NMR ($CDCl_3$) δ 1.05 (t, J = 7.3 Hz, 6 H, $N(CH_2CH_3)_2$), 1.2–2.0 (m, 6 H, CH_2) 3.36 (m, 1 H, CHN), 5.52 (m, 4 H, $N(CH_2CH_3)_2$), 5.63 (m, 1 H, CH=), 5.72 (m, 1 H, CH=); IR (eat film) 1645 cm^{-1} ($\nu_{C=C}$); Anal. ($C_{10}H_{19}N$) C, H, N.

(±)-*trans*-3-(Diethylamino)-4-isopropyl-1-methylcyclohexene [(±)-*trans*-diethylpiperitylamine] was prepared from (±)-*trans*-3-acetoxy-4-isopropyl-1-methylcyclohexene [(±)-*trans*-piperityl acetate], which was obtained by acetylation of (±)-*trans*-3-hydroxy-4-isopropyl-1-methylcyclohexene. Thus, a mixture of piperityl acetate (25 g, 0.13 mol) and diethylamine (27 g, 0.37 mol) was heated to 80 °C in an ampule in the presence of palladium nitrate (576 mg, 2.5 mmol) and 3-methyl-1-phenyl-2-phospholene (1.90 g, 7.5 mmol). After 10 h, the reaction mixture was extracted with ether and the extract was washed with dilute sulfuric acid. The combined water layer was neutralized with sodium hydroxide and extracted with ether. Distillation of the ether solution, after being dried over sodium hydroxide, gave the piperitylamine as a colorless liquid (7 g, 25%): bp 90 °C (1 mm); purity 98%; ^{1}H NMR ($CDCl_3$) δ 0.74 (d, J = 7.0 Hz, 3 H, $CH(CH_3)_2$), 0.91 (d, J = 7.0 Hz, 3 H, $CH(CH_3)_2$), 0.98 (t, J = 7.2 Hz, 6 H, $N(CH_2CH_3)_2$), 1.22 (m, 2 H, CH_2), 1.65 (br s, 3 H, CH_3C=), 1.88 (m, 2 H, CH_2), 2.1–2.7 (m, 2 H, $CHCH(CH_3)_2$), 2.43 (q, J = 7.2 Hz, 4 H, $N(CH_2CH_3)_2$), 3.00 (m, 1 H, CHN), 5.34 (m, 1 H, C=CH); IR (neat film) 1675 cm^{-1} ($\nu_{C=C}$); Anal. ($C_{14}H_{27}N$) C, H, N.

Catalyst Precursor, [Rh(diphos)(COD)]ClO_4,[34] [Rh((-)-BINAP)(NBD)]ClO_4,[30] [Rh((-)-CyDIOP)(NBD)]ClO_4,[19] [Rh((-)-*i*-PrDIOP)(NBD)]ClO_4,[39] [Rh((-)-EtDIOP)(NBD)]ClO_4,[39] [Rh$(PPh_3)_2$(COD)]ClO_4,[34] and [Rh(diphos)$_2$]ClO_4[33] were prepared by the known methods. [Rh(DIPP)(COD)]ClO_4, [Rh(BDPF)(COD)]ClO_4, [Rh((*S*)-(*R*)-BPPFA)(COD)]ClO_4, and [Rh(BPPM)(COD)]ClO_4 were prepared similarly from $[Rh(COD)Cl]_2$[65] and the appropriate diphosphine ligands in the presence of $AgClO_4$ according to the method of Osborn.[34] Preparations of other important complexes are as follows.

[Rh((±)-BINAP)(COD)]ClO_4. To an acetone (30 mL) solution of $[Rh(COD)Cl]_2$ (0.123 g, 0.25 mmol) was added $AgClO_4$ (0.104 g, 0.5 mmol) and the mixture was stirred for 1 h at ambient temperature. The colorless precipitates formed were removed by filtration through filter paper and washed with acetone. To the pale yellow filtrate and the washings was added solid (±)-BINAP (0.311 g, 0.5 mmol) and the resulting orange-vermilion solution was stirred for 1 h at ambient temperature. On concentration of the reaction mixture to ca. 2 mL under reduced pressure, [Rh((±)-BINAP)(COD)]ClO_4 began to crystallize,

