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The role of the functional group in double bond migration in allylic systems catalysed by ruthenium hydride complexes

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Abstract

The influence of functional group Q on course and rate of the reaction of 3-B, 3-C, 3-Si, 3-Sn, 3-N, 3-P, 3-O, 3-S, 3-Se, 3-Cl, 3-Br, and 3-I substituted allylic systems of type Q–$CH_2CH{=}CH_2$ with hydride ruthenium complexes (primarily [$RuClH(CO)(PPh_3)_3$]) has been researched. It has been proved that the basic factors for the reaction course are: coordinating properties of Q group, C–Q bond strength, tendency of Q-allyl to oxidative addition to [Ru], and steric effect of Q. When Q has weak (Q = alkyl, aryl, RO, ArO, ...) or medium (Q = Ph_3CS, RC(O)NR, ...) complexing power, migration of the double bond in Q-allyl occurs. Most often, mixtures of (*E*)- and (*Z*)-1-(propenyl) derivatives are the isomerisation products. Sometimes, mainly or solely products with *E* configuration (e.g. Q = ArNCOMe, $PhSO_2$) have been formed, and in other cases—mainly or solely products with *Z* configuration (e.g. Q = Ph_3CS, Ph_3CO, MeCONH). Basing on mechanistic investigations and quantum calculations, it has been shown that *E*-selectivity of double bond migration results mainly from specific coordination effects, but also from steric effects (of Q and ligands). On the other hand, *Z*-selectivity of isomerisation results from steric effects. It has been also proved that when Q has strong complexing power (Q = EtS, PhS, PhS(O), Me_2N, PhCH=N, $allyl_2P$, ...), the double bond migration is not observed at all. Catalytically inert ruthenium complexes are then formed in the reaction mixture. Some of them have been isolated and their structures have been defined. The bond migration has not been observed also when allylic system has been undergoing an oxidative addition to [Ru] (e.g. Q = Cl, Br, I). A similar influence of Q on reactions between Q-allyl and [Ru]–H groups has also been observed in reactions of Q-allyl with [$RuH_2(CO)(PPh_3)_3$] and hydride complexes generated in situ (e.g. [$RuCl_2(PPh_3)_3$] + Li[AlH_4], {[$RuCl_2$(1,5-COD)]$_x$} + CaH_2). Solvent effects in isomerisation reactions of allyl phenyl ether and allylbenzene or safrole have been researched as well. A very good, quantitative consistence of solvent effect (its complexing power) on the isomerisation with the observed effect of Q group has been shown. The requirements for Q–$CH_2CH{=}CH_2$, enabling its isomerisation to Q–$CH{=}CHCH_3$, have been defined.

Keywords: Allylic compounds; Isomerisation; Ruthenium complexes; Double bond migration; Vinyl compounds

1. Introduction

Functional group Q, present in allylic system molecules of type Q–$CHR^1C(R^2){=}CR^3R^4$ (R^1–R^4 = H, alkyl, aryl, ...), often has an essential influence on their reactivity in reactions catalysed by metal complexes. It mainly results from possibility of complexing the metal atom by this group (or, what is particularly important, by the double bond and functional group simultaneously), and from its steric effect on the reaction centre. An essential influence of functional group on selectivity has been observed, e.g. in hydrogenation of allyl and homoallyl alcohols, catalysed by iridium [1,2] or rhodium [3,4] complexes, and particularly in epoxidation of allyl alcohols [5,6]. Directional effect of an oxygen-containing functional group has been also observed in hydrogenation reactions of unsaturated: esters [2,7], ethers [2] and ketones [7], catalysed by complexes of various transition metals. Decisive influence of the functional group has been also ascertained in metathesis reactions [8–10] and silylative coupling [11] of substituted alkenes, and in redox-isomerisation of ynols to enals or enones [12] catalysed by [$RuCl(Indenyl)(PPh_3)_2$]. Similarly strong Q effect has been observed in Grubbs' carbene mediated chemoselective deprotection of allyl amines [13].

As for reaction of double bond migration in allylic systems of Q–$CHR^1C(R^2){=}CR^3R^4$ type, it is known that functional group Q has a strong influence on the allylic system—1-propenyl sys-

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tem equilibrium, and on *E–Z* equilibrium [14–16]. An influence of Q on rate of double bond migration in reactions with transition metal complexes was often observed, but it was rarely analysed. For instance, in isomerisation reactions of prochiral allylamines ($Q = NR^1R^2$) to corresponding enamines, catalysed by chiral rhodium complexes [17,18], a strong influence of Q (also of R^1 and R^2 in NR^1R^2 group) on yield and enantioselectivity of the reactions was ascertained. Also the rate of the double bond migration in *N*-allylimines ($Q = p$-Y–$C_6H_4CH{=}N$, Y = H, Cl, O_2N), catalysed by $[RhCl(PPh_3)_3]$, strongly depended on electron acceptor character of Y (the rate was decreasing with increase in the electron acceptor character) [19]. However, the authors did not comment on the dependence. A strong influence of allylic system structure on yield and selectivity was observed also in the case of ruthenium catalysed tandem RCM-double bond isomerisation of allyl-homoallyl ethers to dioxane derivatives [20].

