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Review

Transition metal complexes as catalysts of double-bond migration in *O*-allyl systems

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Contents

Abstract

This review provides a literature survey of the double-bond migration in *O*-allyl systems catalyzed by transition metal complexes: allyl aryl, allyl alkyl ethers, cyclic ethers, such as 2,5-dihydrofurane and cyclic acetals, *e.g.* 4,7-dihydro-1,3-dioxepine derivatives and allyl silyl ethers. The most frequently used catalysts are ruthenium and rhodium phosphine complexes, but other compounds, such as palladium halides, cobalt and iron carbonyls, are also presented. Also, isomerization of allyl carboxylates is mentioned. Recently double-bond migration reactions have been coupled with ring closing metathesis in a tandem reaction in both (one-pot or two-step) ways, and this is also reviewed. The specific aspects of double-bond migration mechanisms in *O*-allyl systems are presented. Stereoselectivity (*E*/*Z* products), as a key parameter of double-bond migration, resulting from steric factors or the possibility of chelating coordination of isomerized molecule, is discussed in the article. The advantages of transition metal complexes applied for double-bond migration catalysis are presented.

Keywords: Double-bond migration; Isomerization; Ruthenium complexes; Allyl ethers; 1-Propenyl ethers

1. Introduction

Double-bond migration as one method of isomerization in allyl systems has been well recognized in organic synthesis [1]. While the isomerization of alkenes (*C*-allyl systems), *N*-allylamines, and allyl alcohols has industrial and synthetic applications [2–4], the double-bond migration in allyl ethers is well established in organic synthesis as an initial step of the synthesis of poly(vinyl ethers) [5–8], in the procedure of protection and deprotection of free OH groups [9] among others. The isomerization of appropriate allyl ethers is a convenient method for the synthesis of *O*-(1-propenyl) compounds [10]. Moreover, double-bond migration in *O*-allyl systems has been recently successfully coupled with metathesis in a tandem reaction [11–17].

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Scheme 1.

If it meets all thermodynamic requirements [18,19], the reaction is possible, but it needs a catalyst. The reaction can be catalyzed by strong organic bases [19,20], but the most literature describes various transition metal complexes, with the most important being ruthenium and rhodium phosphine complexes Although iridium, palladium and chromium complexes are used in minority in this reaction, it is possible to achieve very high stereoselectivity in some reactions catalyzed by these complexes because of the very specific steric or coordination factors. Here, we present a catalyst survey for double-bond migration in *O*-systems (allyl ethers, cyclic acetals, and allyl carboxylates). We do not describe transformations in allyl alcohols, since there are already reviews on this quite specific topic [2,3,21].

2. Survey of the catalyst for the double-bond migration in *O*-allyl systems

2.1. Ruthenium catalyzed double-bond migration in allyl ethers

Ruthenium complexes have been the most frequently applied catalysts for double-bond migration, for protection and deprotection of OH groups (Scheme 1).

Crivello has shown many examples of the successful application of ruthenium complexes, such as $[RuCl_2(PPh_3)_3]$, mainly in the preparation of 1-propenyl ethers and studies on their polymerization [22–29]. The author illustrates the advantage of the application of the transition metal complexes in the reaction over base catalyzed (*t*-BuOK) reaction—the latter requires large amounts of the base, highly moisture-free conditions, special solvents and a difficult work-up. The disadvantages make the latter reaction less attractive in organic synthesis. Examples of the application of $[RuCl_2(PPh_3)_3]$ in the isomerization of allyl ethers, described by Crivello, is shown in Table 1.

Our research has focused on the isomerization of many *O*-allyl systems [10], including allyl ethers [30–35], allyl esters [36], allyl acetals and orthoesters [36–38], and others. We have been using two types of pre-catalysts. The first type comprises single complexes, such as: $[Ru(CO)_3(PPh_3)_2]$, $[RuClH(CO)(PPh_3)_3]$, and $[Ru(acac)_3]$ which are very active in these reactions. $[Ru(CO)_3(PPh_3)_2]$ exhibits the highest activity at relatively low temperatures: 40–60 °C, which is quite important for temperature sensitive systems, such as allyl esters of boronic and silicic acids [36]. $[RuClH(CO)(PPh_3)_3]$ shows higher activity at slightly elevated temperatures (60–120 °C). We found this complex to be the most universal catalyst for double-bond migration in *O*-allyl compounds. The important advantage of these catalysts for organic synthesis is the convenience of their use, the simplicity and stability of the catalytic system. Thus, such a catalyst has been applied to obtain many 1-propenyl ethers, particularly for further polymerization [39]. Comparably the lowest activity was found for $[Ru(acac)_3]$ (for example, this last species catalyzes isomerization of allyl phenyl ether in 1 h at 100 °C, while $[RuClH(CO)(PPh_3)_3]$ catalyzes it in 15 min at 60 °C).

The second catalytic system is formed *in situ* in the reaction of $\{[RuCl_2L_n]_x\}$ + phosphine + hydride (optional). Although it is less active, it exhibits the highest stereoselectivity in many cases of isomerization [31,35]. The stereoselectivity is discussed in Section 4.

We have also found a very interesting influence of coordination properties on the course of the reaction—the presence of strongly coordinating groups deactivates the catalyst, and new complexes are formed [10,40]. In order to measure the rate of the retarded reaction, the competitive reactions method has been successful to enable us to obtain a quantitative comparison for the isomerization of various *O*-allyl derivatives [10,30].

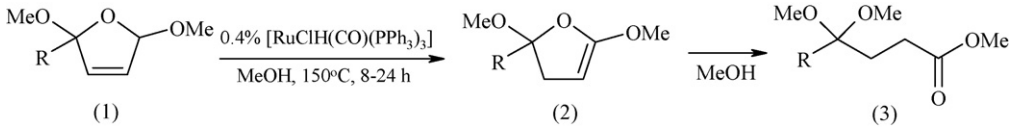
The ruthenium hydride complex $[RuClH(CO)(PPh_3)_3]$, was successfully applied in the isomerization of cyclic *O*-allyl compounds, such as pyran and 1,3-dioxepine derivatives. Suzuki et al. have investigated the isomerization of 2,5-dialkylsubstituted 2,5-dihydrofurans (Scheme 2).

Another hydride complex, $[RuH_2(PPh_3)_4]$, catalyzed the double-bond migration in dihydropyran (to conjugated 2,3-dihydropyran) derivatives as one of many steps of the total synthesis of a natural compound [41].