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and 5 mL of ether was slowly added to complete the precipitation. After the reaction mixture had been allowed to stand overnight at ambient temperature, deep-orange crystals that precipitated were separated, washed with ether, and dried under reduced pressure: 0.36 g (77%); mp 200–205 °C (in an Ar-filled capillary); ^{1}H NMR (CD_2Cl_2) δ 2.00–2.62 (m, 8 H, CH_2), 4.58 (br, 2 H, CH=), 4.84 (br, 2 H, CH=), 6.42–8.22 (m, 32 H, Ar); Anal. ($C_{52}H_{44}ClO_4Rh$) C, H.

[Rh((+)-BINAP)(COD)]ClO$_4$ and [Rh((-)-BINAP)(COD)]ClO$_4$ were similarly prepared from $[Rh(COD)Cl]_2$, $AgClO_4$, and 2 equiv of (+)- or (-)-BINAP, respectively, in acetone in 70–85% yield. The crude product obtained from the concentrated reaction solution by addition of ether was carefully recrystallized from an acetone–ether mixture to give an analytically pure product as deep-orange crystals: mp 164 °C dec (in an Ar-filled capillary); ^{1}H NMR (CD_2Cl_2) δ 2.00–2.62 (m, 8 H, CH_2), 4.58 (br, 2 H, CH=), 4.84 (br, 2 H, CH=), 6.42–8.22 (m, 32 H, Ar); Anal. ($C_{52}H_{44}ClO_4Rh$) C, H, Cl. More well-formed crystals of the complex can be obtained by recrystallization from THF–ether as THF solvated complex: mp 153 °C dec (in an Ar-filled capillary); ^{1}H NMR (CD_2Cl_2) δ 1.60–2.00 (m, 4 H, CH_2 of THF), 2.00–2.62 (m, 8 H, CH_2), 3.40–3.80 (m, 4 H, CH_2O of THF), 4.58 (br, 2 H, CH=), 4.82 (br, 2 H, CH=), 6.42–8.22 (m, 32 H, Ar); Anal. ($C_{52}H_{44}ClO_4Rh\cdot C_4H_8O$) C, H, Cl.

[Rh((-)-DIOP)(COD)]ClO$_4$ was similarly prepared from $[Rh(COD)Cl]_2$ (0.27 g, 0.55 mmol) and (-)-DIOP (0.50 g, 1.15 mmol) in acetone. The crude complex was recrystallized from an acetone–ether mixture to give deep-orange crystals (0.37 g, 45%): mp 183–184 °C dec (in an Ar-filled capillary); ^{1}H NMR ($CDCl_3$) δ 1.09 (s, 6 H, CH_3), 2.37 (m, 8 H, CH_2), 2.71 (m, 4 H, CH_2), 3.67 (m, 2 H, CH), 4.54 (m, 4 H, CH=), 5.26–8.00 (m, 20 H, Ph). Anal. ($C_{39}H_{44}ClO_6Rh$) C, H.

Catalytic Isomerization Reactions. The catalytic isomerization was carried out under argon and special care was exercised to prevent the product enamines from being hydrolyzed by moisture during their isolation and the physical measurements. Representative examples are given below.