Problem of influence of functional group Q on course and rate of reactions between allylic systems and ruthenium complexes is poorly discussed and rarely analysed. One may notice a strong Q influence while comparing isomerisation of alcohols (particularly primary ones) with isomerisation of allyl ethers [21–25]. In the case of the first group, oxidative addition of the alcohol to metal complex, followed by decarbonylation of the isomerisation product (aldehyde or ketone), leads sometimes to formation of various by-products [21]. On the other hand, isomerisation of allyl ethers (hydroxyl group is protected), catalysed by complexes of various transition metals, most often proceeds with quantitative yields [21]. Particularly Trost and Kulawiec (isomerisation of allyl alcohols in the presence of $[RuClCp(PPh_3)_2]$) [26], and McGrath and Grubbs (isomerisation of allyl ethers catalysed by $[Ru(H_2O)_6]^{2+}$) [27], were noting a decisive influence of Q group on the course of these reactions. Earlier, it was known that the rate of allylbenzene isomerisation (Q = Ph) catalysed by $[RuCl_2(PPh_3)_3]$ is higher than in the case of *p*-methoxyallylbenzene ($Q = p$-$MeOC_6H_4$) at 160 °C, but practically equal at 215 °C [28]. A similar effect was observed in isomerisation reactions of p-Y–$C_6H_4CH_2CH{=}CHCH_2Ph$ ($Q = p$-Y–C_6H_4; Y = Cl, Me, MeO, CN), catalysed also by $[RuCl_2(PPh_3)_3]$ [28]. At lower temperatures, the derivative with $Q = p$-NC–C_6H_4 was undergoing isomerisation particularly slowly. Probably stable complexes with low lability formed, in which the ruthenium atom was strongly coordinated by CN group. However, raising the reaction temperature caused dissociation of these complexes, and the derivative with *p*-CN group isomerised under such conditions with the same rate, as other aforementioned 1-aryl-4-phenyl-2-butenes [29].

A strong (but not explained) Q group effect was observed in isomerisation reactions of 2-methylallylic systems to 2-methyl-1-propenyl derivatives [30]. *N*-(2-methylallyl)ethanamide (Q = NHAc) easily isomerised in the presence of $[RuClH(CO)(PPh_3)_3]$ while *N*-(2-methylallyl)phtalimide (Q = *N*-phthaloimidolyl) was completely inert under the same conditions [30]. An unusual (but not explained) Q effect was also observed in isomerisation reactions of *N*,*N*-diallylic ureas $Me_2NCON(CH_2CH{=}CH_2)(CHR^1CHR^2{=}CHR^3)$ type (R^1, R^2, R^3 = H or alkyl) catalysed by $[Fe_2(CO)_9]$ [31]. The reaction was highly *E*-stereoselective, and replacing of Me_2N group with Et_2N group caused a complete lack of isomerisation. In our earlier studies, we also ascertained a very strong influence of functional group Q on the course of reactions between allylic systems and $[Ru(acac)_3]$ [32,33]. When the group had high complexing power (Q = EtS, PhS(O), Me_2N, ...), bond migration did not occur at all. ($[Ru(acac)_3]$) catalyst underwent then a quick transformation into catalytically inert Ru(II) complexes of $[Ru(acac)_2L_2]$ type, where L = Q-allyl containing a Q group of high complexing power.

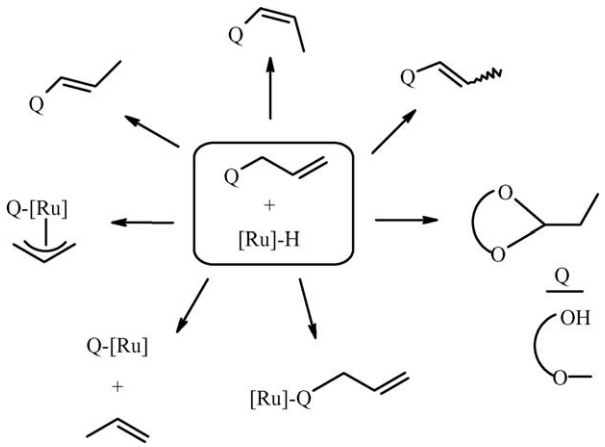
There is also a lack of literature reports concerning isomerisation of allylic systems containing nitrogen, sulphur of phosphorus atoms of high complexing power, catalysed by ruthenium complexes (except for our works). This fact suggests that it is coordination of metal atom by Q that prevents the double bond migration. Non-labile complexes are then formed in the reaction mixture, with transition metal atom coordinated by Q.

This paper describes the influence of functional group Q on course and rate of reaction of Q-allyl with Ru(II) complexes—mainly $[RuClH(CO)(PPh_3)_3]$. We were interested in identifying the Q groups (more than 200 allylic systems had been researched) and conditions (temperature, solvent, ...) enabling Q-allyl isomerisation to Q-(1-propenyl), and also the Q groups (and conditions) enabling transformations other than double bond migration, together with causes of all these effects. We carried out the analysis, basing mainly on the results published earlier [21,34–50].

2. Results and discussion

Investigating reactions of allylic systems of $Q–CH_2CH{=}CH_2$ type with hydride ruthenium complexes (mainly $[RuClH(CO)(PPh_3)_3]$), we observed that the reactions may proceed in various ways—as it is shown in Scheme 1. The scheme presents only the reactions (catalytic or stoichiometric, irreversible) with final products that have been isolated and characterized. Reactions of formation of π-alkene, σ-carbyl, and other complexes (in spite of the fact they have been formed undoubtedly), which have not been isolated or spectroscopically identified, are omitted.

