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Review

Double bond migration in *N*-allylic systems catalyzed by transition metal complexes

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Contents

Abstract

In this review, literature reports on isomerization of *N*-allyl: amines, imines, amides, imides, carbamates and nitrogen-heterocycles to their corresponding *N*-(1-propenyl) compounds, catalyzed by transition metal complexes are discussed. To the best of our knowledge, all applications of isomerization of *N*-allyl compounds, mediated by Rh, Ru, Fe, Ir, Cr, Ti, Co and Os complexes for highly (*E*-, *Z*-, or enantio-) selective syntheses of enamines, enamides, azadienes and other compounds described in the literature are reviewed. All papers dealing with asymmetric isomerization of the prochiral *N*-allyl systems, particularly *N*-allylamines, are analyzed. Also tandem reactions: isomerization-RCM and RCM-isomerization, as well as cascades of reactions leading to heterocyclic systems containing N and O or S atoms in the ring are described. Moreover, procedures for deallylation of *N*-allyl compounds (*via* isomerization), in which the intermediates, i.e. *N*-(1-propenyl) systems, were or may be separated, are reviewed. The first stage of such procedures (the isomerization) is therefore also a method for synthesis of *N*-(1-propenyl) compounds. Relationships between structure and reactivity are analyzed too, particularly the influence of nitrogen atom coordination on the outcome of the reaction between an *N*-allyl system and a transition metal complex. It is clear, as demonstrated by many authors, that participation of the nitrogen atom in coordination of the metal atom determines the stereochemistry of double bond migration. However, too strong a coordination of *N*-allyl by the metal atom precludes double bond migration and favors a cleavage of allyl C–N bond. Such stoichiometric transformations are also analyzed in this paper. Furthermore, our literature survey shows that dependencies between donor–acceptor properties of *N*-allyl compounds and their reactivity are particularly well documented for ruthenium complexes. However, the influence of the type of the central atom on the outcome of reaction of *N*-allyl compounds with a transition metal complex is poorly understood.

Keywords: *N*-allyl compounds; Double-bond migration; Isomerization; Transition metal complexes; *N*-(1-propenyl) compounds

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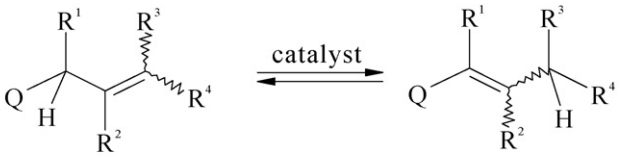
1. Introduction

Isomerization of *N*-allyl systems is one of the more important examples of double bond migration reaction in allylic systems (generally denoted as "Q-allyl") – see Scheme 1. Its importance stems from the significance of the products, namely *N*-(1-propenyl) systems (or more generally, *N*-vinyl systems), such as, for example, enamines and enamides, in organic synthesis. Protonic acids (e.g. H_2SO_4, $HClO_4$), bases (e.g. KOH, NaOH, NaOMe, *t*-BuOK,...), metals on support (e.g. K/Al_2O_3, Pd/C, Pd/Al_2O_3, Rh/C, Ru/C,...), and transition metal complexes ($[RuCl_2(PPh_3)_3]$, $[RhCl(PPh_3)_3]$ $[RuClH(CO)(PPh_3)_3]$, $[RhH(CO)(PPh_3)_3]$, $[RuH(PPh_3)_4]$, $[Fe(CO)_5]$,...) are employed as catalysts for double bond migration reaction in allylic systems (alkenes, cycloalkenes, nonconjugated dienes, allyl arenes, allyl silanes, allyl alcohols, allyl: ethers, amines, imines, amides and others) [1–9].

In this paper, we discuss literature reports on methods for synthesis of *N*-(1-propenyl) systems (generally, *N*-vinyl systems) *via* double bond migration in *N*-allylic systems (such as *N*-allyl: amines, imines, amides, imides; *N*-allyl protected heterocycles) catalyzed by transition metal complexes. Furthermore, syntheses in which double bond migration in *N*-allylic systems is the first step in a tandem reaction, e.g. isomerization-RCM, are also reviewed. In these tandem reactions, the *N*-(1-propenyl) moiety, formed from *N*-allyl, is used for the construction of a carbo- or heterocyclic system. Papers dealing with an isomerization-hydrolysis tandem (one of the variants of deprotection of *N*-allyl compounds) are discussed provided that the *N*-(1-propenyl) intermediate, being the double bond migration product, was or might be separated. All literature reports on asymmetric isomerization of *N*-allyl compounds are reviewed, particularly these on transformation of prochiral *N*-allylamines to chiral enamines. Thus, in Section 2, an attempt is made to demonstrate that isomerization of *N*-allyl compounds catalyzed by transition metal complexes is an exceptionally useful synthetic method for numerous *N*-(1-propenyl) (or generally, *N*-vinyl) compounds which are important for organic synthesis and are, usually, difficult to obtain by different routes. Consequently, we try to show that application of transition metal complexes as catalysts for this transformation is particularly convenient and leads to spectacular results (in terms of chemo-, regio-, stereo- and enantioselectivity).

In this review, different *N*-allyl systems are treated separately, depending on the substituents at the nitrogen atom (first allylamines, then allylimines, etc.). The reason for such an organization of the paper is that we want to emphasize that the nature of the functional group (its donor–acceptor properties, as well as steric bulk) often determines the position of the equilibrium between Q-allyl and Q-(1-propenyl), the rate and selectivity of isomerization. Simple systems of $Q\text{-}CH_2CH{=}CH_2$ type are discussed separately from compounds which contain substituents in the allyl fragment (like $Q\text{-}CH_2CH{=}CR^1R^2$), because these substituents have a strong (sometimes even dramatic) influence on the Q-allyl–Q-vinyl equilibrium and on the isomerization rate. In Section 2 we do not include, however, results which, in our opinion, are hardly useful from the point of view of modern, i.e. selective and convenient, organic synthesis, because of low (i.e. far from equilibrium) allyl substrate conversion, formation of a complicated product mixture, etc. Section 3 is mostly focused on the mechanisms of double bond migration in *N*-allyl systems, catalyzed by transition metal complexes. We, however, review only reactions for which a particular influence of the nitrogen atom (or the whole functional group Q) on the result of the reaction, that is, on reaction rate and chemo-, regio-, stereo and enantioselectivity, was either demonstrated or postulated. Isomerization mechanisms typical for alkenes and allylarenes, such as hydride and π-allyl mechanisms, have been extensively covered in textbooks and other works and are not discussed here (but appropriate references are given). Moreover, in Section 3 much attention is paid to stoichiometric reactions of *N*-allyl compounds and transition metal complexes: cleavage of allyl C–N bond and formation of stable complexes (which are usually not active as catalysts for double bond migration) in the reaction environment. In our literature survey, we focus on data demonstrating how donor–acceptor and steric properties of Q influence the course and mechanism of the reaction between *N*-allyl compounds and a transition metal complex. Our aim is to demonstrate that the presence of a nitrogen atom (or the whole Q group, e.g. imidazole ring) in the molecule of allyl substrate usually determines the outcome of the said reaction between Q-allyl and a metal complex. Research by many authors has proven that Q (i.e. the nitrogen atom or the whole group) decides on the direction of the reaction (stoichiometric versus catalytic), as well as on its rate and stereochemistry.



Q = alkyl (R), aryl (Ar), HO, RO, ArO, CH_2=CH, RCH=CH, R_3Si, Ph_3Si, R_2N, RC(O)NH, ArC(O)NR, 9-carbazolyl, *N*-phtalimidoyl, RS, RCOO, $(RO)_3SiO$, ...; R^1 - R^4 = H, R (alkyl), Ar (aryl), RO, OH, ...

Scheme 1. Double bond migration in allylic systems (Q-allyl).

Scheme 2. Isomerization of *N*-allylamines of $R^1R^2NCH_2CH{=}CH_2$ type catalyzed by transition metal complexes.

$$R^1R^2NCH_2C(R^3){=}CR^4R^5 \xrightarrow{[M]} R^1R^2NCH{=}C(R^3)CHR^4R^5$$

Scheme 3. Isomerization of *N*-allylamines of $R^1R^2NCH_2C(R^3){=}CR^4R^5$ type to enamines of $R^1R^2NCH{=}C(R^3)CHR^4R^5$ type catalyzed by transition metal complexes.

We also review mechanisms of the reactions of *N*-allyl compounds with transition metal complexes. Special attention is paid to investigations of influence of Q-allyl (especially *N*-allyl) donor–acceptor properties on the outcome of reactions with transition metal complexes.

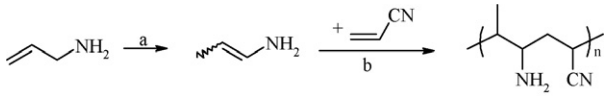
2. Isomerization of *N*-allyl compounds catalyzed by transition metal complexes in organic synthesis

2.1. Isomerization of N-allylamines

Isomerization of *N*-allylamines is important because the isomerization products, i.e. enamines, are significant intermediates in organic synthesis. Only in the case of *N*-allylamines, a practically quantitative transformation of $R^1R^2NCH_2CH{=}CR^3R^4$ systems to $R^1R^2NCH{=}CHCHR^3R^4$ is possible, owing to the favorable equilibrium between these systems [9]. In the case of *N*-allylamides, *N*-allylimides or allyl ethers (with two substituents at C^3 carbon in the allylic fragment of the molecule), this equilibrium is not so beneficial [9,10]. Syntheses of enamines *via* isomerization of *N*-allylamines are shown in Schemes 2–6 and listed in Tables 1–3. Asymmetric isomerization of prochiral *N*-allyl systems, particularly allylamines, is described separately in Section 2.7. Isomerization of *N*-allylamines is usually catalyzed by Rh complexes, and to a lesser extent Fe carbonyls, and Ti and Co complexes (there are two papers on each one). Ruthenium complexes are effective as catalysts of isomerization of allylamines only when the nitrogen atom is shielded by large groups [8,11–15].

$$R^1\text{-}N(CH_2CR^2{=}CH_2)_2 \xrightarrow{[M]} R^1\text{-}N(CH{=}CR^2CH_3)_2$$

Scheme 4. Isomerization di- and polyallylamines (R^1 = alkyl, Me_3Si, allyl; R^2 = H, Me).



Scheme 5. Isomerization of *N*-allylamine and copolymerization of an obtained enamine with acrylonitrile [27]. (a) $[RhH(CO)(PPh_3)_3]$ (1 mol%), PhH, 22 °C and (b) AIBN, *hv*, 10 °C, PhH.

$$R^1R^2CH{=}NCH_2CH{=}CH_2 \xrightarrow{[M]} R^1R^2CH{=}N\text{-}CH{=}CHCH_3$$

$$[M] = [Rh(CO)(PPh_3)_3] \text{ or } [RhCl(PPh_3)_3]$$

Scheme 6. Isomerization of *N*-allylimines to conjugated azadienes catalyzed by rhodium complexes.

Many reports have been published on isomerization of allylamines containing additional substituents in the allyl fragment of the molecule – see Scheme 3 and Table 2.

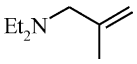
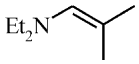
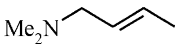
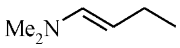
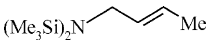
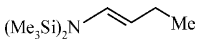
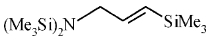
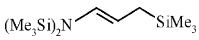
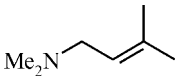
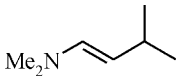
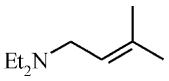
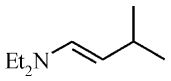
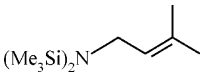
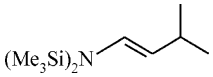
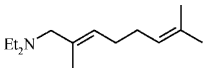
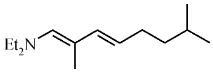
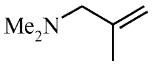
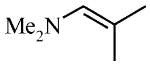
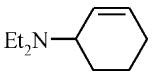
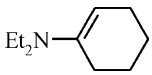
Isomerization reactions of di- and triallylamine to corresponding enamines have also been studied. Poly(1-propenyl)amines (Scheme 4) may be interesting e.g. for the synthesis of dendrimers. Reactions of this type are listed in

Table 1
Isomerization of *N*-allylamines of $R^1R^2NCH_2CH{=}CH_2$ type to enamines of $R^1R^2NCH{=}CHCH_3$ type catalyzed by transition metal complexes

R^1, R^2	Catalyst (mol%)	*t* (°C), *τ* (h)	So	*ε* (%)	*E*/*Z*	Reference
Me, Me	$[MoH_4(dppe)_2]$ (1.0) + *hv*	100, 4	PhMe	100	100/0	[16]
	$[RhH(CO)(PPh_3)_3]$ (1.0)	80, 2	PhH	98	100/0	[12]
Et, Et	$[MoH_4(acac)_2]$ + $[AlEt_3]$ + difos (1.0; 1: 10: 2)	100, 4	PhMe	100	100/0	[16]
	[Ru(COD)(COT)] (1.0)	80, 10	–	70[a]	100/0	[17]
	[Ru(COD)(COT)] (1.0)	70, 20	–	80	100/0	[18]
	$[TiCl_2cp_2]$ + $[NaC_{10}H_8]$ (1; 5:1)	20, 1	–	98	99/1	[19]
	$[CoH(PPh(OEt)_2)_4]$, (5) + *hv*	30	PhH	100		[20]
Me, Ph	$[Rh(CO)Cl]_2$ + NaOH/$BzNEt_3]^+Cl^-$ (0.2)	70, 16	DCM	100	100/0	[21]
	$[RhH(CO)(PPh_3)_3]$ (1.0)	80, 2	PhH	100	96/4	[12,14]
$-(CH_2)_4-$	$[RhH(CO)(PPh_3)_3]$ (1.0)	80, 2	PhH	98	100/0	[12,14]
i-Pr, *i*-Pr	$[RhH(CO)(PPh_3)_3]$ (1.0)	80, 2	PhH	99	100/0	[12,14]
Ph, Bn	$[RhH(CO)(PPH_3)_3]$ (1.0)	80, 23	PhH	99	99/1	[12,14]
Me_3Si, Me_3Si	$[RhH(CO)(PPh_3)_3]$ (1.0)	120, 2	PhH	88	89/11	[12,14]
	$[RClH(CO)(PPh_3)_3]$ (1.0)	100, 3	PhH	98	89/11	[12,14]
	$[Fe(CO)_5]$ (10) + *hv*	rt, 10	Hxn	90[a]	100/0	[22]

t, *τ*—reaction temperature and time, respectively; *ε*—conversion to *N*-(1-propenyl) system; So—solvent; rt—room temperature.
[a] Isolated yield, Hxn—hexane, DCM—CH_2Cl_2.