Diethylnerylamine (1). Typically, a THF (5 mL) solution of [Rh(diphosphine)(COD)]ClO_4 (0.025 mmol) was treated with dihydrogen (1 atm at ambient temperature) for 15 min and the excess dihydrogen was replaced by argon. To this catalyst solution was added the allylamine **1** (0.52 g, 2.5 mmol), and the resulting scarlet-vermilion solution was heated at 40 °C, 23 h. The reaction was quenched by addition of an excess (ca. 0.1 g, 0.5 mmol) of diphos. After removal of the solvent vacuum distillation of the residue using a Kugel-Rohr distillation apparatus gave (*E*)-*N*,*N*-diethyl-3,7-dimethyl-1,6-octadienylamine [(*E*)-diethylcitronellenamine] (**3**), which was analyzed by GLC and ^{1}H NMR and submitted to the measurement of optical rotation. The optical yield was determined by the specific rotation on the basis of its estimated maximum rotation, $[\alpha]^{20}_D$ ±77.6° (*n*-hexane). **3**: bp 120 °C (2 mm); ^{1}H NMR ($CDCl_3$) δ 0.96 (d, 3 H, *J* = 7.2 Hz, CH_3), 1.01 (t, 6 H, *J* = 7.1 Hz, NCH_2CH_3), 1.3 (m, 2 H, $CH_2CH(CH_3)$), 1.58 (br s, 3 H, CH_3), 1.66 (br s, 3 H, CH_3), 1.95 (m, 3 H, CH_2CH= + CH), 2.92 (q, 4 H, *J* = 7.1 Hz, NCH_2CH_3), 3.93 (d of d, 1 H, *J* = 14.6, 8.4 Hz, CH=), 5.11 (br t, 1 H, *J* = 7.3 Hz, CH=), 5.79 (d of d, 1 H, *J* = 14.6, 0.8 Hz, =CHN); IR (neat film) 1660 ($\nu_{C=C}$), 1655 ($\nu_{C=C}$), 985 cm^{-1} (*trans*-CH=CH); MS, *m/e* 208 (M^+).

The diene complexes [Rh(diphosphine)(diene)]ClO_4 themselves were also used as the catalyst precursor without treatment with dihydrogen. In some cases, a catalyst solution was prepared in situ by treatment of $[Rh(COD)Cl]_2$ or $[Rh(NBD)Cl]_2$ with 2 equiv of an appropriate diphosphine and $AgClO_4$ in THF and employed for the isomerization without isolation after removing AgCl by filtration. The neutral complex catalyst $[Rh((\pm)\text{-BINAP})Cl]_2$ was prepared in situ from $[Rh(C_2H_4)_2Cl]_2$[66] and 2 equiv of (±)-BINAP in THF and employed for the isomerization.

Diethylgeranylamine (2) was similarly isomerized to give the (*E*)-enamine **3**. In most cases, the optical yield was determined on the basis of the optical rotation of **3**. In the case of the temperature dependence experiment, extra pure diethylgeranylamine (purity 99.7%) was used as the starting allylamine and the optical yield was determined from the specific rotation of the hydrolyzed product, citronellal, referring to the reported maximum optical rotation of pure (+)-citronellal, $[\alpha]^{20}_D$ +16.50° (neat).[53] The experimental scale enabled us to measure the optical rotation of citronellal neat.

Cyclohexylmethylgeranylamine was isomerized similarly to give the corresponding (*E*)-enamine: bp 130 °C (1 mm); ^{1}H NMR ($CDCl_3$) δ 0.96 (d, *J* = 6.3 Hz, 3 H, CH_3), 0.7–3.0 (m, 11 H, C_6H_{11}), 1.59 (br s, 3 H, CH_3), 1.68 (br s, 3 H, CH_3), 2.43 (s, 3 H, CH_3), 3.98 (d of d, *J* = 13.8, 8.0 Hz, 1 H, CH=), 5.10 (m, 1 H, CH=), 5.95 (d, *J* = 13.8 Hz, 1 H, =CHN).

Cyclohexylgeranylamine was similarly isomerized to *N*-(3,7-dimethyl-6-octenylidene)cyclohexylamine: bp 130 °C (1 mm) [lit.[67] bp 137–139 °C (2 mm)]; ^{1}H NMR ($CDCl_3$) δ 0.89 (d, *J* = 6.4 Hz, 3 H, CH_3), 1.56 (s, 3 H, CH_3), 1.63 (s, 3 H, CH_3), 1.00–3.30 (m, 11 H, C_6H_{11}), 1.83–2.40 (m, 4 H, CH_2CH_2), 5.00 (t of m, *J* = 6.4 Hz, 1 H, CH=); IR (neat film) 1667 cm^{-1}.