Results of investigations carried out by us using more than 200 model systems show unequivocally that functional group Q, present in Q-allyl, exerts a significant influence on course and rate of reaction between Q-allyl and ruthenium complex. The effect of the functional group consists in, first of all, its donor–acceptor (electron factors) and steric properties, influencing the course and rate of the reaction between Q-allyl and ruthenium complex. The following considerations concern essentially the reactions catalysed by $[RuClH(CO)(PPh_3)_3]$. Activity of other hydride Ru(II) complexes (or compounds easily transforming into hydride complexes under conditions of the process), such as $[RuCl_2(PPh_3)_3]$, $[RuClH(PPh_3)_3]$, $[RuH_2(CO)(PPh_3)_3]$, $[RuH_2(PPh_3)_4]$, $\{[RuCl_2(1,5\text{-}COD)]_x\}$, has been investigated in reference to some allylic systems. However, significant departures from the dependences between structure and reactivity, found for $[RuClH(CO)(PPh_3)_3]$, have never been observed.



Scheme 1. Observed reaction paths of allylic compounds with ruthenium hydride complexes (particularly with $[RuClH(CO)(PPh_3)_3]$). Q = 3,3,5,5-tetramethyl-2,5-dioxoborolanyl, alkyl (R), cyclohexyl, vinyl, allyl, $PhCH_2$, aryl (Ar), PhC≡C, H(O)C, Me(O)C, N≡C, HOOC, MeOOC, $(EtOOC)_2CH$, Me_3Si, Ph_3Si, $(EtO)_3Si$, $Me_2(ClCH_2)Si$, $Me_2N(CHMe_2)Si$, Cl_3Si, $ClMe_2Si$, Ph_3Sn, Me_2N, $allyl_2N$, PhNMe, $(Me_3Si)_2N$, $(Me_3Si)allylN$, $R^1C(O)N(R^2)$, RC(O)NAr, *N*-phthaloimidolyl, *N*-carbazolyl, *N*-imidazolyl, PhCH=N, O=C=N, S=C=N, *p*-Me–$C_6H_4SO_2NPh$, Et_3N^+ (Cl^- or Br^-), $allyl_2P$, Ph_2P, $Ph_2P(O)$, Ph_3P^+ (Cl^- or Br^-), HO, RO, $PhCH_2O$, ArO, allylO, $(EtO)_3SiO$, Ph_3SiO, $PhC(Me_2)OO$, RCOO, ArCOO, $(allylO)_2BO$, $(allylO)_3SiO$, $(allylO)_2HCO$, $allylO(CH_2)_nO$, $(allylO)_2PhCO$, $(allylO)_2PO$, RS, allylS, PhS, PhS(O), $Me_3CS(O)$, $PhS(O_2)$, PhSe, Cl, Br, I. [Ru]–H = $[RuClH(CO)(PPh_3)_3]$, $[RuH_2(CO)(PPh_3)_3]$, $[RuClH(PPh_3)_3]$, $[RuH_2(PPh_3)_4]$, $[RuCl_2(PPh_3)_3] + Na[BH_4]$ or $Li[AlH_4]$, $\{[RuCl_2(1,5\text{-}COD)]_x\} + CaH_2$, $\{[RuCl_2(1,5\text{-}COD)]_x\} + CaH_2$ (or $Li[AlH_4]$) + PR_3 and others.

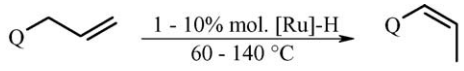
Below we discuss the individual observed paths of reaction between Q-allyl and [Ru]–H.

2.1. Z-stereoselective double bond migration

A highly *Z*-stereoselective double bond migration was observed for some ethers (allyl-trityl, allyl-(2,4,6-tribromophenyl), allyl-(*t*-butyl), allyl-*o*-formylphenyl), allyl sulphides (allyl-trityl, allyl-*t*-butyl, allyl-*i*-propyl), allyl *t*-butyl sulphoxide, allyldiphenylphosphine oxide as well as *N*-allylamides of $R^1CONR^2CH_2CHCH_2$ type ($R^1 = H_2N$, $R^2 = H$; $R^1 = CH_3$, $R^2 = H$; $R^1 = CH_3$, $R^2 = Bu$; $R^1 = CH_3$, $R^2 = H$; $R^1 = Ph$, $R^2 = H$)—Scheme 2 and Table 1. In the case of the ethers, sulphoxide, silane and sulphides, the catalyst was $[RuClH(CO)(PPh_3)_3]$ [42,45,48,49], while *N*-allylamides were isomerised in the presence of a catalytic system generated in situ from a precursor, i.e. $\{[RuCl_2(1,5\text{-}COD)]_x\}$, 2,4-di-*t*-butylphenyl phosphite and calcium hydride [45,46].