Double-bond migration in other partially hydrogenated cyclic acetals, such as 2-substituted 1,3-dioxepine derivatives, has been investigated by many research groups. 2-Mono- and 2,2-disubstitited 4,7-dihydro-1,3-dioxepines were isomerized to their 4,5-dihydroderivatives by $[RuH_2(PPh_3)_4]$ (1) or $[RuClH(CO)(PPh_3)_3]$ (2) (substrate/catalyst ratio 100/1 and 500/1, respectively) [42].

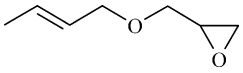
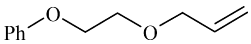
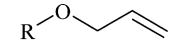
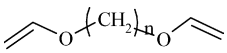
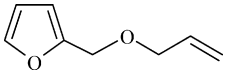
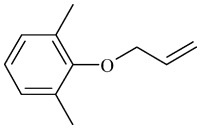
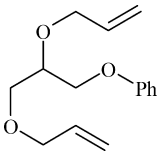
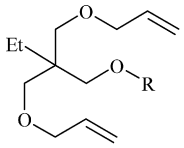
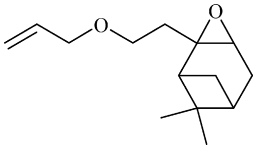
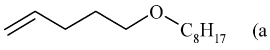
Pertici et al. have isomerized 1,3-dioxepine derivatives and alkyl allyl ethers using the non-hydride Ru(0) complex [Ru(η^4-cod)(η^6-naphthalene)] activated with acetonitrile *in situ* [43] and Table 2. The role of acetonitrile was to replace naphthalene. As a more labile ligand, acetonitrile may provide a free coordination site for the catalyzed double bond transformation. Because of the absence of a hydride ligand, the authors assign a π-allyl mechanism for this reaction (Section 3). Further, they propose coordination of ruthenium to one of the oxygen atoms, which may influence the stereoselectivity of the reaction (Section 4).

The double-bond migration in 2-alkylsubstituted 4,7-dihydro-1,3-dioxepines leads to desymmetrization of the sys-



Scheme 2.

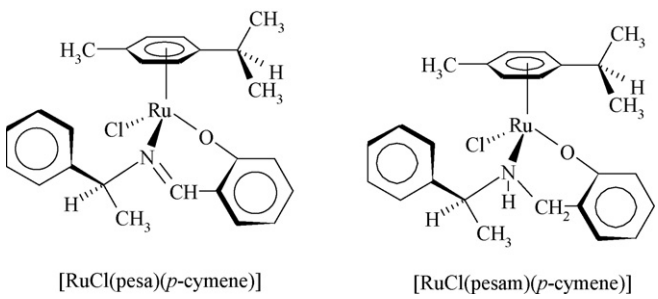
Table 1
Isomerization of allyl ethers catalyzed by $[RuCl_2(PPh_3)_3]$ described by Crivello

Substrate	%Ru	t/τ	α	E/Z	Refs.
	0.2	140/4	100	1	[27]
	0.05	100/0.6	100	<1	[22]
 R=decyl, dodecyl	0.5	120/2	100	?	[23,24]
 n=2,4,6,8,10	0.5	120/2	100	?	[23,24]
	0.5	120/2	100	*Z*	[23,24]
	0.2	130/45	95	1.5	[25]
	1	130/7	80	?	[25]
 R: Bu, Oc, Ph, -COOBu, -COONHBu	0.08	>170/1	>95	–	[26]
	0.1	120/2.5	97	0.6	[28]
 (a	0.1	200/2	>95	0.67	[29]

%Ru: catalyst molar percentage to substrate; *t*: temperature (°C); τ: reaction time (h); α: conversion of allyl to 1-propenyl ether; *E*/*Z*: the ratio of *E* and *Z*; [a]isomerization led to octyl-(1-pentenyl) ether.

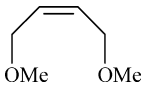
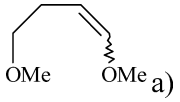
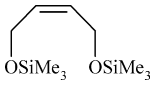
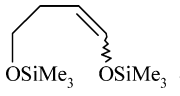
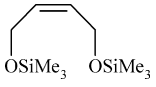
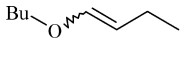
tem, thus, position 2 becomes the chiral center. Brunner et al. have attempted to control the enantioselectivity of double-bond migration in 2-butyl-4,7-dihydro-1,3-dioxepines by screening half-sandwich ruthenium complexes of general formula [RuX(XL)(*p*-cymene)] [44]. The chirality of these complexes comes from the rigid coordination of the unsymmetrical bidentate XL ligand. The pre-catalyst was activated with $Na[BH_4]$ (molar ratio: hydride/pre-catalyst = 200/1). Among the pre-catalysts screened, [RuCl(pesa)(*p*-cymene)], [RuI(pesa)(*p*-cymene)] and [RuCl(pesam)(*p*-cymene)] showed the highest activity (higher than 95%) and enantioselectivity (ee = 26–61%) (Scheme 3). The authors have not proposed the key intermediates leading to such interesting results.

Frauenrath has also investigated the isomerization of unsymmetrical 4,7-dihydro-1,3-dioxepines catalyzed by hydride ruthenium species generated *in situ* from $[RuCl_2(PPh_3)_3]$ and $NaBH_4$ [45] (50 °C, 3 h in methanol with 1/500 ruthenium to substrate molar ratio). The reactions resulted in higher yields (>87%) than in the case of base-catalyzed isomerizations (*t*-BuOK with up to 78% yields). The ruthenium catalytic system was further applied

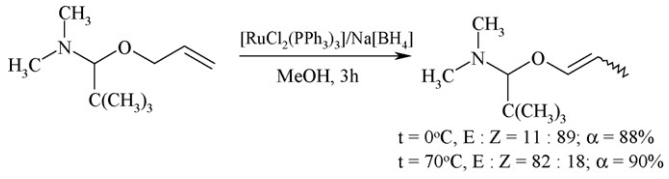


Scheme 3.

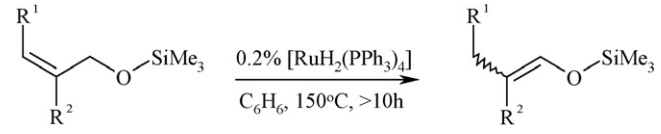
Table 2
Reactions catalyzed by [Ru(1,5-cod)(η⁶-naphthalene)] + CH_3CN [43]

Substrate	Product	Conversion
R^1 = H; R^2 = Ph		80
R^1 = R^2 = Me		90
R^1 = H; R^2 = Et		100
R^1 = H; R^2 = (*E*)-1-propenyl		30
	 a)	100
	 b)	90
	 c)	50

Reaction conditions: 1 mol% [Ru(1,5-cod)(η⁶-naphthalene)], 20 mol% CH_3CN; 2 h; t = 65 °C; THF; resulting stereoisomers: [a] E/Z = 65/35; [b] E/Z = 40/60; [c] E/Z = 90/10.