The optical purity of the imine was determined on the basis of its estimated maximum optical rotation. Thus, cyclohexylamine (15.7 g, 0.16 mol) was added to commercial (+)-citronellal (24.4 g, 0.16 mol, $[\alpha]^{20}_D$ +13.1° (neat)) at ambient temperature. To the resulting emulsified mixture was added 35 g of Molecular Sieves 3A and the reaction mixture was stirred at that temperature for 24 h. After removing Molecular Sieves, the reaction product was distilled to give *N*-(3,7-dimethyl-6-octenylidene)cyclohexylamine (20 g, 54%): bp 97–98 °C (ca. 0.2 mm); purity 100%; $[\alpha]^{20}_D$ + 5.0° (*c* 8.50, *n*-hexane). As the optical rotation of pure (+)-citronellal is reported to be $[\alpha]^{20}_D$ +16.50°,[53] the maximum optical rotation of the imine can be calculated to be $[\alpha]^{20}_D$ +6.3° (*n*-hexane).

(*Z*)-*N*,*N*-Diethyl-7-hydroxy-3,7-dimethyl-2-octenylamine. A solution of the allylamine (114 g, 0.5 mol) and [Rh((+)-BINAP)(NBD)]ClO_4 (229 mg, 0.25 mmol) in THF (70 mL) was heated at 100 °C for 15 h in a pressure bottle. After removal of the THF, distillation of the residue under reduced pressure gave 112 g (98.2%) of a colorless liquid, bp 105–11 °C (1 mm), which was identified as (*E*)-*N*,*N*-diethyl-7-hydroxy-3,7-dimethyl-1-octenylamine from ^{1}H NMR and GLC analysis: purity 98.0%; ^{1}H NMR ($CDCl_3$) δ 0.95 (d, *J* = 6.3 Hz, 3 H, CH_3), 1.02 (t, *J* = 6.3 Hz, 6 H, NCH_2CH_3), 1.20 (s, 6 H, $(CH_3)_2C(OH)$), 1.1–1.6 (br, 7 H, CH_2 + OH), 2.00 (br, 1 H, CH), 3.85 (d of d, *J* = 14.2, 8.0 Hz, 1 H, CH=), 5.68 (d, *J* = 14.2 Hz, 1 H, =CHN); IR (neat film) 3360 (ν_{OH}), 1650 ($\nu_{C=C}$), 938 cm^{-1} (*trans*-CH=CH).

An aliquot of the enamine was hydrolyzed by treatment with 1.2 equiv of 10% H_2SO_4 at 5–10 °C for 0.5 h to give (+)-7-hydroxy-3,7-dimethyloctanal, bp 89–90 °C (1 mm), $[\alpha]^{23}_D$ +11.0° (*c* 20, benzene). The reported maximum optical rotation of the hydroxycitronellal is $[\alpha]^{23}_D$ +10°.[45]

(*E*)-*N*,*N*-Diethyl-7-hydroxy-3,7-dimethyl-2-octenylamine was similarly isomerized with [Rh((-)-BINAP)(NBD)]ClO_4 to give the same enamine as above in 98.2% yield, which gave (+)-7-hydroxy-3,7-dimethyloctanal of $[\alpha]^{23}_D$ +12° (*c* 20, benzene) after hydrolysis with dilute H_2SO_4.

(*E*)-*N*,*N*-Dimethyl-7-phenyl-2-butenylamine (*E*/*Z* = 195/1) (0.53 g, 3 mmol) was heated at 60 °C in the presence of [Rh((+)-BINAP)(COD)]ClO_4 (28 mg, 0.03 mmol) in THF for 48 h to give the corresponding optically active enamine, (-)-(*E*)-*N*,*N*-dimethyl-3-phenyl-1-butenylamine, (0.50 g, 94%): bp 120 °C (2 mm); ^{1}H NMR ($CDCl_3$) δ 1.33 (d, *J* = 7.1 Hz, 3 H, CH_3), 2.45 (s, 6 H, $N(CH_3)_2$), 3.41 (d of q, *J* = 7.3, 7.1 Hz, 1 H, CH), 4.35 (d of d, *J* = 14.1, 7.3 Hz, 1 H, CH=), 5.87 (d, *J* = 14.1 Hz, 1 H, CH=), 7.0–7.4 (m, 5 H, Ar); IR (neat film) 1658 sh, 1650 ($\nu_{C=C}$), 1595, 935 (*trans*-CH=CH), 755, 690 cm^{-1} (Ph); Anal. ($C_{12}H_{17}N$) C, H, N.