We proved that all *Z*-stereoselective double bond migrations occurred according to the hydride mechanism [21,42,45,46,48–50]. It is noteworthy that *Z*-stereoselective double bond migrations in allylic systems catalysed by transition metals complexes are rare. Only Sworen et al. observed 98% *Z*-stereoselectivity in isomerisation of *N*,*N*′-bis[3-(allyloxy)-2-hydroxypropyl]aniline and its acetylated derivative, catalysed by Grubbs' second generation ruthenium-imidazolium carbene complex [10]. Also Wang and Dobson described a reaction of 1-allyl-2-diphenylphosphinobenzene with $[W(CO)_4(NBD)]$, leading to (*Z*)-1-(1-propenyl)-2-diphenylphosphinobenzene [51] coordinated with $[W(CO)_4]$ (through phosphorus atom and a double bond). *Z*-configuration of the alkene (ligand) was forced here simultaneously by coordination and steric effects. A spontaneous *Z*-stereoselective double bond migration was also observed in complexes of [Rh(acac)(CO)L], [RhCl(COD)L], and $[RhCl(CO)L_2]$ types, obtained in reactions of, correspondingly $[Rh(acac)(CO)_2]$, $\{[RhCl(COD)]_2\}$, and $\{[RhCl(CO)_2]_2\}$ with L = allyldiphenylphosphine [52]. The reaction occurred in a solution, and the coordinated allyldiphenylphosphine isomerised slowly to coordinated (*Z*)-(1-propenyl)diphenylphosphine. It was interesting that the double bond did not participate in the coordination—it occurred only through the phosphorus atom [51].

Besides, many *Z*-stereoselective double bond migrations in O- [53–55], N- [56–58], and S- [59] allylic systems were of course described in literature, but they were catalysed by bases. In our opinion, *Z*-stereoselectivity of the reactions investigated by us results from steric effects (Q = Ph_3CO, Me_3CO, Ph_3CSi,



[Ru]-H = $[RuClH(CO)(PPh_3)_3]$ - (A),[42,45,48,49] or $\{[RuCl_2(1,5\text{-}COD)]_x\}$ + 2,4-di-*t*-butylphenyl phosphite + CaH_2 (1 : 1 : 10) - (B)[45,46]

Scheme 2. *Z*-stereoselective isomerisation of Q-allyl catalysed by ruthenium hydride complexes. [Ru]–H = $[RuClH(CO)(PPh_3)_3]$—A [42,45,48,49], or $\{[RuCl_2(1,5\text{-}COD)]_x\}$ + 2,4-di-*t*-butylphenyl phosphite + CaH_2 (1:1:10)—B [45,46].

Table 1
Z-stereoselective isomerisation of Q-allyl catalysed by ruthenium hydride complexes

Q ([Ru]–H: A or B)	ε (%)	*E*:*Z*	Reference	Q	ε (%)	*E*:*Z*	Reference
RCONH– R = Me, Ph, H_2N (B)	100	0:100	[45,46]	Ph_3CS–	99.6	5:95	[42]
MeCON(Bu)– (B)	100	0:100	[45,46]	Me_3CS–	99.7	4:96	[42,50]
RO– R = Ph_3C, 2,4,6-$Br_3C_6H_2$, Me_3C (A)	100	0:100	[48,49]	*i*-PrS–	70	0:100	[42,50]
o-$OHCC_6H_4O$– (A)	70	0:100	[44]	$Me_3CS(O)$–	96	10:90	[42,50]
Ph_3Si– (A)	96	10:90	[21]				

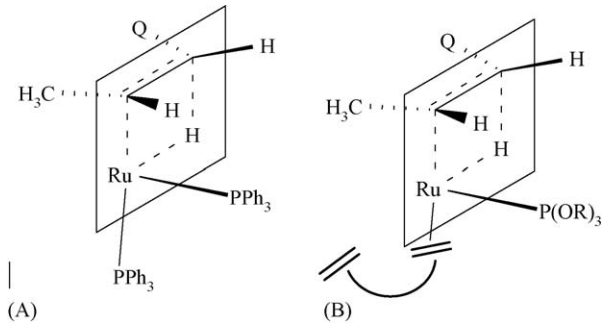
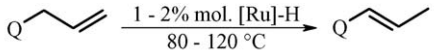


Fig. 1. Proposed structure of β-elimination in the *Z*-stereoselective double bond migration. Such ligands as CO, Cl and solvent, were omitted. A—catalyst: $[RuClH(CO)(PPh_3)_3]$; B—catalyst: $\{[RuCl_2(1,5\text{-}COD)]_x\} + CaH_2 + PR_3$.

Me_3CS, $Me_3CS(O)$, Ph_3CS, 2,4,6-$Br_3C_6H_2O$) or steric and coordination effects (Q = *o*-$OHCC_6H_4$) in transition states of these reactions—particularly at the β-elimination stage. Proposed structures of transition state of the β-elimination stage of *Z*-stereoselective double bond migrations are shown in Fig. 1—basing on our earlier works [42,44,48,50,60].