Table 2
Isomerization of *N*-allylamines of $R^1R^2NCH_2C(R^3)=CR^4R^5$ type to $R^1R^2NCH=C(R^3)CHR^4R^5$ enamines catalyzed by transition metal complexes

Substrate	Catalyst (mol%)	*t* (°C), τ (h)	So	ε (%)	Product	*E*/*Z*	Reference
	$[Rh(CO)Cl]_2 + NaOH/BzNEt_3]^+Cl^-$ (0.2)	70, 16	DCM	80[a]		–	[21]
	$[Rh(binap)(COD)]ClO_4$ (1) + H_2	60, 23	THF	52		100/0	[16]
	[Fe(CO)$_5$] (10) + *hν*	20, 15	Hxn	100		30/70	[22]
	[Fe(CO)$_5$] (10) + *hν*	20, 48	Hxn	100		40/60	[22]
	$[Rh((\pm)\text{-}(binap)(COD)]ClO_4$(1) + H_2	60, 23	THF	100		100/0	[23]
	[CoH(N$_2$)(PPh$_3$)$_3$] (1)	80, 15	THF	100		100/0	[24]
	[Fe(CO)$_5$] (10) + *hν*	20, 48	Hxn	100		40/60	[22]
	[CoH(N$_2$)(PPh$_3$)$_3$] (1)	80, 15	THF	85[a]		(*E*)	[24]
	$[(\mu\text{-}H)Os_3(\mu\text{-}O{=}CNHMe)(CO)_{10}]$ (3)	37, 168	CCl_4	100		*E* + *Z*	[25]
						E, *E*	[88]
	$[TiCl_2cp_2]$ + i-PrMgBr (1)	60, 15	THF	100		(*E*)	[88]
	$[Rh(PPh_3)_2(COD)]ClO_4$ (1)	60, 15	THF	100			
	$[Rh((\pm)\text{-}binap)(COD)]ClO_4 + H_2$ (1)	60, 23	THF	97		–	[23]
	$[Rh((\pm)\text{-}binap)(COD)]ClO_4 + H_2$ (1)	60, 23	THF	94[b]		–, 95[c]	[23]

[a] Isolated yields, there also forms <15% of (*E*)-*N*,*N*-diethyl-3,7-dimethyl-2,4-octadienylamine.
[b] Complete *N*-allyl conversion.
[c] Selectivity to enamine.

Table 3. In every case, isomerization of all allylic systems is observed. Selective conversion of one allylic group (while preserving other groups) is not known.

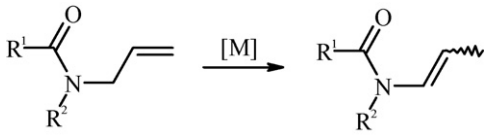
Novak and Cafmeyer showed a possibility of obtaining thermodynamically unstable primary and secondary enamines *via* isomerization of *N*-allylamine and *N*-methyl-*N*-allylamine catalyzed by [RhH(CO)(PPh$_3$)$_3$] [27]. It was feasible because isomerization to an enamine was much faster that consecutive tautomerization of the product to an imine more stable thermodynamically. Moreover, the obtained *N*-(1-propenyl)amine was successfully isolated and copolymerized (without protection–deprotection strategies) with acrylonitrile under free radical conditions, to yield a one-to-one alternating copolymer (see Scheme 5) [27].

Isomerization of *N*-allylamines to enamines can also be catalyzed by strong bases [6,9,28]. A number of isomerization reactions of *N*-allylamines in the presence of *t*-BuOK in DMSO [29–31] or in HMPT [32,33], $LiNH_2$ in liquid NH_3 [33] or in HMPT [33], $NaNH_2$ in liquid NH_3 [32–34], KNH_2 on Al_2O_3 in pentane [35] or in THF [36] as solvents, or K on Al_2O_3 in heptane as a solvent [37] have been described. These procedures are, however, inconvenient in most cases, because of difficult reaction conditions (liquid ammonia, K on Al_2O_3), high catalyst concentration (*t*-BuOK). In our opinion, preparation of enamines is much more convenient when using transition metal complexes as catalysts.

2.2. Isomerization of *N*-allylimines

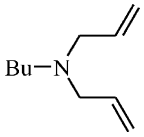
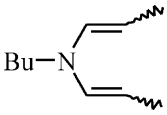
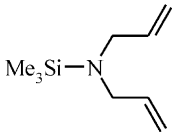
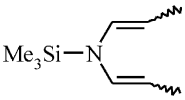
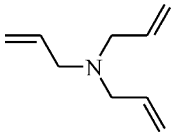
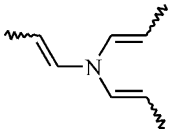
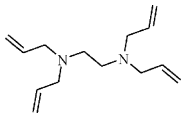
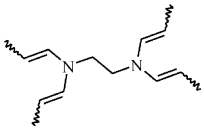
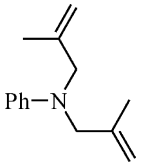
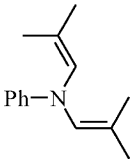
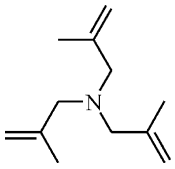
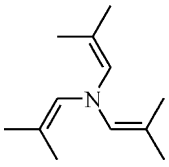
Isomerization of *N*-allylimines allows easy preparation of aza-1,3-dienes, which are interesting substrates for cycloaddition, for example for the synthesis of many heterocyclic systems [38–40]. Only a few such reactions catalyzed by transition metal complexes (rhodium compounds exclusively) are known – see Scheme 6 and Table 4. Asymmetric isomerization of prochiral *N*-allylimines is described in Section 2.7.

Isomerization of *N*-allylimines was also carried out in the presence of: DBU in CH_2Cl_2 [38,39], *t*-BuOK in THF

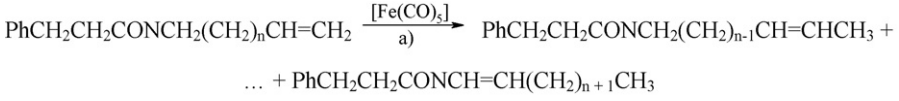


Scheme 7. Isomerization of *N*-allylamides of $R^1(COR^2)NCH_2CH{=}CH_2$ type to enamides of $R^1(COR^2)NCH{=}CHCH_3$ type catalyzed by transition metal complexes.

Table 3
Transition metal complexes as catalysts for isomerization of *N*-allylamines containing 2 or more *N*-allyl units

Substrate	Catalyst (mol%)	*t* (°C), *τ* (h)	So	*ε* (%)	Product	*E*/*Z*	Reference
	[RhH(CO)(PPh$_3$)$_3$] (1)	80, 2	PhH	98		92/8/0[a]	[12,14]
	[RhH(CO)(PPh$_3$)$_3$] (1)	100, 3	PhH	98		95/5/0[a]	[12,14]
	[RuClH(CO)(PPh$_3$)$_3$] (1)	80, 2	PhH	98		95/4/1[a]	[12,14]
	[RhH(CO)(PPh$_3$)$_3$] (1)	80, 2	PhH	98		87/12/1/0[b]	[12]
	[RhH(CO)(PPh$_3$)$_3$] (1)	80, 2	PhH	98		83/10/7/0/0[c]	[14]
	[Rh(DIPHOS)(COD)]BF$_4$ (1)	170, 14	THF	98		–	[26]
	[Rh(DIPHOS)(COD)]BF$_4$ (1)	140, 18	THF	99		–	[26]

[a] *E*,*E*/*E*,*Z*/*Z*,*Z*.
[b] *E*,*E*,*E*/*E*,*Z*,*E*/*E*,*Z*,*Z*/*Z*,*Z*,*Z*.
[c] *E*,*E*,*E*/*E*,*E*,*E*,*Z*/*E*,*Z*,*E*,*Z*/*E*,*Z*,*Z*,*Z*/*Z*,*Z*,*Z*,*Z*.



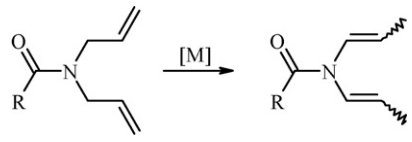
Scheme 8. Synthesis of enamides *via* long-distance migration of double bond in *N*-alkenylamide catalyzed by [Fe(CO)$_5$] [53]. (a) 33 mol% [Fe(CO)$_5$], 16 h, 120 °C, without solvent; *n* = 1, 2 or 3; yield of conjugated *E* and *Z* enamides = 56% (*n* = 1), 32% (*n* = 2), 23% (*n* = 3).

[44] or CsF (in the presence of a crown ether) in THF [44].

2.3. Isomerization of *N*-allylamides of carboxylic acids

N-(1-Propenyl)amides (or generally, *N*-vinylamides, enamides) – products of isomerization of *N*-allylamides of carboxylic or sulfonic acids – may be considered as enamines protected with electron withdrawing groups (EWGs). EWGs enhance the stability of these compounds. Ruthenium, iridium and iron complexes are particularly useful catalysts for the isomerization of *N*-allylamides to enamides. Syntheses of enamides *via* transition metal catalyzed double bond migration in *N*-allylamides of carboxylic acids are presented in Schemes 7–10 and in Tables 5–7.

In the reactions catalyzed by [Fe$_2$(CO)$_9$], an enormously strong (but unexplained) effect of the functional group Q was observed: Me$_2$NCONHallyl easily underwent isomerization, while Et$_2$NCONHallyl did not isomerize at all [50].



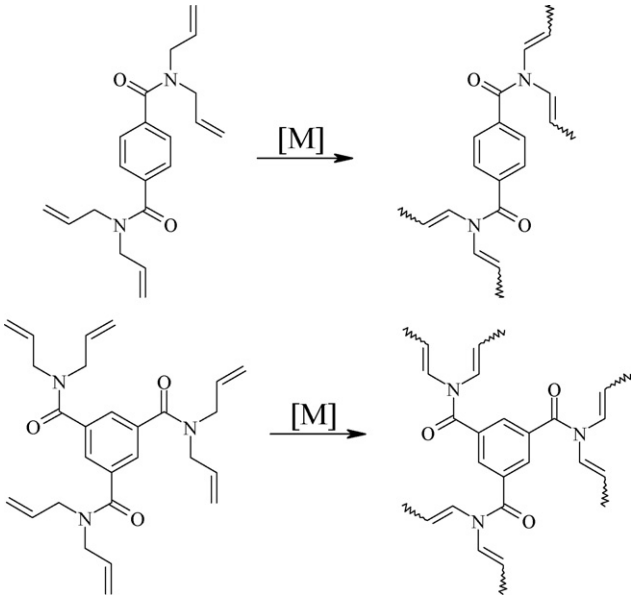
Scheme 9. Isomerization of *N*,*N*-diallylamides of RCON(allyl)$_2$ type.

Table 4
Isomerization of *N*-allylimines of $R^1R^2C{=}NCH_2CH{=}CH_2$ type to azadienes of $R^1R^2C{=}NCH{=}CHCH_3$ catalyzed by rhodium complexes

R^1, R^2	Catalyst (mol%)	t (°C), τ (h)	So	ε (%)	*E*/*Z*	Reference
Ph, H	$[RhH(CO)(PPh_3)_3]$ (1)	145, 2	Xy	>97	[a]	[41]
	$[RhCl(PPh_3)_3]$ (3)	rfx, 1.2	Xy	75[b]	2.7	[42]
Ph, Ph	$[RhH(CO)(PPh_3)_3]$ (1)	145, 5	Xy	100	[a]	[41]
p-Me_2N-C_6H_4-, H	$[RhH(CO)(PPh_3)_3]$ (1)	100, 2	PhH	100	[a]	[41]
	$[RhCl(PPh_3)_3]$ (3)	rfx, 1	Xy	73[b]	1.2	[42]
p-MeO-C_6H_4-, H	$[RhH(CO)(PPh_3)_3]$ (1)	100, 3	PhH	100	[a]	[41]
	$[RhCl(PPh_3)_3]$ (3)	rfx, 1	Xy	74[b]	1.9	[42]
p-NC-C_6H_4-, H	$[RhCl(PPh_3)_3]$ (3)	rfx, 6	Xy	63[b]	2.2	[42]
p-Cl-C_6H_4-, H	$[RhH(CO)(PPh_3)_3]$ (1)	145, 4	Xy	100	[a]	[41]
m-Cl-C_6H_4, H	$[RhH(CO)(PPh_3)_3]$ (1)	145, 6	Xy	100	[a]	[41]
1-Naphthyl, H	$[RhH(CO)(PPh_3)_3]$ (1)	100, 3	PhH	100	[a]	[41]
3-Pyridyl, H	$[RhH(CO)(PPh_3)_3]$ (1)	145, 2	Xy	98	[a]	[41]
2-Furyl, H	$[RhH(CO)(PPh_3)_3]$ (1)	145, 6	Xy	96	[a]	[41]
Et, Me	$[RhH(CO)(PPh_3)_3]$ (1)	130, 2	Xy	100	[a]	[41]
Ph, Me	$[RhH(CO)(PPh_3)_3]$ (1)	145	Xy	100	[a]	[41]
H, *p*-AllylN=CHC_6H_4-	$[RhH(CO)(PPh_3)_3]$ (1)	140, 4	Xy	98[c]	[a]	[43]

Xy—xylene.
[a] *E*/*Z* isomer mixture.
[b] Isolated yield.
[c] Both allyl groups undergo isomerization.