The optical purity of the enamine was determined after converting it into 3-phenylbutanoic acid. Thus, the enamine (0.3 g) was hydrolyzed to 3-phenylbutanal by treatment with 4 N acetic acid (2 mL) at ambient temperature for 1 h. The crude 3-phenylbutanal was oxidized with freshly prepared silver oxide (5 g) in aqueous sodium hydroxide. The reaction separated from solid material being washed with ether and acidified with an excess of concentrated hydrochloric acid, the organic layer was extracted with ether. After usual workup, the volatile product was distilled and identified as 3-phenylbutanoic acid from its IR and ^{1}H NMR, 0.19 g (68%), bp 165–170 °C (2 mm). Anal. ($C_{10}H_{12}O_2$) H. C: calcd, 73.14; found, 72.72. $[\alpha]^{26}_D$ -52.3° (*c* 2.42, benzene). The optical purity was estimated as 90% ee based on its reported maximum rotation, $[\alpha]_D$ -58.5° (benzene).[68]

Isomerization in ^{1}H NMR Tubes. Typically, 0.01 mmol of a rhodium-(±)-BINAP complex was dissolved in 0.4 mL of dry THF-d_8 in an ^{1}H NMR tube. After treatment with hydrogen or without treatment, an allylamine (1 mol) was added at -78 °C and the tube was sealed under Ar. The sample was placed in a thermostated bath for appropriate periods and the reaction was monitored by ^{1}H NMR. The reaction products were further analyzed by GLC.

^{1}H NMR Spectral Data of Some Isomerized Products. (*E*)-*N*,*N*-Dimethyl-1-propenylamine: (THF-d_8) δ 1.27 (d of d, *J* = 6.8, 1.2 Hz, 3 H, CH_3), 2.49 (s, 6 H, $N(CH_3)_2$), 4.17 (d of q, *J* = 13.6 Hz, 6.8 Hz, 1 H, CH=), 5.90 (d of q, *J* = 13.6, 1.2 Hz, 1 H, =CHN).

(*E*)-*N*,*N*-Dimethyl-1-butenylamine: (THF-d_8) δ 1.27 (t, *J* = 6.8 Hz, 3 H, CH_3), 2.49 (s, 6 H, $N(CH_3)_2$), 4.17 (d of t, *J* = 13.6, 6.6 Hz, 1 H, CH=), 5.90 (d of t, *J* = 13.6, 1.2 Hz, 1 H, =CHN).

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***N,N*-Dimethyl-2-methyl-1-propenylamine**: (THF-d_8) δ 1.58 (s, 3 H, CH_3), 1.67 (s, 3 H, CH_3), 2.37 (s, 6 H, $N(CH_3)_2$), 5.31 (m, 1 H, CH=).

(*E*)-*N,N*-Dimethyl-3-methyl-1-butenylamine: (THF-d_8) δ 0.96 (d, J = 6.7 Hz, 6 H, $CH(CH_3)_2$), 2.18–2.37 (m, 1 H, CH), 2.48 (s, 6 H, $N(CH_3)_2$), 4.15 (d of d, J = 13.9, 7.2 Hz, 1 H, CH=), 5.91 (d of d, J = 13.9, 0.8 Hz, 1 H, CH=).