In each of the proposed transition states, Q and Me groups are located at one side of the plane, in which β-elimination occurs, and volumetric ligands bounded with the ruthenium atom—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 bulkiness of the Q group or steric demand of the phosphine ligand (phosphine with high θ) are required for high *Z*-stereoselectivity. In the case of allyl 2,4,6-tribromophenyl ether, the isomerisation had to be carried out at temperature as high as 140 °C (in boiling xylene) [44]. It resulted beyond any doubt from a very strong steric effect of Q (2,4,6-tribromophenoxyl). On the other hand, isomerisation of ethers of ROallyl type is not stereoselective when R = Et, Ph, allyl (so when R and Q have too small volume). Likewise, isomerisation of *N*-allylamides in the presence of $[Ru(PR_3)_x]$–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 θ—e.g. for PPh_3 (tris(2,4,6-tri-*t*-butylphenyloxy)phosphine is required) [48,60]. Therefore, the role of Q in *Z*-stereoselective double bond migration in our opinion consists in augmentation of steric effect of the phosphine ligands. However, the *Z*-stereoselective isomerisation of allyl-(*o*-formylphenyl) ether is in our opinion caused by chelating effect—as it has been described for isomerisation of allyl (*o*-diphenylphosphino)benzene [51]. A complete lack



[Ru]-H = $[RuClH(CO)(PPh_3)_3]$ - A or $\{[RuCl_2(1,5\text{-}COD)]_x\}$ + tris(2,4,6-trimethoxyphenyl)phosphine + $Li[AlH_4]$ (1 : 1 : 5) - B [44,49,50]

Scheme 3. *E*-stereoselective isomerisation of Q-allyl catalysed by ruthenium hydride complexes. [Ru]–H = $[RuClH(CO)(PPh_3)_3]$—A or $\{[RuCl_2(1,5\text{-}COD)]_x\}$ + tris(2,4,6-trimethoxyphenyl)phosphine + $Li[AlH_4]$ (1:1:5)—B [44,49,50].

of stereoselectivity in isomerisation of allyl (*p*-formylphenyl) ether, observed by us [44], is a confirmation of the chelating effect influence.

A significant role in *Z*/*E* is also played for sure by number of phosphine molecules coordinated to the metal atom. Presence of two coordinated phosphine molecules should increase *Z*-selectivity. In such a case, one side of the plane, in which β-elimination occurs, is occupied by bulky phosphine ligands, so Q and CH_3 form *cis* configuration (Fig. 1). Presence of just one coordinated phosphine molecule should favor *E*-selectivity. Then, Q and CH_3 may be present at opposite sides of the forming double bond—Fig. 2 [41,44,49,50,60].

2.2. *E*-stereoselective double bond migration

A highly *E*-stereoselective double bond migration was observed for some *N*-allylamines (Q = $(Me_3Si)_2N$- or *t*-Bu(allyl)N-), *N*-allyl-*N*-arylethanamides (Q = ArN(COMe)-, Ar = Ph, substituted Ph, 1- or 2-naphtyl), allyl-phenyl sulphone (Q = $PhSO_2$), allyldiphenylphosphine oxide and some allyl ethers (e.g. allyl-(*o*-bromophenyl) ether)—Scheme 3 and Table 2. Isomerisation of *N*-allylamines, allyl sulphone, phosphine oxide and *N*-allylamides was catalysed by $[RuClH(CO)(PPh_3)_3]$ [40,41,60], whereas isomerisation of the ether was performed in the presence of a catalytic system generated in situ from a precursor, i.e. $\{[RuCl_2(1,5\text{-}COD)]_x\}$and tris(2,4,6-trimethoxyphenyl)phosphine [49].

Our investigations lead to a conclusion that also *E*-stereoselective isomerisations occurred according to the hydride mechanism [21,49,50,60]. *E*-stereoselectivity of the reactions mentioned above results, in our opinion, mostly from coordination effect—participation of the Q group in coordination of the ruthenium atom [40,41,45,46,49,50,60]. Proposed structures essential for stereoselectivity of these reactions, presenting contribution of Q, are shown in Fig. 2 [41,42,44,49,60].

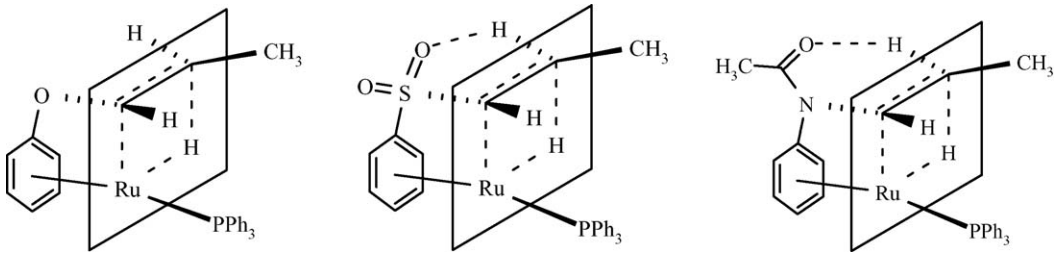


Fig. 2. Proposed structures of β-elimination in the *E*-stereoselective double bond migration in allyl aryl ethers, allyl phenyl sulphone (similarly in allyldiphenylphosphine oxide) and *N*-allyl-*N*-arylamides. Such ligands as CO, Cl and solvent, were omitted.