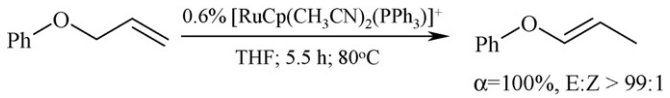
Scheme 4.



Scheme 5.

to the isomerization of *O*-allyl-*N*,*O*-acetals [46]. The isomer composition was a function of reaction temperature which was explained by consecutive *Z*–*E* isomerization, which accelerated with increase in temperature. An example is shown in Scheme 4.

Malanga et al. isomerized 2-allyloxypyrans by [$RuH_2(PPh_3)_4$] (1/100 ruthenium to substrate molar ratio, 150 °C, 4 h) leading to quantitative yields of 1-propenyl derivatives [47]. Further, they described the isomerization of allyl benzyl ether and alkyl allyl acetals (*i.e.* 1-allyloxy-1-ethoxypropane) by the same catalyst [48]. The ruthenium catalyst does not catalyze any transformations of other groups present in the organic reagents (acetal groups are sensitive to an acidic environment). [$RuH_2(PPh_3)_4$] has been used in isomerization of allyl silyl ethers [49]. The



Scheme 6.

reaction was not stereoselective, although the *Z* isomer was the majority product (Scheme 5).

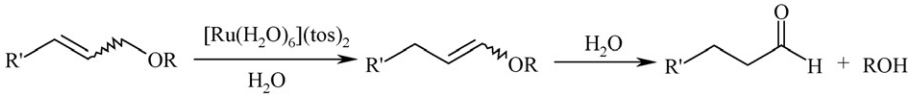
Kirchner et al. investigated non-hydride complexes [$RuCp(EPh_3)(CH_3CN)_2]PF_6$ (E = P, As, Sb) exhibiting high stereoselectivity in the isomerization of allyl phenyl ethers [50] (Scheme 6). The stereoselective aspects are described in Section 4. A disadvantage of this system is its relatively low activity, which results in low isomerization yields.

McGrath and Grubbs presented interesting results for the isomerization of allyl ethers by [$Ru(H_2O)_6](tos)_2$ in aqueous media [51,52]. The resulting enol ethers hydrolyzed under these conditions to propionaldehyde and the corresponding alcohols (Scheme 7).

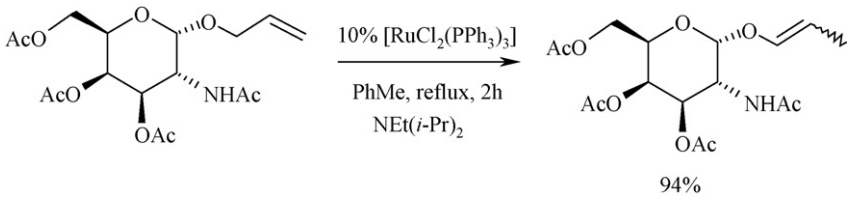
Finally, Roy et al. investigated the possibility for the metathesis of allylated sugar derivatives, for example, *O*-allyl-2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranose with allyltritylamine by first generation Grubbs catalyst [53]. However, they obtained 1-propenyl sugars instead of the desired cross-metathesis product. This result led the authors to the further investigation of double-bond migration catalyzed by carbene ruthenium complexes. They discovered catalytic activity of the carbene complexes in the double-bond migration only in the presence of amines, particularly with ethyldiisopropylamine and allyltritylamine. This system resulted in high stereoselectivity—*Z*/*E* 3–13/1. The mechanisms of amine contribution in the reaction were not explained. Further, the carbene complex was replaced by [$RuCl_2(PPh_3)_3$], resulting in higher yields of the reaction, but still with the contribution of the amines. Sugars with sensitive amide groups required a large amount of the catalyst (even 10% molar) (Scheme 8). Moreover, the authors reported inactivity of [$RuCl_2(PPh_3)_3$] in double-bond migration in the absence of the amines, which was not consistent with the work previously described by Crivello [22,23,25,26].

2.2. Tandem: double-bond migration with metathesis of O-allyl systems

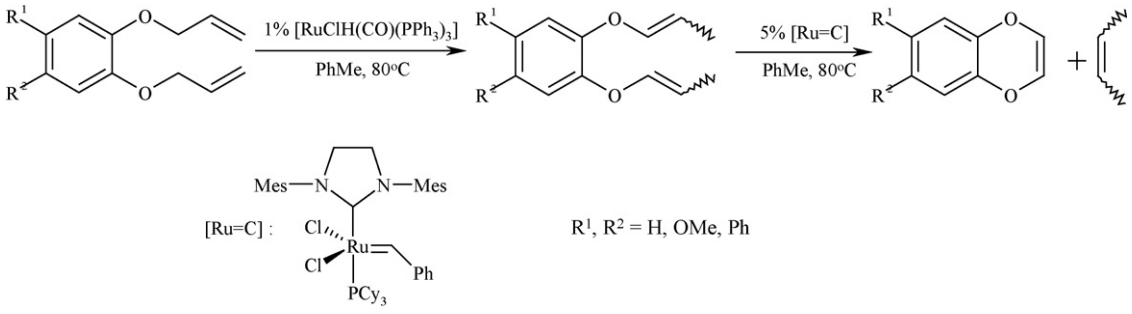
One-pot syntheses including two different reactions have many advantages, although the control of the inter-reaction species is difficult and may not only complicate the description of the whole process, but also lead to unexpected results. Thus, the tandem of double-bond migration with metathesis is puzzling with both successful applications and unclear conversion of carbene to hydride complexes. In most cases RCM (*ring closing metathesis*) has been conjugated with double-



Scheme 7.



Scheme 8.

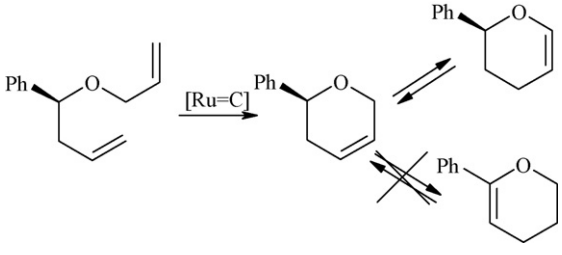


Scheme 9.