Introduction of substituents (e.g. a methyl group) to the allyl part of the molecule of an amide always resulted in a significant decrease in isomerization rate. It was necessary to raise the temperature, increase catalyst concentration or use another, more active catalyst than the one for an unsubstituted system [8,48,53]. For example, a system of $R^1CONR^2CH_2CH{=}CH_2$ type requires only 0.5 mol % of a catalyst $[Fe_2(CO)_9]$, while systems of $R^1CON(R^2)CH_2C(R^3){=}CH_2$ and $R^1CON(R^2)CH_2CH{=}CHR^3$ (R^1–R^3=Me) types need 5 and 10 mol% $[Fe_2(CO)_9]$, respectively [50]. Similar effects were observed by Sergyeev and Hesse: amides with methyl groups in the allyl part of the molecule required higher isomerization temperatures [48,53]. It is noteworthy that amides of $R^1CONR^2CH_2CH{=}CR^3R^4$ type cannot be quantitatively converted to enamides, owing to the state of equilibrium in the system: substituted *N*-allylamide–substituted enamide [48]. Similarly, isomerization of amides of $RCONCH_2(CH_2)_nCH{=}CH_2$ type leads to a mixture of products (see Scheme 8) [53]. It obviously originates from the state of equilibrium between the isomers differing in the position of the double bond in the chain.

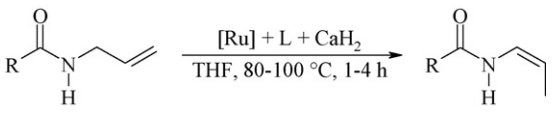


Scheme 10. Isomerization of polyallylamides [8,43]. [M] = 1 mol% $[RuClH(CO)(PPh_3)_3]$, $Cl_2C{=}CCl_2$, 60 °C, 6 h, 98% yield, mixture of isomers.

Isomerization of *N*,*N*-diallylamides leads to *N*,*N*-di-(1-propenyl)amides (Scheme 9 and Table 7). No case of significant regioselectivity in these reactions has been reported to date.

Some poly(1-propenyl)amides have been prepared *via* $[RuClH(CO)(PPh_3)_3]$-catalyzed isomerization of corresponding polyallylamides – see Scheme 10 [8,43]. Such polyenamides may be of potential use for synthesis of dendrimers or crosslinking of polymers.

A catalytic system yielding a quantitative *Z*-selective isomerization of some *N*-allylamides to *Z*-enamides has been found (Scheme 11) [12,15,46]. It is the only case of a quantitative *Z*-stereoselectivity in double bond migration in *N*-allylic systems [12,15,46].



Scheme 11. *Z*-stereoselective isomerization of *N*-allylamides catalyzed by ruthenium hydride complexes (generated *in situ*). R = Me, Ph, NH_2,...; [Ru] = $\{[RuCl_2(COD)]_x\}$; L = tris(2,4-di-*t*-buthylphenoxy)phosphine; *N*-allylamide:[Ru]:L:CaH_2 = 100:1:1:10.

Table 5
Isomerization of *N*-allylamides of $R^1(COR^2)NCH_2CH{=}CH_2$ type to enamides of $R^1(COR^2)NCH{=}CHCH_3$ type catalyzed by transition metal complexes

R^1, R^2	Catalyst (mol%)	t (°C), τ (h)	So	ε (%)	*E*/*Z*	Reference
	$[RhCl(PPh_3)_3]$ (0.5)	110, 24	PhMe	80	0/100	[45]
	$[RuClH(PPh_3)_3]$ (0.5)	110, 15	PhMe	100	33/67	[45]
	$[RuClH(CO)(PPh_3)_3]$ (0.5)	80, 3	PhH	100	59/41	[12,46]
H, Me	$[RhH(CO)(PPh_3)_3]$ (0.5)	80, 3	PhH	100	58/42	[46]
	$[Fe(CO)_5]$ (5)	20, 10	–	70	40/60	[47]
	[Os][a] (3)	rt	CCl_4	100		[25]
	$[CoH(PPh(OEt)_2)_4]$, (5) + *hν*	30, 0.33	PhH[b]	100		[20]
H, CF_3	$[Fe(CO)_5]$ (5) + *hν*	20, 6	–	100		[47]
H, $PhCH_2CH_2$-	$[Fe(CO)_5]$ (20)	100, 15	–	95[c]	61/39	[48]
H, (*E*)-MeCH=CH-	$[Fe(CO)_5]$ (20)	100, 15	–	88[c]	71/29	[48]
H, R[d]	$[Fe(CO)_5]$ (20)	100, 15	PhCl	89[c]	75/25	[48]
H, $MeOOC(CH_2)_3CH_2$-	$[Fe(CO)_5]$ (20)	100, 15	–	86[c]	55/45	[48]
H, $MeOCH_2$-	$[Fe(CO)_5]$ (20)	100, 15	–	72[c]	70/30	[48]
H, TsNHCH(Ph)-	$[Fe(CO)_5]$ (20)	100, 15	–	90[c]	64/34	[48]
Me, $PhCH_2CH_2$-	$[Fe(CO)_5]$ (20)				100/0	[48]
H, Ph	$[RuClH(CO)(PPh_3)_3]$ (0.5)	80, 3	PhH	100	67/33	[12,46]
	$[RhH(CO)(PPh_3)_3]$ (0.5)	80, 3	PhH	100	67/33	[12,46]
H, 2-Thienyl	$[RuClH(CO)(PPh_3)_3]$ (1)	80, 3	PhH	100	77/23	[12,46]
H, AllylNH-	$[RuClH(CO)(PPh_3)_3]$ (1)	80, 3	THF	100[e]	79/21/0	[12,46]
Cy, Me	$[RuClH(CO)(PPh_3)_3]$ (1)	120, 2	–	100	85/15	[12,46]
Bu, Me	$[RuClH(CO)(PPh_3)_3]$ (1)	80, 3	PhH	100	87/13	[12,46]
Bn, Me	$[RuClH(CO)(PPh_3)_3]$ (1)	80, 3	PhH	100	91/9	[12,46]
Bn, Ph	$[IrCl(COD)]_2 + PCy_3 + Cs_2CO_3$ (5:1:2:1)	110, 72	PhMe	>95	92/8	[49]
Me, *p*-Tol	$[IrCl(COD)]_2 + PCy_3 + Cs_2CO_3$ (5:1:2:1)	110, 72	PhMe	>95	98/2	[49]
H, 2-Thienyl	$[RuClH(CO)(PPh_3)_3]$ (1)	120, 2	–	95	83/17	[12,46]
H, H_2N	$[RuClH(CO)(PPh_3)_3]$ (1)	80, 3	PhH	100	42/58	[12,46]
	$[Fe(CO)_5]$ (5)	20, 6	–	100	100/0	[47]
H, Me_2N	$[Fe(CO)_5]$ (5)	110, 3	PhMe	85	92/8	[50]
	$[Fe_2(CO)_9]$ (0.5)	67, 3	THF	79[c]	92/8	[45]
H, PhNH	$[Fe(CO)_5]$ (5) + *hν*	20, 10	MeOH	100	70/30	[47]
H, AllylNH-[e]	$[RuClH(CO)(PPh_3)_3]$ (0.5)	80, 3	THF	100	79/21/0	[46]
Ar[f], Me	$[RuClH(CO)(PPh_3)_3]$ (0.5)	120, 2	–	100	>98/2	[51,52]
o-$O_2NC_6H_4$, Me	$[RuClH(CO)(PPh_3)_3]$ (0.5)	120, 3	–	100	81/19	[51,52]
Me_2N, MeCH=C(Ph)-	$[Fe_2(CO)_9]$ (25)	67, 3	THF	>99	75/25	[50]
Me_2N, R[g]	$[Fe_2(CO)_9]$ (25)	67, 3	THF	>99	>99/1	[50]
Me_2N, R[h]	$[Fe_2(CO)_9]$ (25)	67, 3	THF	>99	>99/1	[50]

[a] [Os] = [(μ-H)(μ-O=CNHMe)$Os_3(CO)_{10}$].
[b] Or $CHCl_3$.
[c] Isolated yield.
[d] R = $CF_3CONHCH(Ph)CH_2$.
[e] Both groups undergo isomerization.
[f] Ar = Y-C_6H_4-, Y = *o*- and *p*-Me, MeO (τ = 16 h), Br, Cl; *m*-MeO, Cl; *p*-O_2N; 1- or 2-naphthyl.
[g] R = 1-cyclopentenyl.
[h] R = methylenecyclohexenyl.

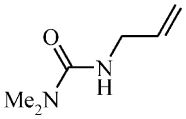
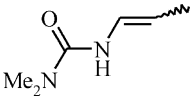
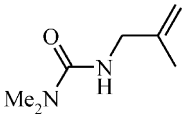
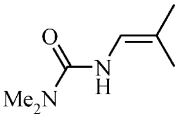
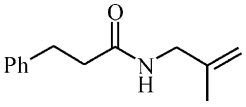
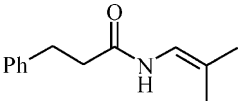
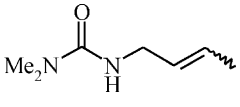
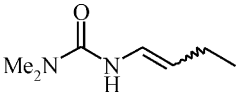
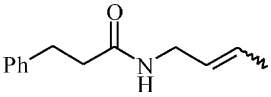
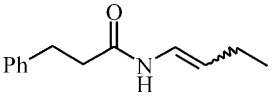
Isomerization of *N*-allylamides to propenyl derivatives may also be carried out using very strong bases: LDA [28,34,36,55], BuLi [28,34,56], and others [28]. In the first step of the reaction with LDA or BuLi, dilithiation of *N*-allylamides occurs (C- and O-lithiation), with an excess of LDA or BuLi. Then a proton donor (H_2O or MeOH) is introduced, and the enamide is formed: both *E*- and *Z*-isomers [36,55,56], mainly *E* [34], mainly or solely *Z* [34,55]. In our opinion, however, these reactions are much less convenient (strictly non-aqueous medium, excess of the base, difficult isolation of products) than reactions catalyzed by transition metal complexes. It is noteworthy that *N*-allylamides (unlike *N*-allylamines) cannot be isomerized in the presence of such bases as *t*-BuOK, $NaNH_2$ or KNH_2. These bases attack the acyl carbon of the amides, eventually causing their transformation into secondary amines [57].

2.4. Isomerization of XY N-allyl type compounds (sulfonamides, carbamates)

Yamada et al. presented a highly stereoselective synthesis of *N*-BOC protected dienamines *via* isomerization of *N*-allylcarbamates (Scheme 12) [58]. Synthesis of a dienamine of $R_2NCH{=}CHC(Me){=}CHR^1R^2$ type is shown in Table 2.

Other isomerization reactions of *N*-allyl sulfonamides and carbamates are presented in Table 8.

Table 6
Isomerization of *N*-allylamides $R^1CONR^2(CHR^3CR^4{=}CHR^5)$ type catalyzed by transition metal complexes

Substrate	Catalyst (mol%)	*t* (°C), *τ* (h)	So	*ε* (%)	Product	*E*/*Z*	Reference
	$[Fe_2(CO)_9]$ (0.5)	67, 3	THF	79[a]		92/8	[50]
	$[Fe_2(CO)_9]$ (5)	67, 3	THF	82[a]			[50]
	$[RuClH(PPh_3)_3]$ (0.8)	110, 72	PhMe	95			[45]
	$[Fe(CO)_5]$ (20)	120, 15	–	63[a]			[48]
	$[Fe_2(CO)_9]$ (10)	67, 3	THF	79[a]		71/29	[50]
	$[Fe(CO)_5]$ (20)	120, 15	–	59[a]		68/32	[48]

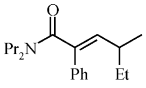
[a] Isolated yield.

Table 7
Isomerization of *N*,*N*-diallylamides of $RCON(CH_2CH{=}CH_2)_2$ type to enamides of $RCON(CH{=}CHCH_3)_2$ type catalyzed by transition metal complexes

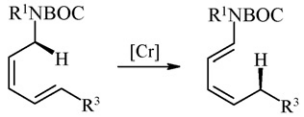
R	Catalyst (mol%)	*t* (°C), *τ* (h)	So	*ε* (%)	*E*/*Z*	Refetrence
Me	$[Fe_2(CO)_9]$ (20)	rfx, 30	PhMe	90		[50]
	$[Fe(CO)_5]$ (5) + *hν*	20, 10	–	80	50/50	[47]
	$[RuClH(CO)(PPh_3)_3]$ (1)	80, 3	PhH	100	44/66/0[a]	[12]
CF_3	$[Fe(CO)_5]$ (5) + *hν*	20, 6	–	100		[47]
	$[RuClH(CO)(PPh_3)_3]$ (1)	80, 3	PhH	100	55/45/0[a]	[46]
4-$MeOC_6H_4$-	$[Fe_2(CO)_9]$ (40)	110, 45	PhMe	86[b,c]		[54]
Me_2N	$[Fe_2(CO)_9]$ (10)	110, 3	PhMe	100	86/14	[50]
Ph	$[RuClH(CO)(PPh_3)_3]$ (1)	80, 3	PhH	100	40/47/15[a]	[46]
t-Bu	$[RuClH(CO)(PPh_3)_3]$ (1)	80, 3	PhH	100	53/47/0[a]	[46]

[a] *E*,*E*/*E*,*Z*/*Z*,*Z*.
[b] Isolated yield.
[c] 3% was (*E*)-(4-$MeOC_6H_4N$(allyl)(1-propenyl).

Table 8
Isomerization of XY *N*-allyl type compounds catalyzed by transition metal complexes

X, Y	Catalyst (mol%)	*t* (°C), *τ* (h)	So	*ε* (%)	*E*/*Z*	Reference
Bn, Ts	$[IrCl(COD)]_2 + 2PCy_3 + Cs_2CO_3$ (5 mol% Ir)	110, 72	PhMe	56[a]	97/3	[49]
Me, Ts	$[IrCl(COD)]_2 + 2PCy_3 + Cs_2CO_3$ (5 mol% Ir)	110, 72	PhMe	64[a]	91/9	[49]
Bn, BOC	$[IrCl(COD)]_2 + 2PCy_3 + Cs_2CO_3$ (5 mol% Ir)	110, 72	PhMe	96[a]	97/3	[49]
$PhCH_2CH_2$, Ts	[Ru][b] (3)	rt, 12	CH_2Cl_2	21[a]		[59]
 , BOC, BOC	$[RuClH(CO)(PPh_3)_3]$ (10)	60, ov	Xy	82[a]		[60]
H, PhO	$[Fe(CO)_5]$ (5)	rfx, 15	PhH	80[a]		[47]

[a] Isolated yield; ov—overnight.
[b] [Ru]=$[Cl_2(Imes)(PCy_3)Ru{=}CHPh]$.