Table 2
E-stereoselective isomerisation of Q-allyl catalysed by ruthenium hydride complexes

Q ([Ru]–H: A or B)	ε (%)	*E*:*Z*	Reference	Q	ε (%)	*E*:*Z*	Reference
MeCON(Ar) Ar = 4-X-C_6H_4– (X = Cl, Br, O_2N) (A)	100	98.9:99.9	[40,41,60]	$PhS(O_2)$ (A)	96	100:0	[42,50]
				$Ph_2P(O)$ (A)	96	96:4	[21]
(*i*-Pr)$_2$N, *t*-BuNallyl (A)	99	99 : 1	[45,46,60]	*o*-BrC_6H_4O (A)	100	96:4	[44,49,50]
t-$BuMe_2SiO$ (B)	100	90:10	[44,49,50]	*o*-$MeOC_6H_4O$ (A)	100	88:12	[44,49,50]

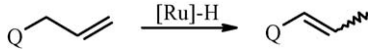
We carried out quantum calculations (semi-empirical and ab initio geometry optimisation followed by an analysis of the shapes of RHF orbitals) for *N*-allyl: amides and amines and *N*-(1-propenyl): amides and amines [40,41,48,60]. It allowed us to analyse possible interactions of substrates and products of double bond migration with ruthenium complexes [41,48,60]. The analysis proved unequivocally that participation of Q in the coordination increases the chance of obtaining *E*-isomer. It is shown particularly clearly in isomerisation reactions of *N*-allylamides [40,41,60]. *N*-aryl-*N*-allyl amides isomerise highly stereoselectively to *E*-enamides in the presence of $[RuClH(CO)(PPh_3)_3]$ (because of Q participation in the coordination), and *N*-alkyl-*N*-allylamides isomerise to a mixture of *E*- and *Z*-enamides (lack of Q participation) [48,60]. Steric effects play also significant part in these reactions. The steric effects are lowest when methyl group is possibly far from ligands coordinated with the metal atom (as in *E*-isomer). Significance of coordination (Q participation in coordination of the metal atom) and steric (interaction of Q and Me with ligands) effects for stereochemistry of double bond migration were also described by other authors. A highly enantioselective isomerisation of *N*-allylamines catalysed by cationic rhodium complexes may be an example [61–63]. Participation of nitrogen atom (so Q) in the coordination plays an essential role there. Then, isomerisation of dienamines and dienyl ethers (catalysed by "$Cr(CO)_3$") was highly *E*,*Z*-stereoselective, because it proceeded via U-shaped η^5-intermediates formed stereospecifically by the oxidative addition of a C–H bond to "$Cr(CO)_3$" [64,65]. Quantitative *E*-stereoselectivity was also observed in isomerisation of allylbis(trimethylsilyl)amine photocatalysed by $[Fe(CO)_5]$ [66]. However, the authors did not try to explain its cause.

In the case of allyl-(*t*-butyldimethylsilyl) ether isomerisation in the presence of [Ru]–H generated in situ from $\{[RuCl_2(1,5\text{-COD})]_x\}$, tris(2,4,6-trimethoxyphenyl)phosphine and $Li[AlH_4]$, high *E*-selectivity (*E*/*Z* = 7.3) results in our opinion from fusion of steric and coordination effects [49,60]. However, main role is played by steric effects. Synergy of Q and phosphine ligand steric effect is apparent. When triphenylphosphine was used instead of tris(2,4,6-trimethoxyphenyl)phosphine, *E*/*Z* decreased to 1.1 [49,60]. Then, when allyl ethyl ether (Q = Et is significantly smaller than Q = *t*-$BuMe_2Si$) was isomerised, *E*/*Z* decreased below 1.0 in spite of the fact that bulky tris(2,4,6-trimethoxyphenyl)phosphine was the ligand. Steric and coordination effects determined also high *E*-stereoselectivity of *N*-allylamides isomerisation catalysed by iridium catalyst generated in situ from $[Ir(COD)Cl]_2$, tricyclohexylphosphine and Cs_2CO_3 [67]. The reaction proceeds according to the π-allyl mechanism, and the η-allyl hydride intermediate is consistent with the almost exclusive formation of *E*-enamide, since in this case only hydrogen atoms occupy the "endo" position [67]. Unusual *E*-stereoselectivity of isomerisation of 1-alkenes to 2-alkenes, isolated dienes to *E*,*E*-conjugated dienes, and allylamines to *E*-enamines catalysed by $[TiCl_2(C_5Me_5)_2]/NaC_{10}H_8$ was observed by Akita et al. [68]. 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 isomerisation reactions of *N*-allylamides catalysed by $[Fe(CO)_5]$, proceeding according to the π-allyl mechanism [69]. *E*-isomer was preferred due to steric effects—interactions between methyl group and ligands were smaller, when this isomer was formed.

2.3. Non-stereoselective double bond migration

Most double bond migrations studied are non-stereoselective: mixtures of isomeric 1-propenyl compounds are formed [21,32–39,43,44,48–50,60]—Scheme 4.

Lack of stereoselectivity in these reactions results from, in our opinion, a lack of specific coordination or steric effects. However, it is noteworthy that propenyl systems are most often the only products of these reactions, and the catalytic system is stable. In that case, also the non-stereoselective reactions are interesting for organic synthesis—e.g.: transformation of terminal alkenes to mixture of internal isomers [21,36], isomerisation of allyl ethers to 1-propenyl ethers [21,34,35,43,44,46,49,50], allylsilanes to vinylsilanes [21,70], *N*-allylamines and *N*-allylamides to enamines [21,34,45,46,60] and enamides [21,34,37,38,40,41,45], isolated dienes and polyenes to conjugated systems [21,36], 2-vinyl-1,3-dioxanes and dioxolanes to ethylidene derivatives [21,35,36], vegetable oils (rapeseed, soybean, sunflower and linseed) to oils containing conjugated double bonds [21,71,72], di- and polyallylic systems to di- and poly(1-propenyl) compounds [21,37,38,50].