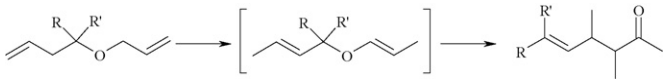
bond migration leading to heterocyclic systems. Recent literature describes both possibilities: isomerization—RCM or RCM with consecutive isomerization leading to different products. Schmidt presented metathetical cyclization to isolated, unsaturated heterocycles, which were further isomerized to conjugated derivatives [11,13]. On the other hand, double-bond migration in *O*-allyl systems to *O*-1-propenyl derivatives followed by RCM was described among others by van Otterlo [54]. In the latter work the authors subjected aromatic diallyl ethers to isomerization by [RuClH(CO)(PPh_3)$_3$]. After a quantitative conversion, without separation of the product, 1-propenyl derivatives was cycled to benzo[1,4]dioxin by second-generation Grubbs catalyst, which was not deactivated by the byproducts of the first step (Scheme 9).

Van Otterlo applied this same idea to the synthesis of heterocyclic systems containing nitrogen and even sulfur groups [14]. In the first step allyl aryl amines and ethers were isomerized by [RuClH(CO)(PPh_3)$_3$]. It is surprising in respect to our previous results [55] that during isomerization of *N*-allyl fragment (10% [RuClH(CO)(PPh_3)$_3$], toluene, 105 °C, 24 h), $-S(O)_2-CH_2-CH=CH_2$ fragment did not isomerize at all. Further, the Grubbs catalyst was used for RCM—that is why it is not a typical one-pot tandem reaction. Cossy's publication [56] is thus very intriguing in respect to the previously described research of van Otterlo. Cossy has reported the isomerization of various *O*-allyl systems solely on Grubbs second-generation catalyst, but he did not mention any metathesis products. The *O*-allyl compounds had substituents in the allyl fragment; the reaction conditions were mild (r.t., CH_2Cl_2 as a solvent, in up to 12 h). The ambiguity in catalytic pathways of the Grubbs catalyst has been observed by Rutjes et al. [57], when they were trying to obtain RCM products of benzyl 2-(3-butenyloxy)acrylate and its derivatives. Unfortunately, apart from the expected metathesis of the substrate allyl systems, they observed RCM products of the 1-propenyl compounds. Thus, during the reaction, double-bond migration of the allyl compounds occurred in parallel and was followed by RCM. The authors showed that the Grubbs catalyst was responsible for the isomerization. The complex might have undergone transformation to hydride complexes. However, the researchers were not able to suppress the competitive isomerization neither by preliminary purification of the complex, nor by the addition of tricyclohexylphosphine oxide (as others have suggested [58]). A similar problem was discussed by Snapper et al. when *O*-allyl derivatives were cycled *via* RCM and further isomerized to conjugated heterocyclic systems (see example in Scheme 10) [16].

Isomerization led only to the conjugated system of the less crowded position, most likely because of lower steric hindrance on the double-bond migration catalyst. The authors did not succeed in the separation and characterization of the real double-bond migration catalyst. They also showed that the second-generation Grubbs catalyst the freshly purified (by chromatography) does not catalyze the double-bond migration. After activation with gaseous hydrogen the previously purified catalyst did catalyze the double-bond migration. Schmidt presented a similar approach by coupling RCM with isomerization [11,13]. Allyl (3-butenyl) ethers were cycled on Grubbs catalyst. Then the carbene complex was treated with Na[BH_4] or NaH (he showed the inactivity of these simple hydrides in isomerization), in order to generate hydride ruthenium complex, which further catalyzed double-bond migration. However, he did not



Scheme 10.



Scheme 11.

notice competitive double-bond migration on the Grubbs catalyst before treatment with the hydrides. Later, Schmidt presented a better way to convert the Grubbs carbene to a double-bond migration catalyst by the addition of 2-propenol and NaOH to the reaction mixture after metathesis [11,59]. This system is a relatively efficient catalyst for double-bond migration (in the case of the investigated allyl (3-butenyl) ethers, the reaction was complete in 2 h at 100 °C). However, the author was not able to identify the real isomerization catalyst, even in such well-defined systems. He also rejected previous suspicions [60] that it might be $[RuClH(CO)(PCy_3)_2]$—the product of thermal decomposition of the carbene complex $[Ru(=CHOEt)Cl_2(PCy_3)_2]$.

Also Wagener et al. tried to eliminate competitive double-bond migration in RCM reaction of the Grubbs catalyst [12]. In their work, undesirable isomerization was inhibited by the addition of a coordinating solvent such as THF. On the other hand, raising the reaction temperature from 23 to 60 °C resulted in significant isomerization contribution (*i.e.* for allyl alcohol isomerization increases from 4 to 40%). Moreover, in some cases (*N*,*N*-di(2-allyloxyethyl)aniline) metathesis did not occur at all, while isomerization proceeded completely.

As we can see, the tandem between the double-bond migration (isomerization) and RCM might be a successful tool for synthesis of a broad range of heterocycles. On the other hand, isomerization may compete with metathesis leading to an undesirable mixture of products. Moreover, the activity of the Grubbs carbene catalyst in isomerization is still under debate and the real species must be isolated and characterized.

2.3. Other tandem reactions involving the double-bond migration of O-allyl systems

Another example of coupling two catalytic reactions is tandem: double-bond migration with Claisen rearrangement (Scheme 11).

Dixneuf et al. presented two catalytic systems active in these reactions (Scheme 12): ruthenium(II) complexes with bisoxazoline derivatives (1) [61] and compounds generated *in situ* from $\{[RuCl_2(p\text{-cymene})]_2\}$ or $[Ru_3(CO)_{12}]$ with *N*-substituted imidazolium salts (2) [62]. The authors did not describe the real catalyst. Moreover, they did not explain whether the consecutive Claisen rearrangement is catalyzed by the ruthenium complex. However, since classical Claisen reactions usually occur about 200 °C (thermal concerted reaction), a successful reaction in 120 °C may indeed result from the catalytic activity of the ruthenium complexes.

2.4. Rhodium, cobalt and other metals as catalysts of the double-bond migration in allyl ethers

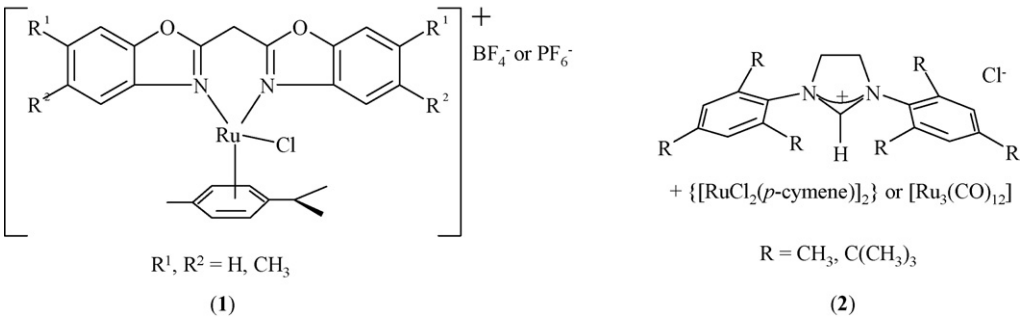
There are numerous reports of other metal complexes active in double-bond migration, but the most important studies have been described below, particularly with thorough mechanistic discussion or specific stereochemical considerations.