Scheme 12. Isomerization of *N*-protected-*N*-dienyl carbamates: synthesis of *N*-BOC protected conjugated dienamines [58]. R^1, R^2 = H, H; Me, H; H, PvO$(CH_2)_3$–; H, (*E*)-$MeO_2CCH{=}CH(CH_2)_3$–; [Cr] = 20 mol% [$Cr(CO)_3$(naphthalene)]; 20 °C; 4 h; acetone; isolated yields = 88–97%.

2.5. Isomerization of N-allyl nitrogen heterocyclic compounds

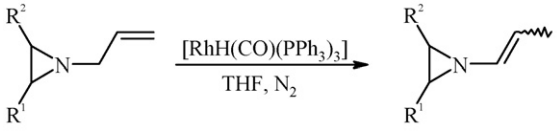
Isomerization of nitrogen heterocyclic systems containing an *N*-allyl unit has also been investigated. Obviously, these systems may also be considered *N*-allylamides, *N*-allylamines, and so forth. Most reactions of such a type described in the literature are shown in Table 9. Some substrates from Table 9 are not cyclic compounds, but rather *N*,*N*-diallyl systems. However, in the course of the reaction they first undergo RCM to *N*-allyl heterocyclic compounds, and then the latter compounds are isomerized to *N*-(1-propenyl) nitrogen-heterocyclic compounds.

Alphonse and Yudin recently published a paper on *Z*-stereoselective isomerization of *N*-allylaziridines to 1-propenylaziridines, catalyzed by [$RhH(CO)(PPh_3)_3$] – the most important examples are shown on Scheme 13 [74]. These reactions are also isomerizations of *N*-allylamines and *N*-allyl nitrogen-heterocycles, however, considering their unusual *Z*-selectivity we discuss them separately.

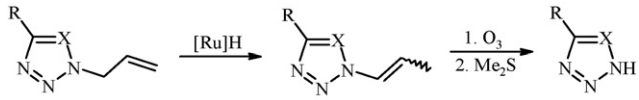
This is the first case of obtaining mainly *Z*-enamines *via* double bond migration in *N*-allylamines, catalyzed by transition metal complexes. The conversion was in most cases quantitative, and *Z*-selectivity was in the range of 75–96% (depending on the substrate structure and reaction conditions).

2.6. Isomerization as a step in deallylation of N-allyl compounds

Allyl group is one of the protecting groups for the nitrogen atom in amines, amides, imides and nitrogen-containing heterocycles [28,75]. A deprotection step for derivatives containing an *N*-allyl group appears in syntheses and transformations of many natural and biologically active products. Usage of allyl moieties as protecting groups in amines and other *N*-allyl compounds is becoming more and more popular since, in contrast to more classical protecting groups. *N*-allyl groups remain inert



Scheme 13. *Z*-Stereoselective isomerization of *N*-allylaziridines to *N*-(1-propenyl) derivatives catalyzed by [$RhH(CO)(PPh_3)_3$] [74]. Conversion = 100%; R^1, R^2 (*t* (°C), τ (h), substrate/Rh, *Z*/*E* = –$(CH_2)_4$– (−78, 24, 66, 95/5); MeO_2C, H (60, 72, 10, 82/18); Ph, H (60, 24, 20, 91/9); *cis*-Ph, Me (−78, 24, 66, 96/4).



Scheme 14. Deallylation of triazoles and tetrazoles. X = CR′ or N; [Ru]H = 5 mol% [$RuClH(CO)(PPh_3)_3$]; 120 °C, PhMe; R, R′ = see Table 9.

in both acidic and basic media and are nucleophile-resistant. Some deallylation procedures of *N*-allyl derivatives consist of two steps – the first step is isomerization of the *N*-allyl group to an *N*-(1-propenyl) group, and the second one is a formal exchange of the 1-propenyl group for a hydrogen atom (*via* hydrolysis, oxidation, and other reactions). The first step of these procedures may as well be treated as a method for synthesis of *N*-(1-propenyl) systems, particularly when deallylation is not a one-pot procedure. The isomerization step may be catalyzed by strong bases, metals on support and transition metal complexes, see a microreview by Escoubet et al. [28]. In that paper, an extensive survey of various deallylation methods of *N*-allyl compounds was carried out – including methods *via* isomerization of *N*-allyl compounds, catalyzed by transition metal complexes. Herein, only these papers on deallylation of *N*-allyl compounds are discussed in which isolation of *N*-(1-propenyl) compounds is described. Thus, these deprotection procedures are also methods for synthesis of *N*-(1-propenyl) compounds from *N*-allyl compounds.

Kamijo et al. developed method of synthesis for *N*-unsubstituted triazoles and tetrazoles *via* deallylation of *N*-allyl derivatives (Scheme 14) [67,76]. The double bond migration products were isolated, therefore it is also a method of synthesis of *N*-(1-propenyl) nitrogen-heterocycles.

Isolated isomerization products (see Table 9) were subjected to an ozonolysis and finally treated with Me_2S, eventually yielding *N*-unsubstituted heterocycles. Alcaide and co-workers presented a selective deprotection of *N*-allyl group (in amines) in the presence of *O*-allyl group [77–80]. Grubbs carbene complex [$(PCy_3)_2Cl_2Ru{=}CHPh$] was the catalyst, but it was probably converted *in situ* into a hydride complex. In the key step, the *N*-allyl group undergoes a quantitative isomerization to an enamine. As a matter of fact, the enamine was not isolated (it was hydrolyzed during chromatographic work-up on silica gel), however a modification of the procedure, enabling preparation of pure intermediate *N*-(1-propenyl) compounds is obvious. It was noteworthy that the *O*-allyl groups remained intact. This finding implies the value of this deprotection method and an advantage of the ruthenium catalyst over palladium catalysts. The procedure is also equally interesting considering double bond migration in allyl systems (synthesis of propenyl derivatives). This is the only known case of such a high regioselectivity of isomerization of a *N*-allyl group to *N*-(1-propenyl) without isomerization of an *O*-allyl group. Fig. 1 shows examples of compounds which have been subjected to a selective (leaving other allyl groups intact) isomerization, and eventually to *N*-deallylation.

High selectivity of the catalyst towards a *N*-allyl group and passivity towards an *O*-allyl group is probably a result of

Table 9
Double bond migration in *N*-allyl nitrogen heterocyclic compounds catalyzed by transition metal complexes

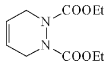
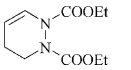
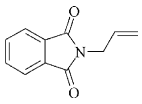
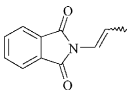
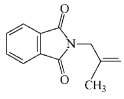
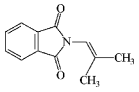
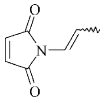
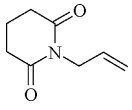
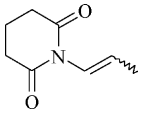
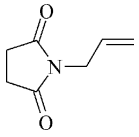
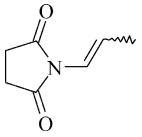
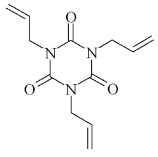
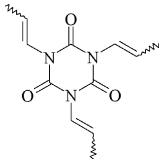
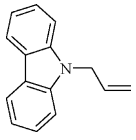
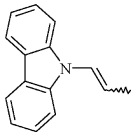
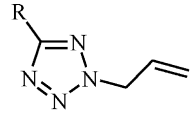
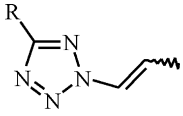
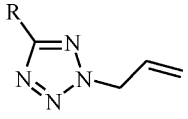
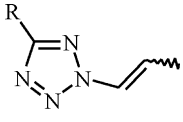
Substrate	Catalyst (mol%), So	*t* (°C), *τ* (h)	*ε* (%), *E*/*Z*	Product	Reference
	$[RhH(PPh_3)_4]$ (1), Xy	138, 44	92		[45]
	$[RuClH(PPh_3)_3]$ (0.5), Xy	138, 22	90		[45]
 R = CHO	$[Pd(OAc)_2]$, dppp	110, 24	78		[61]
R = COOMe	$N(i\text{-}Pr)_2Et$, CF_3COOH	110, 24	80		
	$[Ru_4H_4(CO)_{12}]$ (3), D_2O + EtOH	100, 72	90		[62]
	$[RuCl_2(PPh_3)_3]$ (3), D_2O + EtOH	100, 8	93		[62]
	$[IrCl(COD)]_2 + PCy_3 + Cs_2CO_3$ (5:1:2:1), PhMe	110, 72	71[a], 91/9		[49]
	$[RuCl_2(PPh_3)_3]$ (1), –	150, 13	90[a]		[63]
	$[Fe(CO)_5]$ (10), Xy	rfx, 1	62[a]		[64,65]
	$[RuClH(CO)(PPh_3)_3]$ (1), CH_2Cl_2	60, 3	100		[8,66]
	$[Fe(CO)_5]$ (50), Xy	138, 15	83		[45]
	$[Ru_4H_4(CO)_{12}]$ (2), –	175, 100	88		[63]
	$[RuClH(CO)(PPh_3)_3]$ (1), TCE	80, 6	>98		[8,66]
	$[Ru(CO)_3(PPh_3)_3]$ (1), TCE	80, 6	100		[8,66]
	$[RuClH(CO)(PPh_3)_3]$ (1), TCE	80, 6	> 95		[8,66]
	$[Fe(CO)_5]$ (10), Xy	rfx, 1	79		[64,65]
	$[RuClH(CO)(PPh_3)_3]$ (1), CH_2Cl_2	60, 3	100		[8,66]
	$[IrCl(COD)]_2 + PCy_3 + Cs_2CO_3$ (5:1:2:1), PhMe	110, 72	68[a], 90/10		[49]
	$[Fe(CO)_5]$ (10), Xy	rfx, 2	94		[65]
	$[RuCl_2(PPh_3)_3]$ (1), TCE	160, 6	36		[8,43]
	$[RuClH(CO)(PPh_3)_3]$ (1), TCE	160, 6	70		[8,43]
	$[RuClH(CO)(PPh_3)_3]$ (1), CH_2Cl_2	60, 3	100		[8,66]
 R = *N*-morpholinyl	$[RuClH(CO)(PPh_3)_3]$ (5) PhMe	120, 3	85[a], 87/13		[67]
 R = $Me_2(NC)C$-	$[RuClH(CO)(PPh_3)_3]$ (5) PhMe	120, 24	77[a], 73/27		[67]

Table 9 (*Continued*)

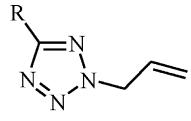
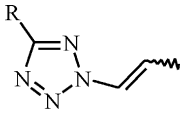
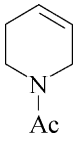
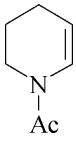
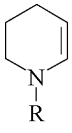
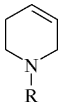
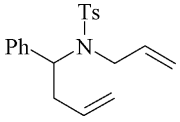
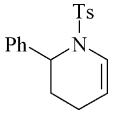
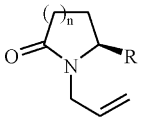
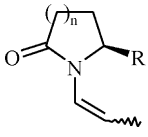
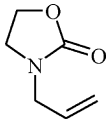
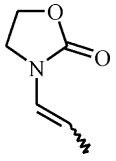
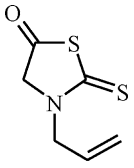
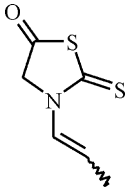
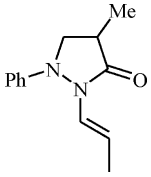
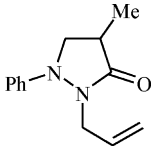
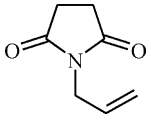
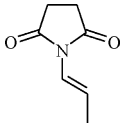
Substrate	Catalyst (mol%), So	*t* (°C), *τ* (h)	*ε* (%), *E*/*Z*	Product	Reference
 R = *N*-(3-methoxy-carbonylcarbazol-1-yl)	$[RuClH(CO)(PPh_3)_3]$ (5) PhMe	120, 24	51[a], 59/41		[67]
	$[RhH(PPh_3)_4]$ (0.4), Xy	138, 48	88		[45]
 R = [b]	$[RhCl(PPh_3)_3]$ (1) H_2O-MeCN				[68]
	1. [Ru][c](5); 2. [Ru] + H_2 (5) CH_2Cl_2		74[a]		[69]
 n = 1, R = H n = 1, R=COOEt n = 2, R = H n = 3, R = H	$[(PCy_3)_2Cl_2Ru{=}CHPh]$ (5), PhMe	110	75[a], 20/80 71[a], 53/47 72[a], 0/100 90[a], 55/45		[70]
	$[(PCy_3)_2Cl_2Ru{=}CHPh]$ (5), PhMe	110,	87[a], 90/10		[70]
	$[(PCy_3)_2Cl_2Ru{=}CHPh]$ (5), PhMe	110	46[a], 70/30		[70]
	$[(PCy_3)_2Cl_2Ru{=}CHPh]$, (5), PhMe	110	87[a], 100/0		[70]
	$[(PCy_3)_2Cl_2Ru{=}CHPh]$, (5), PhMe	110	83[a], 100/0		[70]

Table 9 (*Continued*)