Estimation of the Maximum Optical Rotation of (*E*)-*N,N*-Diethyl-3,7-dimethyl-1,6-octadienylamine (3) and Determination of the Absolute Configuration. The enamine **3** (8.3 g, 40 mmol; purity 82.6%; $[\alpha]^{21}_D$ −73.1 (*c* 5.27, *n*-hexane)), prepared by the present isomerization from **1**, was acidified to pH 4 by addition of 30% aqueous acetic acid below 40 °C (under ice-cooling), and the resulting solution was stirred for further 15 min. The organic layer was extracted with several portions of *n*-hexane, and the combined extracts were washed with aqueous sodium carbonate, dried over magnesium sulfate, and distilled under reduced pressure to give 5.0 g (80%) of (+)-citronellal (bp 94–96 °C (8 mm); purity 97.3%; $[\alpha]^{21}_D$ +16.4° (neat)), which was transformed into *l*-menthol without further purification. Thus, to a solution of the citronellal (5.0 g) in benzene (20 mL) was added gradually 7.32 g of $ZnBr_2$ at 5–10 °C, and the resulting suspension was stirred for 15 min. After filtration of $ZnBr_2$, the reaction mixture was washed with water and then aqueous sodium carbonate and dried over sodium sulfate. Distillation of the product, after removal of the solvent, gave 3.5 of isopulegol (bp 50–60 °C (2 mm)),[51] which was hydrogenated to *l*-menthol in ethanol with Raney nickel catalysts (100 °C, 100 kg/cm^2 H_2, 2 h). After usual workup the resulting *l*-menthol was isolated with preparative gas chromatography for the measurement of optical rotation. During this isolation, any procedure involving crystallization was avoided. The sample of *l*-menthol in our hand was found to be 99.1% pure containing 0.9% of isomenthol by GLC analysis and showed optical rotation of $[\alpha]^{21}_D$ −47.1° (*c* 2.70, EtOH) after correction for the small amount of isomenthol. The optical purity of the *l*-menthol was determined to be 94.2% ee based on the optical rotation of pure *l*-menthol.[52] Thus, the maximum optical rotation of (−)-(*E*)-*N,N*-diethyl-3,7-dimethyl-1,6-octadienylamine (**3**) was estimated to be $[\alpha]^{21}_D$ −77.6° (*n*-hexane), and the absolute configuration of (−)-**3** was determined to be *R*.