Many studies describe the Wilkinson complex $[RhCl(PPh_3)_3]$ as an efficient double-bond migration catalyst, particularly in the procedure of de/protection of OH groups, where the *O*-allyl derivative after other transformations is isomerized following with hydrolysis in mild conditions [63–66]. Since the Wilkinson complex undergoes a progressive deactivation (by poisoning with aldehydes formed from undesired hydrolysis of propenyl ether) and also catalyzes hydrogenation of propenyl fragment, Boons converted it to $[RhBu(PPh_3)_3]$ (by treating with BuLi), which formed $[RhH(PPh_3)_3]$ *in situ* [67].

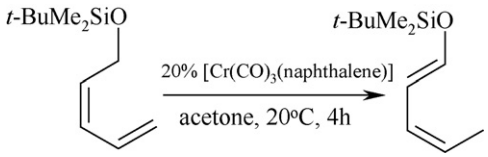
Cobalt complexes, most often $[CoH(CO)_4]$ formed by activation of $[Co_2(CO)_8]$ with molecular hydrogen or trialkylsilanes R_3SiH, were used in the isomerization of allyl ethers followed by polymerization of their 1-propenyl derivatives [68–70]. The polymerization activity has been assigned to $[Co(SiR_3)(CO)_4]$, which was also present in the reaction mixture.

The photochemical or thermal activation of $[Fe(CO)_5]$ led to an active catalyst for the double-bond migration in allyl ethers [71,72]. Crivello and others investigated the very high *Z*-stereoselectivity of the iron system and explained it by the typical π-allyl mechanism of the reaction [73–75]. The authors pointed to the relatively low price of pentacarbonyliron(0), but they did not take into account its very high toxicity and the relatively high amounts used in the catalytic reaction (molar ratio Fe/allyl system = 10–20/100, while for ruthenium catalyzed reactions the ratio is usually 10 times smaller).

Chromium(0) carbonyls have also been applied for the isomerization of diene ethers of allyl types to the conjugated systems [76]. While the activity of $[Cr(CO)_3(naphthalene)]$ was



Scheme 12.



Scheme 13.

much lower than that of the ruthenium complexes, the reaction catalyzed by the chromium complex was very stereoselective leading exclusively to the product of *Z,Z* configuration (Scheme 13).

Crivello and Rajaraman have investigated the catalytic activity of homoleptic carbonyls in the reaction of double-bond migration in allyl octyl ether [77]. The carbonyls ($[Co_2(CO)_8]$, $[Co_4(CO)_{12}]$, $[Rh_6(CO)_{16}]$, $[Fe_3(CO)_{12}]$, $[Ir_4(CO)_{12}]$, $[Ru_3(CO)_{12}]$, $[Os_3(CO)_{12}]$, $[Fe(CO)_5]$, $[Cr(CO)_6]$, $[Re_2(CO)_{10}]$, $[W(CO)_6]$, $[Mn_2(CO)_{10}]$, $[Mo(CO)_6]$ were activated thermally (at 130 °C). While only Cr, Re, W, Mn and Mo carbonyls were not active in the reaction at all, the activity of the remaining carbonyls was comparable (71–89% yield of isomerization).

As previously mentioned, Frauenrath investigated the desymmetrization of 2-alkylsubstituted 4,7-dihydro-1,3-dioxepines by ruthenium complexes, but also using nickel $[NiCl_2L_2]$ species with bidentate and often chiral ligands L_2, such as: diop, chiraphos, dppe [78,79]. The hydrogen-activated nickel complex (using gas or hydride donor $LiBHEt_3$, RMgX) with chiral ligand catalyzed the isomerization with high enantioselectivity, up to 90% ee. Also iridium complexes, such as $[Ir(1,5\text{-cod})(PMePh_2)_2]PF_6$, were activated with hydrogen and further used in isomerization in the procedure of de/protection of OH groups [80,81]. The role of hydrogen was assigned to partial hydrogenation of 1,5-cod, which led to the relinquishment of the coordination site. The advantage of iridium complexes over the Wilkinson catalyst is that they do not catalyze competitive hydrogenation of the propenyl unsaturated fragment. Moreover, there are some reports of their high stereoselectivity in isomerization to 1-propenyl ethers (in most cases $E/Z > 30$) [82,83].

Despite the broad application of palladium complexes in homogeneous catalysis [84], there are relatively few reports on their activity in the double-bond migration. Kirmse used $[PdCl_2(PhCN)_2]$ for the isomerization of allyl (2-formylphenyl) ether derivatives [85], while Bauld applied plain $PdCl_2$ for the isomerization of allyl (4-methoxyphenyl) ether carrying out the reaction for 10 days at room temperature [86]. Golborn and Scheinmann compared the catalytic activity of various transition metal complexes for double-bond migration in $ArOCR^1HCR^2=CR^3R^4$. They found that $[CoCl_2(PPh_3)_3]$, $[Mn_2(CO)_{10}]$, $[NiBr_2(PR_3)_2]$ and $RhCl_3$ were not active at all, while among $\{[RhCl(1,5\text{-cod})]_2\}$, $[RhCl(PPh_3)_3]$, $[RhH(CO)(PPh_3)_3]$, $[RuCl_2(PPh_3)_3]$ and $[PdCl_2(PhCN)_2]$ only ruthenium and palladium complexes isomerized allyl (2,6-dimethylphenyl) ether quantitatively. The rhodium complexes were less active and led up to 50% conversion of allyl to 1-propenyl derivative (reaction in refluxing benzene for 35 h). Hydride platinum(II) complexes described by Clark and Kurosawa, for example, *trans*-$[PtH(PPh_3)_2]ClO_4$, also catalyze double-bond migration in allyl aryl and allyl alkyl ethers [87]. The authors discussed thoroughly the reaction mechanism [88] and they also found an undesired side-reaction leading to $[Pt(\eta^3\text{-allyl})](PPh_3)_2]ClO_4$ complex (catalytically inactive) formed from the hydride precursor and allyl ether.