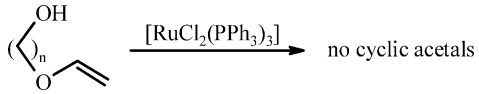
Scheme 4. Non-stereoselective isomerisation of Q-allyl catalysed by ruthenium hydride complexes. Q = alkyl (Et, Bu, ...), aryl (mainly *E*-isomers were the products (>96%), but such is the *E*/*Z* equilibrium in these cases [21]) (Ph, *p*-$MeOC_6H_4$, 3,4-methylenedioxyphenyl, 2,5-dihydroxyphenyl, 3-thienyl), $PhCH_2$, PhC≡C, CH_2=CH, CH_2=$CHCH_2$, CH_3COCH_2, HOOC, *i*-BuOOC, $(EtOOC)_2CH$, ArylO (Ph, *p*-$PhOOCC_6H_4O$), AlkylO (EtO, BuO, $PhCH_2O$, ...), allylO, allylO$(CH_2)_nO$, HO$(CH_2)_nO$, (allylO)$_2$C(R)O (R = H or Ph), (allylO)$_2$BO, $(EtO)_3SiO$, (allylO)$_3$SiO, Me_3Si, $(EtO)_3Si$, $Me_2(CH_2Cl)Si$, Me_2(*i*-Pr_2N)Si, 1-carbazolyl, R(MeCO)N (R = H, Me, allyl, ...), $(Me_3Si)_2N$, 1-phthaloimidolyl, *p*-$MeC_6H_4SO_2NH$, Y$(CH_2)_nCH_2$ (Y = Br or HO; *n* = 2 or 5), 3,3,4,4-tetramethyl-1,3-dioxoborolanyl.

It was noteworthy that the reactions proceeded at moderate temperatures—mostly 60–120 °C. Only some of the reactions proceeded with a suitable rate at higher temperatures. For instance, isomerisation of allyl phenyl acetylene had to be carried out at high temperature, i.e. 160 °C [21]. Below 120 °C the isomerisation practically did not proceed, but a rich red complex was formed. A complex of the same colour formed in the reaction of $[RuClH(CO)(PPh_3)_3]$ with diphenylacetylene. Probable course of the reaction of allyl phenyl acetylene with $[RuClH(CO)(PPh_3)_3]$ was shown in Scheme 5.

Formation of stable acetylene complexes of Ru [73] and other metals [74,75], via ligand exchange – e.g. PPh_3 – for acetylene ligands, is well known. However, first of all reactions between $[RuClH(CO)(PPh_3)_3]$ and alkynes of RC≡CH type (R = Ph, *t*-Bu or Bu) [76] were described. As a result of 1,2-insertion of [Ru]–H to the alkyne, complexes of $[RuCl(CH{=}CHR)(CO)(PPh_3)_2]$ type were formed in these reactions. In our opinion, significant increase in the reaction temperature causes however an elimination with reproduction of [Ru]–H, and double bond migration in PhC≡Callyl occurs practically quantitatively. Also isomerisation of allyl (2-pyridyl) ether required high temperature (140 °C) and high [Ru] concentration (5 mol%) [21,44,50]. For sure, complexing properties of functional group Q (Q = 2-pyridyloxyl) determined this fact. Pyridine itself (if used as a solvent) dramatically decreases the isomerisation rate for various Q-allyls [21,50] (see also Section 2.6.1). Complexing power of allyl (2-pyridyl) ether is surely close to the one of pyridine, what causes low reactivity of the system.

2.4. Double bond migration or cyclisation of allyloxyalcohols ($Q = HO(CH_2)_nOallyl$; $n = 1$, 2–6)

We have observed that allyloxyalcohols undergo isomerisation consisting in double bond migration or isomerisation consisting in cyclisation. $[RuClH(CO)(PPh_3)_3]$ catalyses double bond migration selectively, and $[RuCl_2(PPh_3)_3]$ catalyses double bond migration and cyclisation [21,43,50]—Scheme 6.We have shown that cyclisation is not a simple addition of OH group to enol ether double bond, because vinyloxyalcohols do not undergo it [43,50].



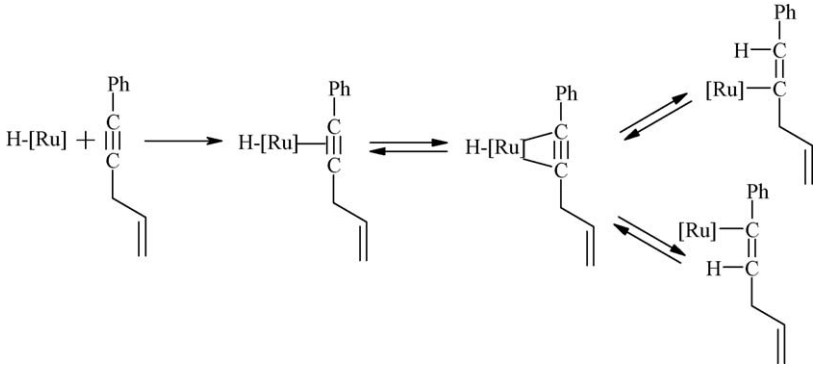
Investigations of the reaction mechanism we have carried out so far lead to a conclusion that it is a two-step reaction. First, an oxidative addition of $HO(CH_2)_nOallyl$ to [Ru] occurs, then the hydrido-π-allylic complex formed undergoes an intramolecular nucleophilic attack of the OH group [50].