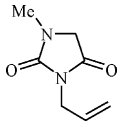
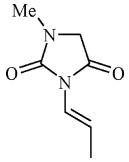
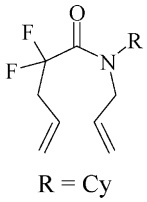
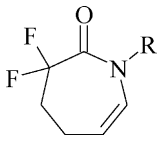
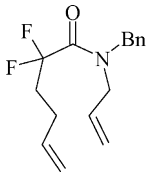
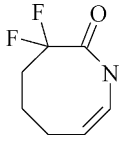
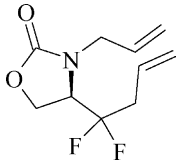
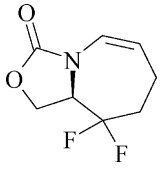
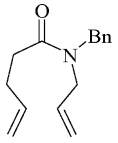
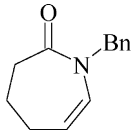
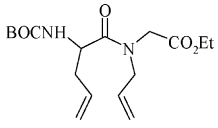
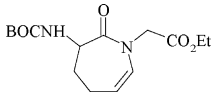
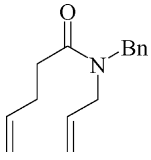
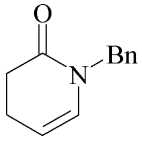
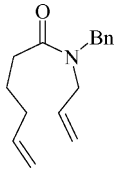
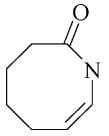
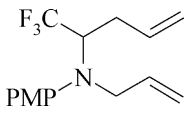
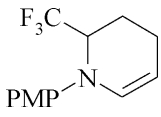
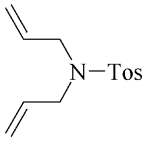
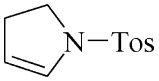
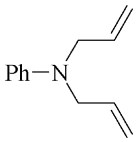
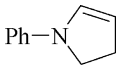
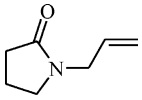
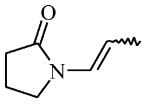
Substrate	Catalyst (mol%), So	*t* (°C), *τ* (h)	*ε* (%), *E*/*Z*	Product	Reference
	$[(PCy_3)_2Cl_2Ru{=}CHPh]$, (5), PhMe	110	65[a], 100/0		[70]
 R = Cy R = p-$MeOC_6H_4$	$[Cl_2(Imes)(Pcy_3)Ru{=}CHPh]$ (5-10), PhMe	rfx, 1-2	93[a] 95[a]		[71]
	$[Cl_2(Imes)(Pcy_3)Ru{=}CHPh]$ (10), PhMe	rfx, 2	65		[71]
	$[Cl_2(Imes)(Pcy_3)Ru{=}CHPh]$ (5-10), PhMe	rfx,	85[a]		[71]
	$[Cl_2(Imes)(Pcyd)Ru{=}CHPh]$ (10), PhMe	rfx, 2	67[a]		[71]
	$[Cl_2(Imes)(Pcy_3)Ru{=}CHPh]$ (5-10), PhMe		51[a]		[71]
	$[Cl_2(Imes)(Pcy_3)Ru{=}CHPh]$ (10), PhMe	rfx, 3	82[a]		[71]
	$[Cl_2(Imes)(Pcy_3)Ru{=}CHPh]$ (10), PhMe	rfx, 2	57[a]		[71]
	$[Cl_2(Imes)(Pcy_3)Ru{=}CHPh]$ (5-10), PhMe	rfx, 2	75[a]		[71]

Table 9 (*Continued*)

Substrate	Catalyst (mol%), So	*t* (°C), τ (h)	ε (%), *E*/*Z*	Product	Reference
	$[Cl_2(Imes)(Pcy_3)Ru{=}CHPh]$ (5-10), PhMe	rfx,	65[a]		[71]
	$[Cl_2(Pcy_3)_2Ru{=}CHPh]$ (5), CH_2Cl_2	40, 24	84		[72]
	$[RhH(PPh_3)_4]$ (5), EtOH	rfx, 8	85		[73]
	$RhCl_3{*}H_2O + NaOPr$ (5 + 15), PrOH	rfx, 0.17	95		[73]

Xy = xylene; TCE = $Cl_2C{=}CCl_2$.
[b] R = CH_2CH_2(indol-2 or 3-yl).
[a] Isolated yield.
[c] Step I: RCM; step II: isomerization of *N*-allyl product of RCM.

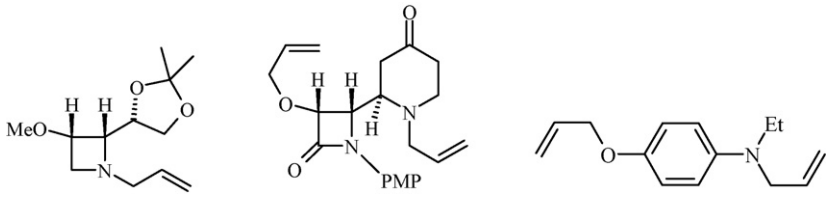
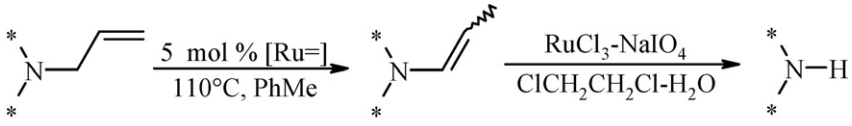


Fig. 1. *N*-Allyl and *N*,*O*-diallyl systems, which may be isomerized selectively and then *N*-deallylated [77–80].



Scheme 15. Deprotection of *N*-allyl compounds by ruthenium catalyzed isomerization-oxidation protocol [70]. [Ru] = $[Cl_2(PCy_3)_2Ru{=}CHPh]$.

nitrogen-assisted ruthenium-catalyzed double bond migration. The main limitation of this method was RCM, which some diallyl substrates were undergoing.

Alcaide et al. described a convenient, two-step methodology for a ruthenium catalyzed deallylation of amides, lactams, imides, pyrazolidones, hydantoins and oxazolidinones (Scheme 15) [70].

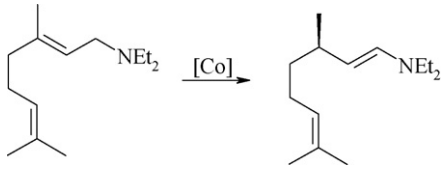
The first step (isomerization) was catalyzed by Grubbs carbene complexes, and the second step (oxidation) by $RuCl_3$. This protocol is tolerant towards different functionalities as well as stereocenters present in the molecule. The isomerization products were isolated before the oxidation step, therefore a series of new *N*-(1-propenyl) derivatives was obtained (see Table 9).

2.7. Asymmetric isomerization of N-allylic systems

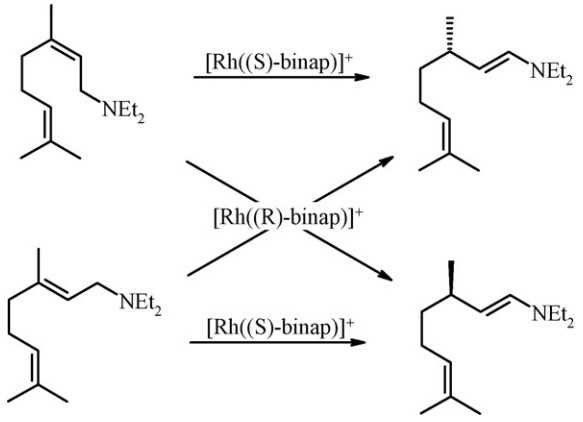
In 1978, Kumobayashi et al. reported the first enantioselective double bond migration in *N*-allylic systems (Scheme 16) [24].

However, both the yield of the enamine and the enantiomeric excess (ee) were not high, in spite of testing many chiral cobalt catalytic systems (mainly with chiral phosphines) [24]. In 1982, Tani et al. obtained spectacular results in asymmetric isomerization of *N*,*N*-diethylgeranyl- or *N*,*N*-diethylnerylamine to optically active enamines catalyzed by cationic rhodium complexes with chiral binap ligands – Scheme 17 [81].

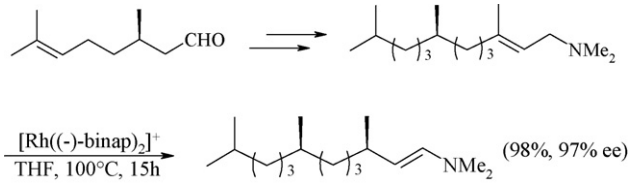
Further investigations have led to a deep understanding of isomerization of prochiral allylamines catalyzed by rhodium cationic complexes with chiral diphosphine ligands [23,26,82–92]. Relationships between the structure of allylamines and rhodium complexes and the reaction rate, stability



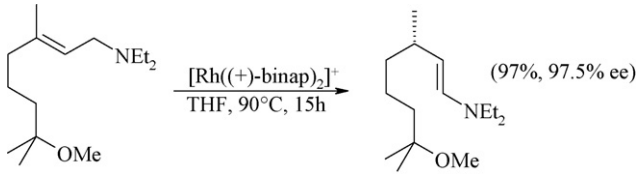
Scheme 16. Enantioselective isomerization of *N*,*N*-diethylgeranylamine to citronellal-*trans*-enamine catalyzed by a chiral cobalt catalyst [24]. [Co] = Co(II) salts + (+)-DIOP + $[AlH(i\text{-}Bu)_2]$; yield of enamine = 23% (32% ee).



Scheme 17. Isomerization of *N*,*N*-diethylgeranylamine or *N*,*N*-diethylneryl-amine to optically active (*R*)- or (*S*)-enamines catalyzed by {Rh[(+)-binap](cod)}ClO_4 or {Rh[(−)-binap](cod)}ClO_4 [81].



Scheme 19. Synthesis of vitamin E side chain [26].



Scheme 20. Synthesis of (*S*)-(−)-7-methoxycitronellalenamine – intermediate in methoprene synthesis [26].

and effectiveness of the catalytic system, chemo- and enantioselectivity of double bond migration, etc. have been examined in detail. It has been shown that there are some structural limitations in the substrate allylamines. Only allylamines of a general formula $R^1R^2C{=}CHCH_2NR^3R^4$ are allowed, that is, both C(1) and C(2) should not have alkyl substituents. Moreover, the electron-donating property of the amine group appears to be essential for the catalysis.

High conversion, and high chemo- and enantioselectivity are obtained only when R^3, R^4=Et, Et or H, Cy. Mechanism of the reactions has been studied thoroughly, both from experimental and quantum chemical point of view. All results of these investigations have been described in detail elsewhere – also in review papers [26,85,86,90–92]. Section 3 of this paper contains a discussion of the reaction mechanism, especially of the specific role of the nitrogen atom in coordination of the rhodium atom.

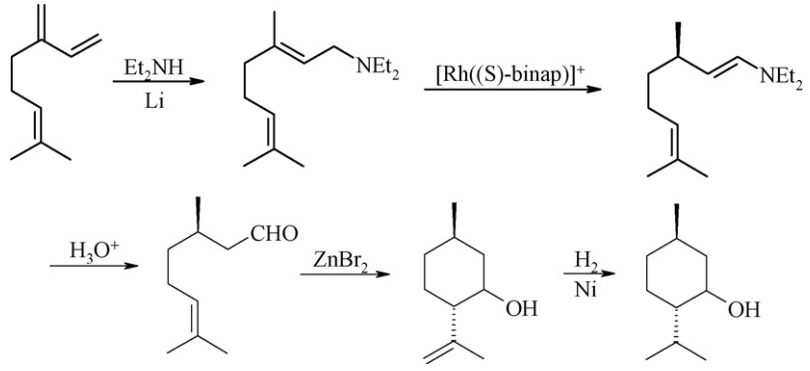
Realization of an industrial synthesis of (−)-menthol from myrcene was a spectacular final of this research (Scheme 18) [85,86,90–92]. As R. Noyori wrote in his Nobel Lecture "this resulted from a fruitful academic/industrial collaboration between groups at Osaka University (S. Otsuka and H. Tani), Nagoya University (R. Noyori), Institute for Molecular Science (H. Takaya), Sizuoka University (J. Tanaka and K. Takanabe) and Takasago International Co." [91].

For the Rh(I)-catalyzed synthesis of (+)- or (−)-citronellal *via* isomerization of neryl and geranylamines, several variants of binap ligands have been tested and patented by Takasago [93–98], Hoffmann La Roche [99,100] and Bayer [101]. Both optical isomers of citronellal have also been used for the production of both citronellol enantiomers (*via* hydrogenation) and both hydroxycitronellal enantiomers (H_2O addition) [26].

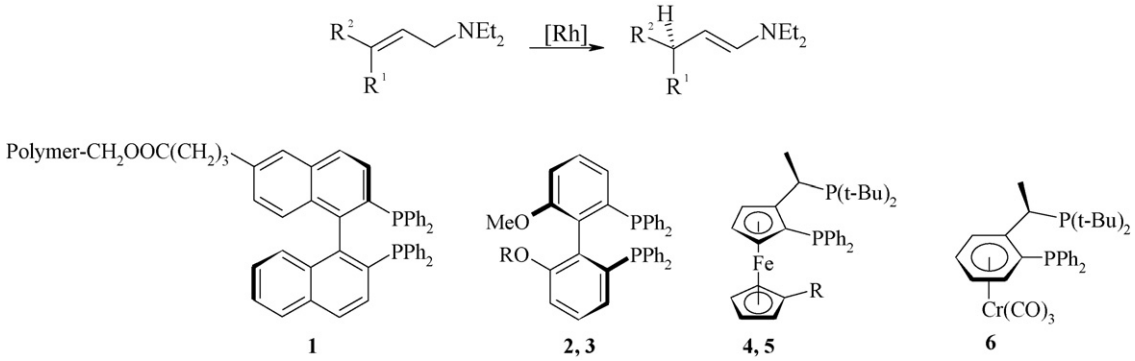
Moreover, highly optically pure (*R*)-(+)-citronellal is the starting material for the synthesis of the optically pure vitamin E side chain [26]. This route may be one of the most practical methods. Asymmetric isomerization of geranylamine derivative, obtained from (*R*)-(+)-citronellal, is an important step of this multistep synthesis – Scheme 19.

Also methoprene synthesis contains a step of isomerization of a prochiral *N*-allylamine – 7-methoxygeranylamine (obtained by addition of MeOH to diethylgeranylamine) – Scheme 20.

However, in 1988 Schmid et al. showed that binaphthyl derivatives are not the only ligands, whose Rh complexes catalyze enantioselective isomerization leading to chiral cintronellalenamine [102]. These researchers found that equally effective (as binap complexes) catalysts for *N*,*N*-diethylnerylamine isomerization are complexes of $[RhL^*(nbd)]^+$ and $[RhL^*(cod)]^+$ types, where L* is chiral 2,2′-bis(diphenylphosphino)-6,6′-dimethyl-biphenyl (biphemp) or its derivatives [92]. The reactions were carried out in THF, at a temperature of 60–80 °C,



Scheme 18. Takasago menthol synthesis *via* asymmetrical isomerization of *N*,*N*-diethylgeranylamine catalyzed by $\{[Rh(S)\text{-binap}]\}^+$ complex [26].