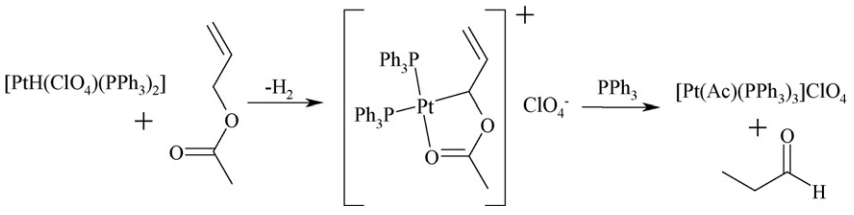
2.5. The double-bond migration in allyl carboxylates

The isomerization of allyl carboxylates to their 1-propenyl derivatives is a very difficult challenge, because the esters are very prone to competitive reactions. The oxidative addition of ester C(O)–O bond is the most frequent side reaction which leads to a permanent coordination of the decomposed ester or its fragment resulting in deactivation of the catalyst.

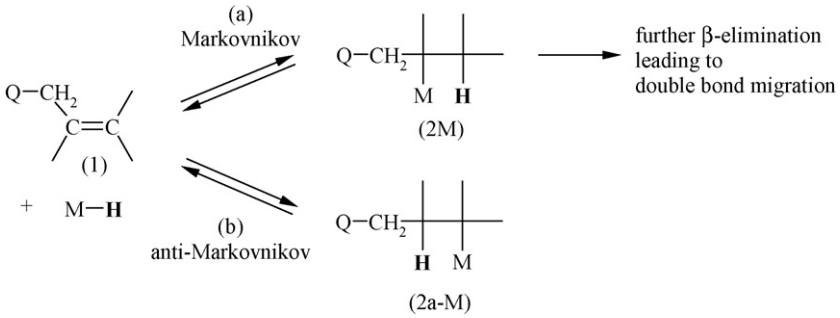
Tatsumi et al. have isolated the products formed during attempts to isomerize allyl acetate with *trans*-$[Mo(N_2)_2(dppe)_2]$ [89]. The major isolated product, $[Mo(CH_3COO)(dppe)(ortho\text{-}C_6H_4PhPCH_2CH_3PPh_2)]$, was formed by above mentioned C(O)–O bond cleavage, coordination of acetate, and propene release from allyl fragment and hydrogen coming from the *ortho*-metalation of the dppe aryl ring.

Clark and Kurosawa isolated and characterized the platinum complex formed in attempts to isomerize allyl acetate by $[PtH(PPh_3)_2]ClO_4$ [87]. The stoichiometric reaction led to an oxidative addition of the allyl fragment to $H–C^1$ bond, and hydrogen release (Scheme 14). While heated, the complex produced acetaldehyde and rearranged to the acyl platinum derivative.

One of the very few studies presenting a successful double-bond migration in the allyl fragment of allyl carboxylate was reported by Iranpoor [90]. He isomerized allyl 2-norbornanecarboxylate derivative and allyl acetate using photochemically activated $[Fe(CO)_5]$. Although Iranpoor reported 60 and 75% conversion, respectively, the catalyst concentrations were very high (80 and 50 mol%, respectively). Unfortunately, the author did not explain such high catalyst concentration or any



Scheme 14.



Scheme 15.

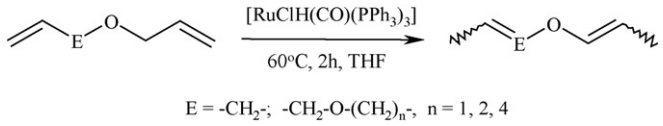
catalyst transformations. We have reported the isomerization of allyl acetate and allyl butanoate (both up to 45% conversion), allyl methyl carbonate and allyl benzoate (both 80%) with [RuClH(CO)(PPh_3)$_3$] [40,91]. We also isolated the catalyst side-reaction product: [RuCl(η^2-*O*,*O*-AcO)(CO)(PPh_3)$_2$], but the complex was previously described by Sanchez-Delgado as a product of acetic acid reaction with [RuClH(CO)(PPh_3)$_3$] [92].

3. The mechanism of the double-bond migration in *O*-allyl systems

Double-bond migration mechanisms have been described for various alkene systems and have become classics and textbooks [84,93–95]. *O*-Allyl systems undergo isomerization following the alkene mechanisms, however, some specific considerations characteristic for these systems have been observed:

In the hydride mechanism a 1,2-insertion step (or addition of M-H to C=C double bond) begins the catalytic cycle. Since, the organic reagent is usually not symmetric, there are two possible insertion orientations: (a) the productive Markovnikov addition and (b) the non-productive anti-Markovnikov addition (Scheme 15).

The orientation of addition is a function of the steric hindrance of the coordination sphere with the functional group Q [40], the character of the metal hydride, which consecutively determine the M-C bonding character [52]. The ratio (b)/(a) was investigated on deuterated *C*-allyl systems and was assigned for Rh complexes as 1:15 [96]. Then for [$CoH(CO)_4$] – strong Brønsted acid – the ratio was estimated at 2:1 [97,98]. However, *O*-propenyl system behavior in this step may differ from these of plain olefins. The oxygen atom in *O*-propenyl compounds introduces the possibility of transition coordination with metal, leading to some pre-orientation of the organic fragment before



E = -CH_2-; -CH_2-O-$(CH_2)_n$-, n = 1, 2, 4

Scheme 16.

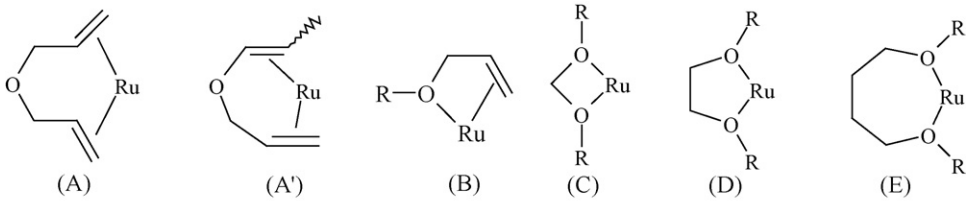
the insertion. On the other hand the withdrawing character of the oxygen atom may change the stability of appropriate products (2M and 2a-M) and thus favor one of the insertion orientation (a) or (b). For example, Clark and Kurosawa found insertion proportion (b)/(a) as 1/2 [88] in isomerization of allyl ethers. Our research on [Ru]-H species catalyzing isomerization of allyl ethers lead to the conclusion that the majority of 1,2-insertions are non-productive anti-Markovnikov processes [35,91].