Registry No. **1**, 40137-00-6; **2**, 40267-53-6; (±)-**3**, 67362-90-7; (*R*)-**3**, 67392-56-7; (*S*)-**3**, 67392-54-5; (*R*)-BINAP, 76189-55-4; (*S*)-BINAP, 76189-56-5; (±)-BINAP, 76144-87-1; (−)-DIOP, 32305-98-9; (−)-Cy-DIOP, 82239-68-7; (−)-*i*-PrDIOP, 82239-67-6; (−)-EtDIOP, 82239-66-5; (−)-BPPM, 61478-28-2; (*S*)-(*R*)-BPPFA, 55650-59-4; diphos, 1663-45-2; DIPP, 91159-11-4; BDPF, 12150-46-8; [Rh(diphos)(COD)]ClO_4, 32799-70-5; [Rh((−)-BINAP)(NBD)]ClO_4, 76155-69-6; [Rh((−)-Cy-DIOP)(NBD)]ClO_4, 82268-72-2; [Rh((−)-*i*-PrDIOP)(NBD)]ClO_4, 82268-70-0; [Rh((−)-EtDIOP)(NBD)]ClO_4, 82283-92-9; [$Rh(PPh_3)_2$-(COD)]ClO_4, 32799-30-7; [$Rh(diphos)_2$]ClO_4, 30513-14-5; [Rh(DIP-P)(COD)]ClO_4, 91159-08-9; [Rh(BDPF)(COD)]ClO_4, 91159-10-3; [Rh((*S*)-(*R*)-BPPFA)(COD)]ClO_4, 69228-79-1; [Rh(BPPM)(COD)]-ClO_4, 67322-49-0; [Rh(COD)Cl]$_2$, 12092-47-6; [Rh((±)-BINAP)-(COD)]ClO_4, 82864-73-1; [Rh((+)-BINAP)(COD)]ClO_4, 82822-45-5; [Rh((−)-BINAP)(COD)]ClO_4, 82889-98-3; [Rh((−)-DIOP)(COD)]-ClO_4, 70832-57-4; cyclohexylgeranylamine, 70548-83-3; (*E*)-*N,N*-diethyl-7-hydroxy-3,7-dimethyl-2-octenylamine, 68759-12-6; (*Z*)-*N,N*-diethyl-7-hydroxy-3,7-dimethyl-2-octenylamine, 57745-79-6; *N,N*-dimethylallylamine, 2155-94-4; cyclohexylmethylgeranylamine, 87560-13-2; myrcene, 123-35-3; methylcyclohexylamine, 100-60-7; (*E*)-*N,N*-diphenyl-3,7-dimethyl-2,6-octadienylamine, 87560-06-3; geranyl chloride, 5389-87-7; lithium diphenylamide, 5856-89-3; phenylgeranylamine, 65559-74-2; lithium anilide, 20732-26-7; *N,N*-dimethyl-3-methyl-2-butenylamine, 2588-79-6; 3-methyl-2-buten-1-ol, 556-82-1; 1-chloro-3-methyl-2-butene, 503-60-6; dimethylamine, 124-40-3; (*E*)-*N,N*-dimethyl-2-methyl-2-butenylamine, 91159-12-5; methyl (*E*)-2-methyl-2-butenoate, 6622-76-0; (*E*)-1-chloro-2-methyl-2-butene, 23009-73-6; (*E*)-*N,N*-dimethyl-3-phenyl-2-butenylamine, 82822-01-3; ethyl (*E*)-3-phenyl-2-butenoate, 1504-72-9; (*E*)-*N,N*-dimethyl-2-butenylamine, 51752-08-0; (*E*)-1-chloro-2-butene, 4894-61-5; *N,N*-dimethyl-1-methyl-2-propenylamine, 52113-79-8; *N,N*-dimethyl-2-methyl-2-propenylamine, 6000-82-4; 3-chloro-1-methyl-1-propene, 563-47-3; 3-chloro-1-butene, 563-52-0; (±)-3-diethylaminocyclohexene, 91159-13-6; 3-hydroxycyclohexene, 822-67-3; diethylamine, 109-89-7; (±)-*trans*-diethylpiperitylamine, 91159-14-7; (±)-*trans*-piperityl acetate, 91159-15-8; cyclohexylmethylgeranylamine (*E*)-enamine, 91159-16-9; *N*-(3,7-dimethyl-6-octenylidene)cyclohexylamine, 70548-84-4; (*E*)-*N,N*-diethyl-7-hydroxy-3,7-dimethyl-1-octenylamine, 85793-96-0; (+)-7-hydroxy-3,7-dimethyloctanol, 34212-48-1; (−)-(*E*)-*N,N*-dimethyl-3-phenyl-1-butenylamine, 82822-02-4; 3-phenylbutanoic acid, 4593-90-2; (*E*)-*N,N*-dimethyl-1-propenylamine, 13222-51-0; (*E*)-*N,N*-dimethyl-1-butenylamine, 22644-52-6; *N,N*-dimethyl-2-methyl-1-propenylamine, 6906-32-7; (*E*)-*N,N*-dimethyl-3-methyl-1-butenylamine, 91159-17-0.

Alkylation of the α and γ Meso Positions of Tetraphenylporphyrin upon Reduction of Allyl and Propargyl Bromide by Iron(II) Tetraphenylporphyrin: A New Route to Porphodimethene Complexes

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Abstract: Reduction of allyl bromide by sodium ascorbate or sodium dithionite, under anaerobic conditions, is catalyzed by (5,10,15,20-tetraphenylporphinato)iron(II). 1,5-Hexadiene has been found to be the only organic product. During this reaction, the iron porphyrin complex is slowly transformed into a mixture of stereoisomers of the (5,15-diallyl-5,10,15,20-tetraphenylporphinato)iron(II) complex. These new complexes, which were found to be very sensitive to dioxygen, have been demetalated into the corresponding stable diallylporphodimethenes whose structure has been established by elemental analysis and spectroscopic techniques. In the case of propargyl bromide, a similar alkylation of the meso positions of the iron porphyrin occurs, by either an allenyl or a propargyl group, leading to stereoisomers of the (diallenyl-, (dipropargyl-, and (allenylpropargylporphodimethene)iron(II) complexes. The mechanism of these reductions is discussed and compared to the general mechanism of reduction of alkyl halides by iron(II) porphyrins in the presence of a reducing agent in excess.

Cytochrome P-450 is able to catalyze the reduction by NADPH of several substrates including nitroarenes and halogenated compounds.[1,2] We have recently described a biphasic heme model system using an iron porphyrin and a phase-transfer agent in

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