Scheme 21. Isomerization of *N*,*N*-diethyl- neryl and geranylamines in the presence of diphosphino ligands (1.0 mol%) and $[Rh(cod)_2]CF_3SO_3$ in refluxing THF [103]. Ligand 2, R = H; ligand 3, $R = (CH_2)_2(OCH_2CH_2)_{60}$-$OCH_2$-polymer; ligand 4, R = H; ligand 5, $R = Si(Me)_2CH_2NHC(O)NH(CH_2)_3Si(OH)(O_2Si)_n$.

in sealed tubes, for 1.5–88 h. Four similar ligands were examined, differing slightly in steric and electronic parameters. In all cases, high asymmetric induction was obtained (ee 98–99.5%), and the yield was moderate or high (60–96%, best result for biphemp). As in the case of binap, it was possible to obtain selectively a chosen enamine enantiomer, using ligand with *S* or *R* configuration. TON was satisfying or good; the best result, obtained for a complex with (*S*)-biphemp, amounted to 960 (comparing to 920–940 for [Rh(binap)] catalyzed isomerization [23]). The other were in the range of 160–560 (however, optimization of TON was not the objective of the work).

In 2001, Chapuis et al. reported the first example of the use of a chiral diphosphino ligand, neither C_2-symmetric nor atropic, which enabled the [Rh(diphosphine)(cod)]X catalyzed preparation (*S*)- or (*R*)-citronellal from diethylneryl- or diethylgeranylamine with similarly high enantioselectivity, under homogeneous or silica-gel- or polymer-supported conditions (see Scheme 21 and Table 10) [103].

It is noteworthy that after 37 recycles of catalyst 1 (see Table 10) by simple decantation-filtration techniques, no decrease in the chiral and chemical efficiency of the polymer-supported catalyst was observed.

It has been shown that complexes of [RhL(diene)]X type (L = ligand 4 in Scheme 21) are most active when the diene is cod, and X is ClO_4, CH_3SO_3 or PF_6. The complexes having nbd as the diene, and BF_4 or SbF_6 as X are less active. An influence of the counter-ion X on the selectivity has been observed as well: when X is BF_4 or SbF_6, enantioselectivity is slightly lower than in the other cases. Isomerization kinetics has also been investigated, and it has been confirmed that Michaelis–Menten kinetics occurs here (the reaction is being slowed by the enamine forming). Moreover, it has come out again that an exchange of the prochiral substrate (geranylamine with geraniol) leads to a significant decrease in conversion, and especially in enantioselectivity of double bond migration.

It is worth noting an attempt to synthesis of chiral aminoacids *via* double bond migration in imines – Scheme 22 [104]. Generated *in situ* cobalt complexes with chiral diphosphines were employed as catalysts for these reactions. However, optical purity of the obtained aminoacids was not high (ee ≤25%).

2.8. Tandem isomerization-RCM

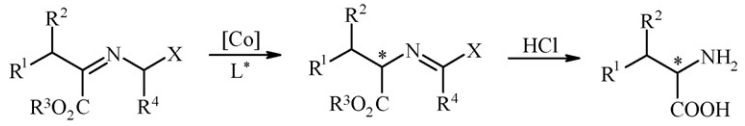
Double bond migration in *N*-allylic compounds is also carried out in tandem with RCM. Formed *N*-(1-propenylic) group is used in the second step of the tandem to construct a cyclic system. For example, Van Otterlo et al. applied this tandem transformation to the synthesis of six-, seven- and eight-membered nitrogen containing benzo-fused heterocycles – Scheme 23 [54].

Arisawa and co-workers offered an extremely facile and selective isomerization of *N*-allylsulfonamides by combining a ruthenium-carbene catalyst and vinyloxytrimethylsilane –

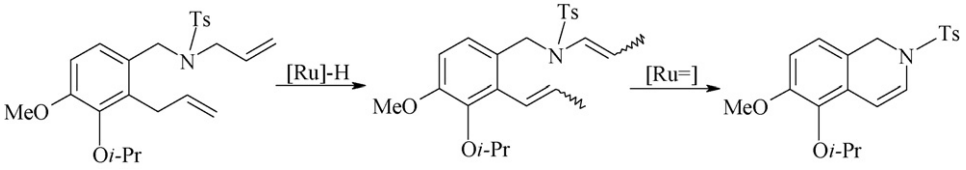
Table 10
Selected results of isomerization of allylamines catalyzed by $[Rh(cod)_2]CF_3SO_3$ and diphosphino ligands in refluxing THF – see Scheme 21 [103]

R^1	R^2	L (mol% of Rh)	Conversion (%) (after 20 h)	ee (%) (config.)
Me	$Me_2C{=}CH(CH_2)_2$	(*R*)-1 (0.25)	100	98 (−)
$Me_2C{=}CH(CH_2)_2$	Me	(*R*)-1 (0.25)	100	98 (+)
Me	$Me_2C{=}CH(CH_2)_2$	(*S*)-2 (1.0)	100	97 (+)
$Me_2C{=}CH(CH_2)_2$	Me	(*S*)-2 (1.0)	100	97 (−)
Me	$Me_2C{=}CH(CH_2)_2$	(*S*)-3 (0.25)	48	96 (+)
Me	$Me_2C{=}CH(CH_2)_2$	(*R*,*S*)-4 (0.25)	99	92 (−)
$Me_2C{=}CH(CH_2)_2$	Me	(*R*,*S*)-4 (0.25)	100	97 (+)
Me	$Me_2C{=}CH(CH_2)_2$	(*R*,*S*)-5 (0.25)	81	96 (−)
$Me_2C{=}CH(CH_2)_2$	Me	(*R*,*S*)-5 (0.25)	99	96 (+)
Me	$Me_2C{=}CH(CH_2)_2$	(*R*,*S*)-6 (0.25)	99	96 (−)

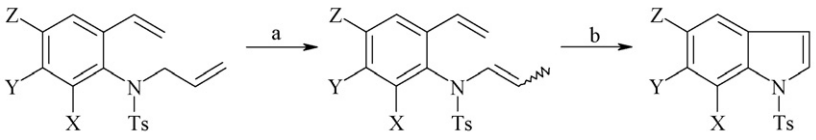
R^1, R^2, L – see Scheme 21.



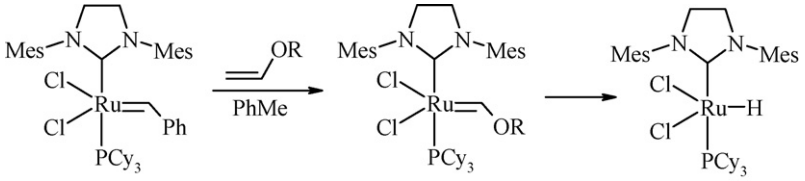
Scheme 22. Synthesis of chiral aminoacids *via* enantioselective isomerization of imines catalyzed by Co complexes with chiral diphosphines [104]. R^1 = H, alkyl, aryl; R^2 = H, alkyl; R^3 = alkyl; R^4 = H, alkyl; X = electron withdrawing group.



Scheme 23. Synthesis of isoquinoline derivatives *via* Ru-catalyzed isomerization and ring closing metathesis [54]. [Ru]-H = 0.5 mol% [$RuClH(CO)(PPh_3)_3$], PhMe, 110 °C, 2h; [Ru=] = 5 mol% [$Cl_2PCy_3(Imes)Ru{=}CHPh$], PhMe, 110 °C, 3 h.



Scheme 24. Ruthenium catalyzed synthesis of the indole ring *via* RCM of double bond migration products [105–108]. X, Y, Z = H, H, H; MeO, H, H; MeO, MeO, MeO; H, Cl, H;. . . (a) isomerization step: 5 mol% [$Cl_2PCy_3(Imes)Ru{=}CHPh$]; 5 mol% [$SiMe_3CH{=}CH_2$]; CH_2Cl_2; 1.5 h; 50 °C; (b) RCM step: 5 mol% [Ru]; PhH or PhMe; 80–110 °C; 1–17 h.

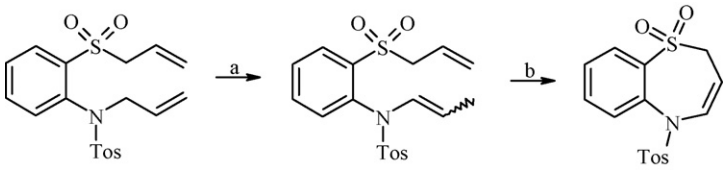


Scheme 25. Transformation of the ruthenium carbene complex into the ruthenium hydride complex [108]. R = Et or $SiMe_3$.

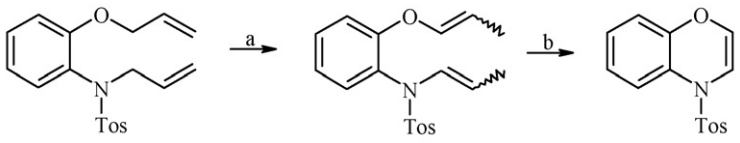
Scheme 24 [105–108]. A new ruthenium hydride complex is formed *in situ*, which catalyzes double bond migration and cycloisomerization, but does not catalyze RCM (Scheme 25) [108]. In the second step, the obtained enamides are subjected to RCM under typical conditions. It is the first example of application of isomerization-RCM tandem in indole ring synthesis.

Isomerization proceeded quantitatively, while RCM products (substituted indoles) were isolated with yields up to 100% (usually higher than 70%). The utility of this reaction was demonstrated in a novel and efficient synthesis of an indole ring from 2-vinyl-*N*-allyl-(*p*-toluenesulfonamide) derivatives using isomerization-RCM ruthenium mediated tandem reactions. It was noteworthy that the Ts group might be equally well replaced by an Ac, Bz or BOC group [105,106,108]. When the isomerization step (Scheme 24a) was carried out at higher temperatures (xylene, rfx), cycloisomerization products, i.e. 3-methyleneindole derivatives [105,108,109], were the main products of the process. On the other hand, without addition of vinyloxytrimethylsilane, only RCM proceeded and dihydroquinoline derivatives were formed [105,106,108]. Modification of reaction conditions allowed to obtain various products from derivatives of *N*-allyl-2-vinylaniline: 1-propenyl, indole, methylene indole derivatives or dihydroquinolines.

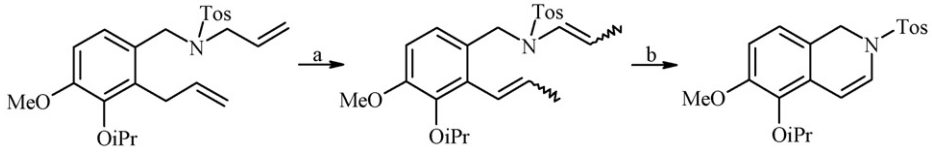
Van Otterlo et al. showed a possibility of synthesis of heterocycles containing sulfur and nitrogen or oxygen and nitrogen atoms *via* Ru-mediated isomerization and RCM reactions (Schemes 26 and 27) [110]. The isomerization required large amounts of catalyst, and the RCM proceeded particularly slowly.



Scheme 26. Ru-catalyzed isomerization and RCM towards a seven-membered *N*,*S*-heterocycle [110]. (a) 10 mol% [$RuClH(CO)(PPh_3)_3$], PhMe, 105 °C, 24 h (84%); (b) 5 mol% [$Cl_2PCy_3(Imes)Ru{=}CHPh$], PhMe, 50 °C, then 5 mol% [$Cl_2PCy_3(Imes)Ru{=}CHPh$], 80 °C, 24 h (total yield 41%).



Scheme 27. Ru-catalyzed isomerization and RCM towards a six-membered *N*,*O*-heterocycle [110]. (a) 1 mol% [RuClH(CO)(PPh3)3], PhMe, 95 °C, 2 h (quant.); (b) 5 mol% [Cl_2PCy_3(Imes)Ru=CHPh], PhMe, 45 °C, 2 h (90%).



Scheme 28. Tandem isomerization-RCM of *ortho*-*C*,*N*-diallylbenzylamine derivative catalyzed by ruthenium complexes. (a) 0.5 mol% [RuClH(CO)(PPh3)3], PhMe, 60 °C, 1 h, quant.; (b) 5 mol% [Ru=], PhMe, 110 °C, 3 h, 76% over two steps.

In our opinion, this was a result of a competitive reaction of *S*-allyl bond cleavage, analogous to the one observed by us in reactions of [RuClH(CO)(PPh_3)$_3$] with allyl sulfides, allyl sulfoxides and sulfones [13,15,111]. It is noteworthy that double bond migration occurred only in the *N*-allyl fragment while the S(O_2)allyl moiety was not undergoing transformation under the reaction conditions (see Scheme 26). Moreover, no isomerization was observed when the *S*(O_2)allyl group was replaced with *S*-allyl [110].

These results are consistent with ours: presence of a sulfide sulfur atom, not protected by large groups (e.g. Ph_3C or Me_3C), renders isomerization on Ru complexes impossible [13,15,111]; isomerization of *N*-allyl systems occurs significantly faster than that of *S*-allyl systems [15].

As one can see, both *O*- and *N*-allyl groups undergo the reaction without obstruction. There is no need to use high catalyst concentrations or long reaction times. However, when Tos was replaced by BOC, a significantly higher amount of the catalyst was required for both steps, and a significant prolongation of reaction time was necessary. In our opinion, a cleavage of C–O bond in BOC was a competitive reaction in this case [15]. In the case of reactions of allyl carboxylates, and of allyl methyl carbonate with [RuClH(CO)(PPh_3)$_3$], we have observed a cleavage of C–O bond [15].

In another work, Van Otterlo et al. obtained a variety of six-, seven- and eight-membered nitrogen- and oxygen-containing benzo-fused heterocycles *via* a Ru-catalyzed isomerization and RCM of C,*N*-diallyl substrates [54,80,112]. An example of a synthesis of a six-membered nitrogen-containing benzo-fused heterocycle is shown on Scheme 28.