The possibility of coordination *via* oxygen atom may change the rate-determining step. We have compared the rate of isomerization of diallyl ethers by a typical hydride mechanistic catalyst—[RuClH(CO)(PPh_3)$_3$] [35] (Scheme 16).

Based on our observations – the longer the chain (therefore the longer the *E* fragment in the Scheme 16), the slower the reaction – we suspect that the rate determining step is a result of the stability of one or several transition chelate complexes proposed in Scheme 17.

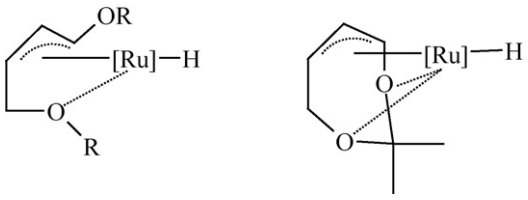
While in the short-chained ethers the only possibility is the chelation *via* C=C double bond (structures A and A′), which turns out to be less stable, in the long-chained ethers there are many possible chelate structures including the interactions of both oxygen lone pair and C=C double bond (B–E) of apparent higher stability. The latter slows the net reaction.

A π-allyl mechanism with characteristic relatively high *Z*/*E* [99] might be more desirable for stereoselective synthesis of *Z*-products. Pertici et al. postulated the simultaneous coordination of oxygen ether atoms at the stage of hydride-π-allyl complex formation in the isomerization of *O*-allyl systems [43]

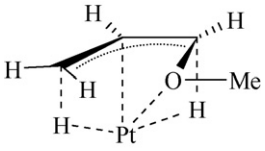


R = allyl or 1-propenyl

Scheme 17.



Scheme 18.



Scheme 19.

(Scheme 18). On the basis of such a co-ordination, the authors explained the high stereoselectivity of the reaction.

4. Aspects of stereoselectivity

Since most of the double-bond migration products are mixtures of *E* and *Z* isomers, achieving stereoselective results is a challenge. Moreover, it is a key parameter for further application of the double-bond migration reactions in organic synthesis, and thus, a lot of research has been oriented to stereoselective reactions. The oxygen atom in *O*-allyl systems has introduced a new possibility of coordination, which has been assigned to one of crucial factors for the stereoselectivity.

Clark and Kurosawa observed the high stereoselectivity ($Z/E > 4$) of allyl methyl ether isomerization by $[PtH(PPh_3)_2]ClO_4$ [88]. Since a high *Z*/*E* ratio is usually associated with π-allyl mechanism, the authors provide one of the very few examples of *Z*-stereoselectivity based on the hydride mechanism accompanied with its explanation. They claim that simultaneous coordination of the hydride complex and oxygen atom in the transition state is responsible for forming *Z* isomer in the majority (Scheme 19).

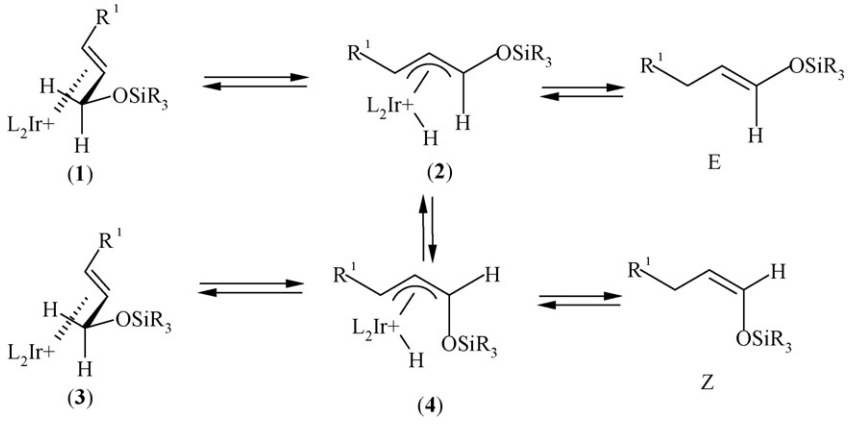
Cationic iridium complexes activated with hydrogen, *e.g.* $[Ir(cod)(PPh_2Me)_2]PF_6$ [80] and $[Ir(cod)_2]PF_6/PR_3$ [100], catalyze double-bond migration in *O*-allyl systems with high *E*-stereoselectivity. π-Allyl mechanism has been assigned for this reaction. The authors suggest that the hydride-π-allyl complex formation step has a key role for stereoselectivity (Scheme 20).

Because of steric reasons, hydride-π-allyl complex of *syn* configuration ((**2**) in Scheme 21) forms faster. *syn* complex, which has hydrogen atoms in *endo* position, leads to the observed *E*-product formation. Moreover, in the presence of bulky R^1 substituents it does not occur at all, which was explained by high steric hindrance disabling the formation of π-allyl complex. Miyaura pointed out the influence of substituents in allyl fragment on reactivity and stereoselectivity of allyl silyl ether derivatives [83]. He also achieved high *E*-stereoselectivity in the isomerization of unsubstituted allyl silyl ethers in acetone. However, apart from lower reactivity of the substituted ether (in allyl fragment), the stereoselectivity in that case was also lower. The observation was explained by comparable rates of *anti* (**4**) and *syn* (**2**) π-allyl complexes formation.

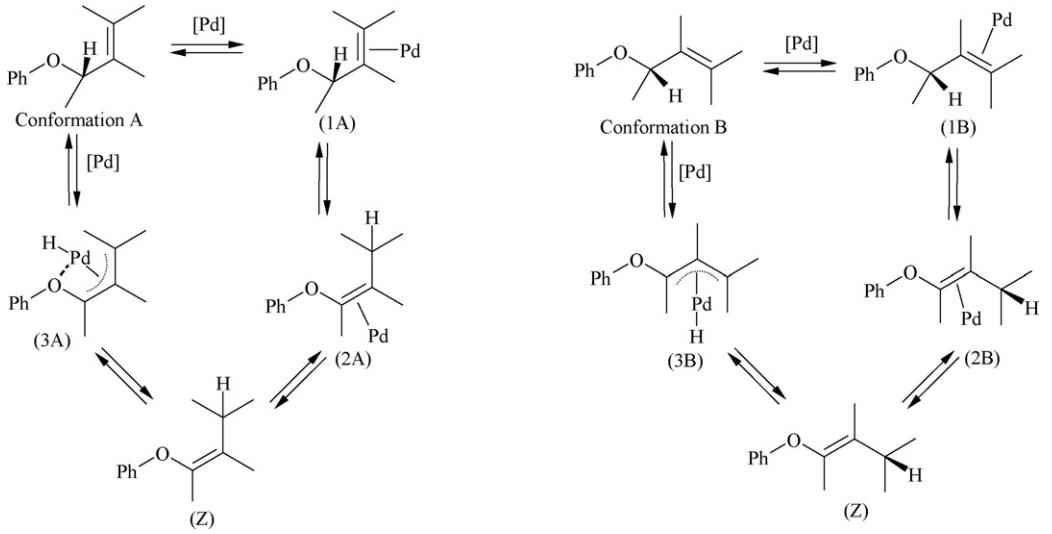
Golborn investigated the isomerization of allyl aryl ethers by $[PdCl_2(PhCN)_2]$ [101]. In the case of unsubstituted (in allyl fragment) allyl ether the isomerized *Z*-1-propenyl derivatives formed with some excess. 1,3-hydrogen shift mechanism has been assigned for this reaction with both possibilities: the formation of hydride-π-allyl transient complex or suprafacial hydrogen shift on the opposite space in respect to metal. In contrast to the previous researcher, Golborn suspects that stereoselectivity depends on the orientation of allyl moiety in relation to metal, and thus, he claims the key step of stereoselectivity is the formation of π-allyl complex A or B (Scheme 21).