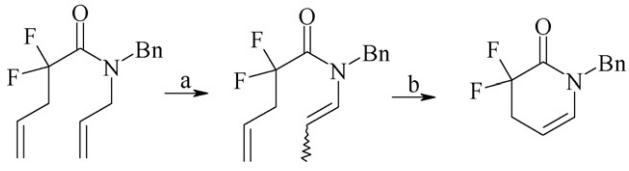
Fustero et al. described an efficient and regioselective synthesis of fluorinated and nonfluorinated lactams from *N*,*C*- or *N*,*N*-diallylamides [71]. The lactams were formed in tandem reactions: RCM-isomerization or isomerization-RCM catalyzed by Ru complexes. Selected examples of the RCM-isomerization tandem are presented in Table 9, because they are indeed examples of isomerization of *N*-allyl nitrogen heterocycles formed in RCM of *N*,C- or *N*,*N*-diallylamides. As the RCM catalyst, a ruthenium carbene complex was used, which was undergoing (without use of any additives) an *in situ* transformation to a hydride complex. The latter species catalyzed the isomerization, which was significantly slower than metathesis. The only limitation to the method involves the formation of nine-membered rings. The sole example of synthesis of a lactam starting from isomerization of an *N*,C-diallylamide is shown on Scheme 29 [71].

However, unlike the aforementioned RCM-isomerization tandem, the first catalyst in isomerization-RCM tandem was a ruthenium hydride species, and a ruthenium carbene was used in the second step.

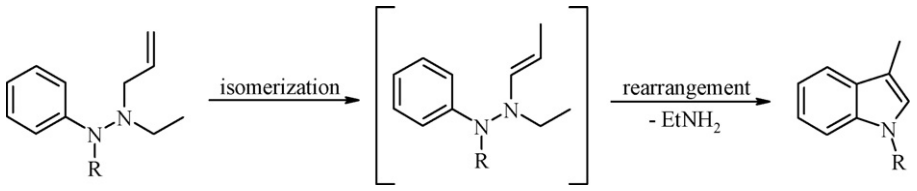
2.9. Isomerization in a cascade of reactions

Nielsen et al. recently described a simple and convenient method for synthesis of *N*-substituted-3-methylindoles from *N*-allyl-*N*′-arylhydrazines [113] (Scheme 30).

This is the first example of a catalyzed isomerization of allyl phenylhydrazines using transition metal catalysis. The catalyst was a ruthenium hydride species generated *in situ* from a ruthenium carbene complex and Li[BEt_3H]. The intermediate enehydrazine (not isolated) then undergoes a cascade of reactions (under the reaction conditions), including a [3,3]-sigmatropic rearrangement, leading to the indole. The Authors found also that *N*-acyl-*N*′-allylhydrazines did not undergo conversion into corresponding *N*-acylated indoles. It was a result of deactivation of the ruthenium catalyst. It is likely that inactive, chelate complexes were formed.



Scheme 29. Synthesis of a fluorinated lactam *via* Ru-catalyzed isomerization and RCM of a *N*,*C*-diallyl substrate [71]. (a) 10 mol% [RuClH(CO)(PPh_3)$_3$], PhMe, 3 h, rfx, 71% yield; (b) 10 mol% [Cl_2(PCy_3)(Imes)Ru = CHPh], CH_2Cl_2, 3 h, rfx, 66% yield.



Scheme 30. Fischer indole synthesis *via* cascade isomerization-rearrangement of *N*-allyl-*N*′-arylhydrazines [113]. R^1, R^2 = H, Me; H, Ph; Me, Me; Me, Ph; isomerization: 5 mol% of $[Cl_2(PCy_3)_2Ru{=}CHPh]$, 20 mol% of $Li[BEt_3H]$, PhMe, 100 °C, 12 h; yield of indoles: 56–62%.

3. Mechanisms and stereoselectivity

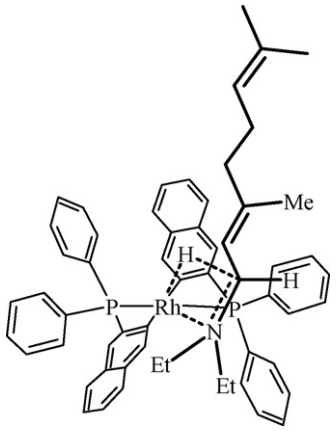
Double bond migration in *N*-allylic systems usually proceeds according to the same mechanisms as in other compounds, i.e. C-, O-, S-, P and Si-allylic systems [1–4,8,15]. Classic mechanisms, hydride and hydride-π-allyl, were most frequently observed or suggested. However, in a number of cases, mechanisms with a specific participation of nitrogen atom were postulated. These reactions are discussed below. When a high stereoselectivity (and, particularly, enantioselectivity) was observed in a reaction, the result can almost always be attributed to a specific participation of nitrogen atom in the coordination of the metal atom (or to a specific participation of the Q functional group as a whole), and of course also to steric effects.

The most spectacular example of influence of nitrogen atom participation in metal atom coordination on the reaction outcome is the asymmetric isomerization of derivatives of geranylamine and nerylamine, catalyzed by rhodium cationic complexes with chiral diphosphines. The coordination of the nitrogen atom by the rhodium atom during the whole catalytic cycle determines the configuration of the complexes forming, and thus governs the configuration of the product (Scheme 31).

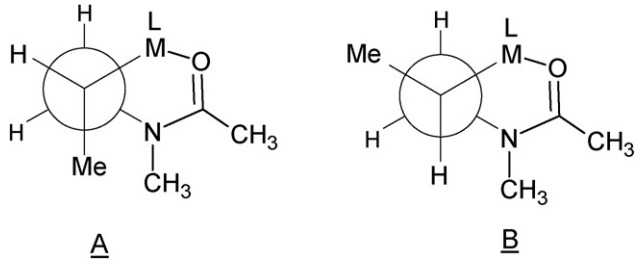
In the case of the enantioselective isomerization of diethylgeranylamine and diethylnerylamine (as well as some other structurally similar allylamines) to chiral enamines (see Section 2.7 of this review) catalyzed by cationic binap-based complexes of rhodium, steric and coordination effects play a dominant role. The mechanism of this reaction, investigated in detail by Inoue et al. [87], is shown in a simplified form on Scheme 31.

The enantioselectivity-determining step consists of an oxidative addition of Rh C^1–H bond, accompanied by formation of an iminium complex [85,87]. Enantioselectivity is a result of forcing the specific complex geometry by the binap ligand (Scheme 32) [85,87].

A detailed analysis of the mechanism of isomerization of prochiral allylamines may be found in works of Tani et al. [23] and Inoue et al. [87], and also in a review by Noyori [85]. It is worth to note that attempts to change the allylic substrate or the catalytic system have always led to a decrease (even dramatic) of chemo- and enantioselectivity of the reaction. Apparently, *N*,*N*-diethylneryl and *N*,*N*-diethylgeranylamines constitute a



Scheme 32. Enantioselectivity-determining step in Rh-binap catalyzed isomerization of diethylgeranylamine [85,87].

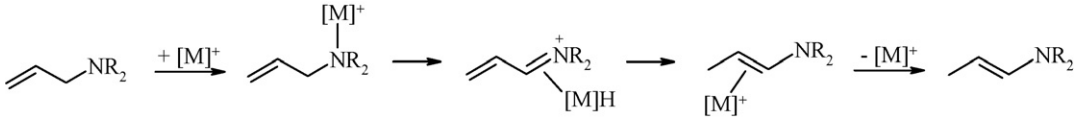


Scheme 33. *E*-Stereoselectivity as a result of steric and coordination effects [48].

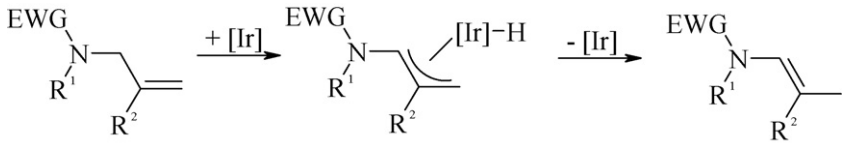
"key-and-lock" system with the cationic binaphtyl (or biphenyl) diphosphine complexes of Rh(I).

Sergeyev and Hesse obtained 100% *E*-stereoselectivity in isomerization of $PhCH_2CH_2CON(Me)allyl$ in the presence of $[Fe(CO)_5]$ [48]. They attribute this result to participation of the functional group Q (i.e. the amide group) in coordination of the metal atom, and to steric effects in the metal hydride elimination step (Scheme 33).

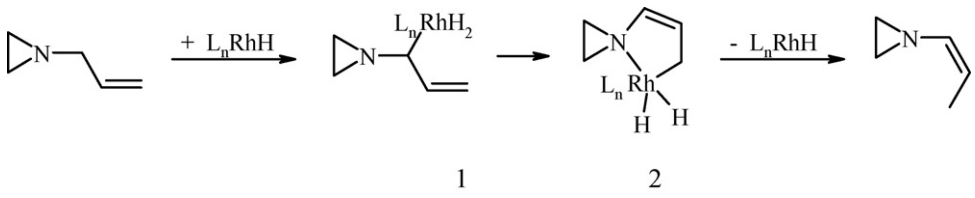
Complex B is less sterically hindered (there is a weak H–Me repulsion in B and a strong Me–Me repulsion in A), and that is why the reaction path leading through complex B to isomer *E* is preferred [48]. The effect is less obvious in the case of amides



Scheme 31. Mechanism of rhodium-catalyzed isomerization of allylamines [26,85–87,90,91].



Scheme 34. Proposed mechanism for Ir catalyzed isomerization of (EWG)N(R^1)CHCH(R^2)=CH_2 (EWG, R^1 – see Table 8; R^2 = H or Me) [31].



Scheme 35. Proposed mechanism for *Z*-stereoselective isomerization of *N*-allylaziridines catalyzed by [RhH(CO)(PPh_3)$_3$] [74].

of RCONHallyl type, therefore in these reactions the observed *E*-selectivity is low (*E*:*Z* ≤ 75:25). Moderate *E*-selectivity in isomerization of *N*-allylamides catalyzed by Ru and Rh complexes was explained in an analogous manner by Stille and Becker [45].

On the other hand, *E*-selectivity in isomerization of *N*-allylamides, imides and carbamates of (EWG)N(*R*)allyl type (EWG = electron withdrawing group) catalyzed by an Ir complex generated *in situ* from [IrCl(COD)]$_2$, PCy_3 and Cs_2CO_3 is a result of steric effects in the opinion of the Authors [49]. They suggest a typical hydride-π-allyl mechanism (see Scheme 34). The hydride-η-allyl intermediate is consistent with the almost exclusive formation of *trans*-enamine, since in this case only hydrogen atoms occupy the "endo" position. This also explains the low reactivity of systems having a methyl group at C^2 in the allyl moiety (i.e. R^2 = Me, Scheme 32), due to steric hindrance.

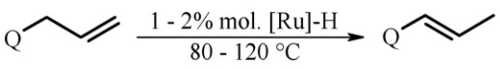
Alphonse and Yudin obtained exclusively *Z*-enamines in reactions of isomerization of aziridine derivatives – see Scheme 13 [74]. The kinetic preference for the formation of the *Z*-enamine is explained by a mechanism involving coordination of the aziridine nitrogen atom and the terminal carbon by rhodium, causing a *pro-Z* configuration of complex 2 (Scheme 35). In our opinion, coordination *via* nitrogen atom stabilizes the σ-carbyl complex 2.

A highly *E*-stereoselective double bond migration was observed for some *N*-allylamines (Q = (Me_2N, PhNMe, $Me_3Si)_2$N-, *t*-Bu(Allyl)N-, . . .) and *N*-allyl-*N*-arylethanamides (Q = ArN(COMe)-, Ar = Ph, substituted Ph, 1- or 2-naphtyl) catalyzed by [RuClH(CO)(PPh_3)$_3$] or [RhH(CO)(PPh_3)$_3$] (Scheme 36) [12,15,46,51,52,114,14].

Our investigations lead to a conclusion that also *E*-stereoselective isomerizations proceed according to the hydride mechanism [15,46,14]. *E*-stereoselectivity of these reactions results, in our opinion, mostly from the coordination effect, namely participation of the Q functional group (R^1R^2N- or RC(O)N-) in coordination of the ruthenium or rhodium atom [15,46,14]. Proposed structures essential for stereoselectivity of these reactions, presenting contribution of Q, are shown in Fig. 2 [8,13–15,46,52].

We carried out quantum-chemical calculations (semi-empirical and *ab initio* geometry optimization followed by an analysis of the shapes of RHF orbitals) for *N*-allyl: amides and amines and *N*-(1-propenyl): amides and amines [15,46,52]. It allowed us to analyze possible interactions of substrates and products of double bond migration with ruthenium or rhodium complexes [15,46,52]. The analysis proved unequivocally that participation of Q in the coordination increases the chance of obtaining *E*-isomer. It is particularly clear in the case of isomerization of some *N*-allylamides [15,46,51,52]. *N*-Aryl-*N*-allyl amides isomerize highly stereoselectively to *E*-enamides in the presence of [RuClH(CO)(PPh_3)$_3$] or [RhH(CO)(PPh_3)$_3$] (because of Q participation in the coordination), and *N*-alkyl-*N*-allylamides isomerize to a mixture of *E*- and *Z*-enamides (lack of Q participation) [15,46,51,52]. In the case of *N*-aryl-*N*-allylamides, the coordination occurs mainly through the allylic double bond and the arene fragment, while in the case of *N*-allylamines – through the double bond and the nitrogen atom. Steric effects play also a significant role in these reactions. Unfavorable steric influence in complexes shown in Fig. 2 (between other ligands and methyl group) would be significantly higher if the enamines or enamides had *Z*-configuration.

Isomerization of dienamines and dienyl ethers (catalyzed by generated *in situ* "$Cr(CO)_3$") was highly *E*,*Z*-stereoselective



Scheme 36. *E*-Stereoselective isomerization of Q-allyl catalyzed by ruthenium or rhodium hydride complexes. Q = Me_2N, PhNMe, $Me_3Si)_2$N-, *t*-Bu(Allyl)N-,. . .; ArN(COMe)-, Ar = Ph, substituted Ph, 1- or 2-naphtyl; [M]-H = [RuClH(CO)(PPh_3)$_3$] or [RhH(CO)(PPh_3)$_3$].

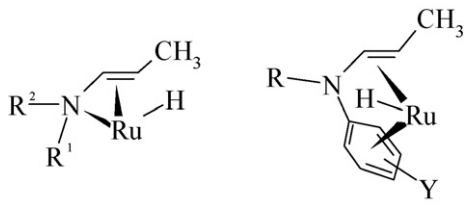
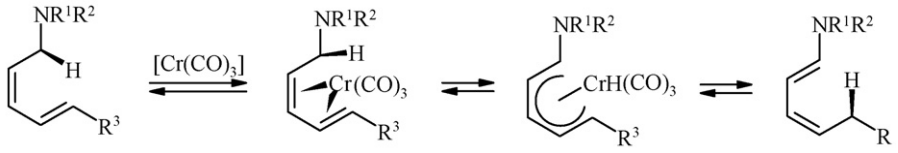


Fig. 2. Proposed structures of complexes determining the stereochemistry of isomerization of *N*-allylamines and *N*-allyl-*N*-arylamides catalyzed by [RuClH(CO)(PPh_3)$_3$] or [RhH(CO)(PPh_3)$_3$]. Such ligands as PPh_3, CO, Cl, and solvent, were omitted.



Scheme 37. A chromium-catalyzed stereocontrolled double bond migration in *N*-BOC-*N*-allyl systems. Suggested mechanism of the reaction (R^1, R^2 – see Scheme 12) [58,100].

(Scheme 37). In the opinion of the Authors, it is because it proceeded *via* U-shaped η^5-intermediates formed stereospecifically by the oxidative addition of C–H bond to "$Cr(CO)_3$" [58,100].

A quantitative *E*-stereoselectivity was also observed in isomerization of *N*-allylbis(trimethylsilyl)amine photocatalyzed by $[Fe(CO)_5]$ [22]. However, the Authors did not try to explain its cause.

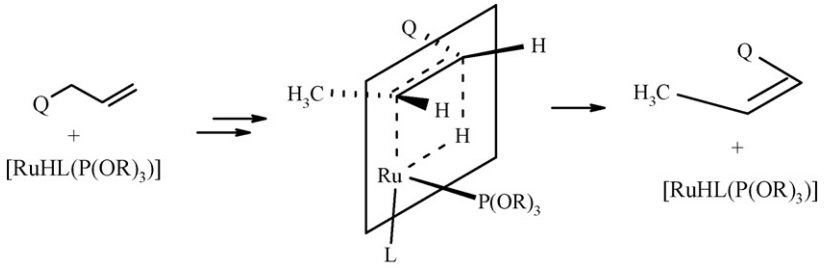
Steric and coordination effects determined also high *E*-stereoselectivity of *N*-allylamides isomerization catalyzed by iridium catalyst generated *in situ* from $[Ir(COD)Cl]_2$, tricyclohexylphosphine and Cs_2CO_3 [78]. The reaction proceeds according to the π-allyl mechanism, and the η^3-allyl hydride intermediate is consistent with the almost exclusive formation of *E*-enamide, since in this case only hydrogen atoms occupy the "endo" position [78]. Unusual *E*-stereoselectivity of isomerization of 1-alkenes to 2-alkenes, isolated dienes to *E*,*E*-conjugated dienes, and allylamines to *E*-enamines catalyzed by $[TiCl_2(C_5Me_5)_2]/NaC_{10}H_8$ was observed by Akita et al. [19]. Authors stated that the stereoselectivity resulted from steric effects at β-elimination stage (migration proceeded according to the hydride mechanism). Some *E*-stereoselectivity was also observed in isomerization reactions of *N*-allylamides catalyzed by $[Fe(CO)_5]$, proceeding according to the π-allyl mechanism [76]. *E*-isomer was preferred due to steric effects – interactions between the methyl group and ligands were minimized when this isomer was formed.

The only example of a highly *Z*-stereoselective double bond migration in *N*-allylamides is a reaction catalyzed by ruthenium hydride complexes generated *in situ* from $\{[RuCl_2(1,5\text{-}COD)]_x\} + CaH_2 + P(OAr)_3$ (Ar = 2,4,6-tri-*t*-butylphenyl) (Scheme 38, see also Scheme 11) [12,15,46].

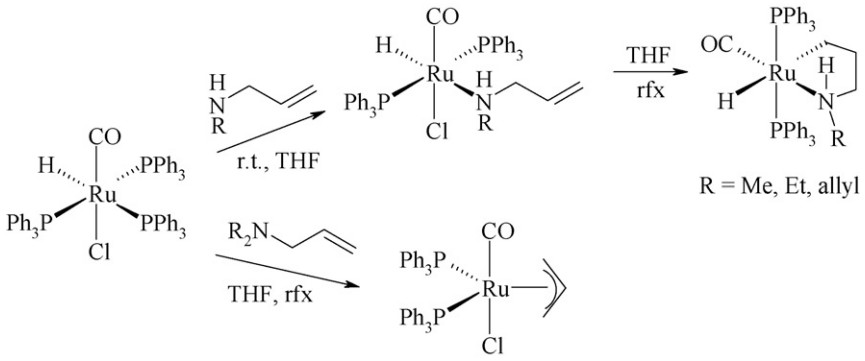
In the proposed transition state, Q and CH_3 groups are located at one side of the plane in which β-elimination occurs, while bulky ligands bound to the ruthenium atom are at the other side. Such a geometry of the transition state minimizes repulsive steric interactions between, on one side, Q and Me, and on the other side – bulky ligands coordinated to the ruthenium atom. It is noteworthy that either bulk of the Q group or steric demand of the phosphine ligand (i.e. a phosphine with high θ angle) is required for high *Z*-stereoselectivity. Likewise, isomerization of *N*-allylamides in the presence of $[RuL_n(PR_3)_x]$-H, generated *in situ* using $\{[RuCl_2(1,5\text{-}COD)]_x\}$, PR_3 and CaH_2, is not stereoselective for PR_3 with too low a θ – e.g. for PPh_3 or $P(OPh)_3$. In this case tris(2,4,6-tri-*t*-butylphenyloxy)phosphine is required [12,15,46]. Therefore the role of Q in *Z*-stereoselective double bond migration in our opinion consists in augmentation of the steric effect of the phosphine ligands. Presence of ligand L (diene or second molecule of $P(OR)_3$) in the ruthenium coordination sphere should favor an increase in *Z*-selectivity of isomerization.

The examples analyzed above show that the participation of the nitrogen atom or the whole Q group in coordination of the metal atom usually determines the stereochemistry of double bond migration in Q-allyls. However, the fact whether Q-allyl is a "soft" or a "hard" donor, is also very important for the outcome of reactions between Q-allyl and transition metal complexes [15]. It is evident for reactions of Q-allyl (also *N*-allyl) with ruthenium complexes [15]. Namely when Q = Me_2N, O=C=N, *N*-imidazolyl or PhCH=N-, isomerization of Q-allyl to Q-(1-propenyl) does not occur for many Ru(0), Ru(II), and Ru(III) complexes [8,15,66,116,11]. In these cases, Q-allyl is so strongly coordinated by ruthenium atom that forming complexes are inert, inactive. Furthermore, sometimes allyl-nitrogen bond cleavage is observed, as a result of C–N bond weakening caused by strong coordination of nitrogen atom by the metal atom [15].

Hiraki et al. studied reactions of primary, secondary and tertiary allylamines with $[RuClH(CO)(PPh_3)_3]$ (Scheme 39) [115]. They found that at room temperature, primary and secondary allylamines were coordinated through the nitrogen atoms, and not through the double bonds. However, at boiling temperature of the reaction mixture, the allylamine was



Scheme 38. Proposed mechanism for *Z*-stereoselective double bond migration in *N*-allylamides catalyzed by ruthenium hydride complex generated *in situ* from: $\{[RuCl_2(1,5\text{-}COD)]_x\} + CaH_2 + PR_3$. L = diene or second $P(OPh)_3$. Such ligands as Cl, diene and solvent, were omitted. Q = MeCONH, H_2NCO, etc. (see Scheme 11); R = 2,4,6-tri-*t*-butylphenyl; L = COD or second phosphine ligand.



Scheme 39. Reaction of primary, secondary and tertiary allylamines with [RuClH(CO)(PPh$_3$)$_3$] [115].

inserted into the Ru–H bond of [RuClH(CO)(PPh$_3$)$_3$] to form the five-membered 3-aminopropyl-C^1,N chelate ring. The resulting alkyl complex was stabilized by chelation through the nitrogen atom. A completely analogous reaction of allyl sulfides with [RuClH(CO)(PPh$_3$)$_3$] was observed by Hiraki et al. [117]. To the contrary, in reaction of tertiary allylamines with [RuClH(CO)(PPh$_3$)$_3$], allyl-nitrogen bond cleavage and formation of a π-allyl complex were observed [115].

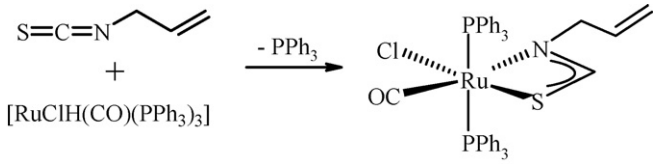
These stoichiometric transformations of allylamines are accompanied by a parallel catalytic process, that is, by double bond migration. In reactions of *N*-methylallylamine and *N*,*N*-dimethylallylamine with [RuClH(CO)(PPh$_3$)$_3$] (at high Ru concentration) formation of *E*-enamines was observed [115]. These results correspond well with the results of our later research. We found that isomerization of *N*- or *S*-allyl systems in the presence of Ru complexes is possible only when coordinating properties of nitrogen or sulfur atom have been limited [15,111]. This may be achieved by using bulky substituents bound to the heteroatoms or by transformation of amines into amides or imides, and sulfides and sulfoxides into sulfones [15].

Formation of π-allyl complexes was also observed in reactions of allylamines with some cationic platinum(II) hydrides [118]. Also in these reactions, allylamines coordinated the metal atom through the nitrogen atom and not through the double bond. Double bond migration was not observed.

However, Onishi et al. showed that double bond migration in an *N*-allyl amine and amide photocatalyzed by [CoH((P(OEt)$_3$)$_3$] (photogenerated from [CoH((P(OEt)$_3$)$_4$]) was initiated by coordination of the substrates trough C=C double-bond rather than N- or O-donor atom [20]. Allylacetamide and *N*,*N*-diethylallylamine gave similar spectral changes to those observed for 1-hexene or allylbenzene, indicating the ligation to [CoH((P(OEt)$_3$)$_3$] *via* double bond in a π-fashion, rather than *via* the oxygen or nitrogen atom. The Authors indicated the impossibility of back-bonding if the coordination occurred solely *via* nitrogen or oxygen atoms.

In the reaction of allyl phenyl isothiocyanate with [RuClH(CO)(PPh$_3$)$_3$], an irreversible addition of [Ru]-H to Q occurred, and the allylic fragment did not participate in the coordination (Scheme 40).

An intramolecular cyclization of an *N*-allyl amine promoted by a transition metal complex was observed: in reaction of



Scheme 40. Reaction of allyl isothiocyanate with [RuClH(CO)(PPh$_3$)$_3$] [15].

N-allylaniline with {[RhCl(ethene)$_2$]$_2$}, a complex with coordinated *N*-phenylazetidine was formed [119].

The type of the central atom in the complex has a very important influence on the outcome of reactions of *N*-allyl (generally, Q-allyl) compounds with the metal complex. However, it is not clear why e.g. isomerization of *N*-allylamines proceeds easily in the presence of [Fe(CO)$_5$] and many Rh(I) complexes, but Ru(0) and Ru(II) complexes catalyze this reaction in special cases only, i.e. when the substituents in R^{1}R^2*N*-allyl are bulky [15].

4. Conclusion

Double bond migration in *N*-allyl compounds (*N*-allyl: amines, imines, amides, imides, carbamates and others) is a convenient method for synthesis of *N*-(1-propenyl) compounds such as enamines, 2-aza-1,3-dienes, enamides, and others. In tandem with RCM, double bond migration reaction is also a useful method for synthesis of heterocycles containing nitrogen atoms and additionally an oxygen or sulfur atom in the ring. In spite of the fact that double bond migration in *N*-allyl compounds may be catalyzed by strong bases and metals on support, transition metal complexes are used most frequently. Particularly effective catalysts include complexes of: Rh (especially for allylamines and imines and also for amides), Ru (especially for allylamides and imides and also for allylamines or carbamates), Fe (for allylamines and amides), Ir (for amides and carbamates). Complexes of other metals – such as Mo, Co, Os, Cr, and Ti – have also been used, and spectacular results have been obtained (high *E*- or *Z*-stereoselecitvity). Moreover, when the *N*-allyl system is prochiral, and a cationic complex of Rh(I) with chiral diphosphines (derivatives of binap or bis(diphenylphosphino)biphenyl) is used as the catalyst, optically active products of double bond migration are obtained: enamines, imines or enamides. Highly chemo-, regio- and enantioselective isomerization of

N,*N*-diethylgeranyl- and nerylamines to optically active citronallal enamine found an industrial application for synthesis of (−)-menthol and other optically active derivatives of terpenes. Isomerization proceeded most frequently under homogeneous conditions, at moderate temperatures, in solvents or without them. Successful reactions catalyzed by rhodium complexes immobilised on a polymer or SiO_2 were also reported. Among of all described isomerizations of Q-allyl (Q = alkyl$_2$N, arylN=CH, Oalkyl, Oaryl, Salkyl, Ar, RCH=CH, Sialkyl$_3$,. . .) catalyzed by transition metal complexes, double bond migration in *N*-allyl compounds proceeds most often regio-, stereo- and enantioselectively. High stereoselectivity (also enantioselectivity) of double bond migration in *N*-allyl systems is almost always a result of specific coordination effects. Most often, they involve participation of nitrogen atom in coordination of the metal atom in intermediate stages essential for stereochemistry of the reaction. It is the case e.g. of asymmetric isomerization of allylamines (on cationic Rh(I) complexes) or *E*-stereoselective isomerization of *N*-allylamines (on Ru complexes). In isomerization reaction of *N*-allylamides, participation of oxygen atom or arene unit in the coordination (in *N*-allyl-*N*-arylamides) is suggested. However, sometimes stereochemistry of double bond migration is determined mainly by steric effects – as in e.g. *Z*-stereoselective isomerization of *N*-allylamides (on Ru hydride complexes). Donor–acceptor properties of *N*-allyl substrates have very strong or even decisive influence on the course of the reaction. Too strong a coordination of nitrogen atom by the metal atom renders double bond migration impossible (catalytically inactive complexes are formed) or leads to C–N bond cleavage. Effects of such a type have been described in detail for reactions of Q-allyl (Q = Me$_2$N, PhCH=N, O=C=N, S=C=N, *N*-imidazolyl,. . .) with Ru(0), Ru(II) and Ru(III) complexes.

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