The *Z*-stereoselectivity is explained by the more facile coordination of A over B conformation. Moreover, the resulting 3A complex is additionally stabilized by the interaction between an oxygen atom (from ether) and palladium. Such a stabilization is not possible in the 3B complex. Thus, pathway A is favored, leading to an excess of the *Z* product.

Catalytic system forming *in situ* from a non-hydride precursor, such as $\{[RuCl_2L_n]_x\}$ (L = 1,5-cod, nbd, benzene) with a bulky phosphine (tris(2,4,6-trimethoxyphenyl)phosphine), has been applied to isomerization of allyl aryl and allyl silyl ethers [31,35,40]. The system was particularly successful in the case of branched aryls or silyl groups, such as 2-Br–C_6H_4–, 2-MeO–C_6H_4– and *t*-$BuMe_2Si$–. In comparison



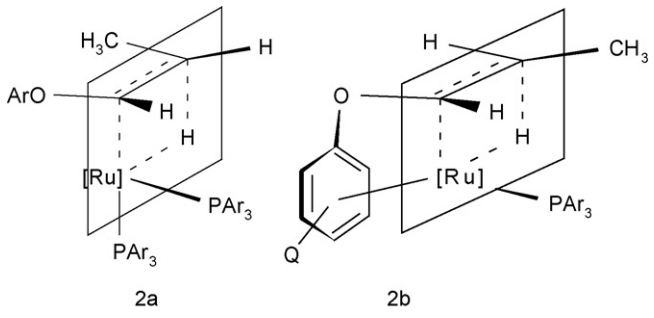
Scheme 20.



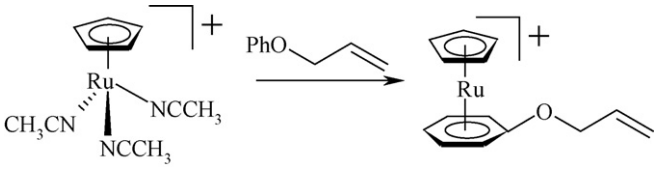
Scheme 21.

to [RuClH(CO)(PPh_3)$_3$] isomerization, *E*-stereoselectivity of *t*-$BuMe_2Si$–O–allyl ether by {[$RuCl_2$(1,5-cod)]$_x$} with P(2,4,6-$MeOC_6H_2$)$_3$ and Li[AlH_4] (in the molar ration of 1:1:5) increased from 0.34 to 7.3 (*E*/*Z*). Adding triphenylphosphine instead of trimethoxy derivatives led to the *E*-stereoselectivity of 1.1 (*E*/*Z*). Moreover, the isomerization of allyl 2-bromophenyl ether by {[$RuCl_2$(1,5-cod)]$_x$} with P(2,4,6-$MeOC_6H_2$)$_3$ (in the molar ration of 1:1) led to *E* isomer almost exclusively (*E*/*Z* = 20). While plain [$RuCl_2$(COD)]$_x$ does not isomerize allyl ethers, the external addition of phosphine not only enables its application as a double-bond migration catalyst, but also completely changes the isomeric product composition—the ratio of *E*/*Z* is reversed. While *Z* isomer, as more stable [10], is dominant for regular catalysis with [RuClH(CO)(PPh_3)$_3$], *E* isomer is superior here. Controlling the bulkiness of externally added phosphines to the precursor [$RuCl_2$(COD)]$_x$ influences the number of phosphines, which are coordinated in the transition state of β-elimination. Such a superposition of relative electronic and steric properties [102] together with the possibility of the coordination of aryl ring, might be a quantified response, which of the transient structures (2a or 2b) is dominant in β-elimination (Scheme 22).

High stereoselectivity was achieved in the isomerization of allyl phenyl and allyl benzyl ethers catalyzed by a series of cyclopentadienyl ruthenium complexes: [$RuCp(EPh_3)_n$



Scheme 22.



Scheme 23.

$(CH_3CN)_{3-n}]^+$, where E = P, As, Sb [50]. *E* isomers of enol ethers were actually the only products of isomerization (*E*:*Z* > 99:1). Although the authors do not propose any explanation of the results, however, they do identify the complex present in the reaction mixture and formed in the reaction of allyl phenyl ether and the catalyst (Scheme 23).

The *E*-stereoselectivity in $[RuCp(EPh_3)_n(CH_3CN)_{3-n}]^+$ is constant even with prolongation of reaction time from 5.5 to 24 h and with four-fold increase of catalyst amount. This suggests very strong coordination effects, decide the stereoselectivity.

5. Conclusion

There are versatile transition metal complexes for catalyzing double-bond migration in *O*-allyl systems. Their activity is comparable with strong bases (*t*-BuOK), thus, the reactions catalyzed by these complexes have been applied successfully mostly in synthetic chemistry. Their specificity in isomerization and additional activity in other reactions (reduction, polymerization) have been used for OH group protection, and double-bond migration coupled with polymerization. Recently, the double-bond migration catalysts have been applied in tandem reaction with a ring-closing metathesis. The isomerization may be alternatively forced before or after the RCM. Although the metathesis complexes might be easily converted to the double-bond migration catalysts, it is still unclear what is the real active catalyst of the latter reaction. Finally, transition metal catalysts for the double-bond migration are potentially very stereoselective, which results from the possibility of many steric and coordination interactions. However, the aspects of stereoselectivity are

not universal and most often are specific for a given *O*-allyl system with a specific geometry of the active complex.

Acknowledgements

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