2.5. Isomerisation occurs, but an irreversible transformation of the catalytic system occurs in parallel

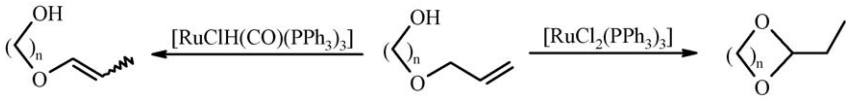
Sometimes, we have found that double bond migration occurs, but most often the reaction cannot be concluded. The Q-allyl—Q-(1-propenyl) equilibrium could not be achieved in spite of using very large quantities of the catalyst (up to 20 mol%), as transformations of the catalytic system occurred in parallel, leading to complexes catalytically inert—Scheme 7.

Thus, isomerisation of allyl-benzyl ether ($Q = PhCH_2O$) to enol ether was accompanied by formation of benzaldehyde and gradual deactivation of the catalytic system. In order to achieve practically quantitative conversion of allyl-benzyl ether, many times larger quantity of the catalyst ($[RuClH(CO)(PPh_3)_3]$, $[RuH_2(CO)(PPh_3)_3]$, $[RuCl_2(PPh_3)_3]$, ...) was required, than for isomerisation of other allyl ethers. Formation of benzaldehyde in the isomerisation reaction of allyl-benzyl ether is possible in a transformation shown in Scheme 8.

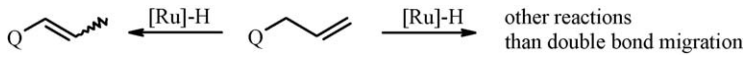
As one can see, a cleavage of Q-allyl (C–O) bond occurs. It was noteworthy that aldehyde was formed in the reaction not only when $[RuClH(CO)(PPh_3)_3]$ was used as a catalyst, but also in the case of $[RuH_2(CO)(PPh_3)_3]$, $[RuCl_2(PPh_3)_3]$, and $\{[RuCl_2(NBD)]_x\}$. $PhCH_2Oallyl$ underwent a complete conver-



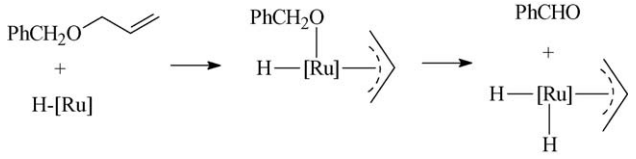
Scheme 5. Reaction of $[RuClH(CO)(PPh_3)_3]$ with allyl phenyl acetylene—a proposition.



Scheme 6. Isomerisation or cyclisation of allyloxyalcohols catalysed by hydride or non-hydride ruthenium complexes, respectively. $n = 2$–6.



Scheme 7. Isomerisation or others reactions some allylic systems with ruthenium hydride complexes ([RuClH(CO)(PPh_3)$_3$] or [$RuH_2(PPh_3)_4$]) [21,50]. Q = HO, $HOCH_2$, CH_3COO, $PhCH_2O$, $CH_3CH_2CH_2COO$, PhCOO, MeOCOO, *o*-$OHCC_6H_4$, C_6Cl_5O, Ph_3Sn, Bu_3Sn, *i*-PrS, $PhS(O_2)$, *t*-BuS(O).



Scheme 8. Reaction of allyl-benzyl ether with [RuClH(CO)(PPh_3)$_3$]—a proposition.

Scheme 10. Isomerisation of allyl carboxylates catalysed by [RuClH(CO)(PPh_3)$_3$] [21,37,50]. (a) R = Me, Bu; *y* = 45% (*E*/*Z* = 0.3); *t* = 60 °C; *ι* = 3 h; 10 mol% [Ru]. (b) R = MeO; *y* = 80% (*E*/*Z* = 0.4); *t* = 80 °C; *ι* = 6 h; 13 mol% [Ru]. (c) R = Ph; *y* = 80% (*E*/*Z* = 0.4); *t* = 120 °C; *ι* = 3 h; 10 mol% [Ru].

sion, but the reaction products always contained, besides (*Z*)- and (*E*)-$PhCH_2OCH{=}CHCH_3$, also PhCHO (5–15%). The aldehyde reacted with [Ru]–H, gradually forming catalytically inert complexes of unknown structure. It was verified that an addition of RCHO (R = Ph or Et), to the reaction mixture caused a total blocking of the catalyst's activity in the isomerisation reaction of PhOallyl catalysed by [RuClH(CO)(PPh_3)$_3$].

We also observed the Q-allyl bond cleavage in isomerisation reactions of allyl pentachlorophenyl ether (Q = C_6Cl_5O) [21,44,50]. Despite using various ruthenium catalysts, various solvents and possibly low temperatures, the double bond migration in this ether was always accompanied by other reactions—a series of products formed (including pentachlorophenol). We think that it results from high complexing power of Q (C_6Cl_5O), leading to weakening of Q-allyl (C–O) bond.

A slow decay of catalytic system activity was also observed in the reaction of [RuClH(CO)(PPh_3)$_3$] with allyl *o*-formylphenyl ether [21,44,50]. Isomerisation of this ether proceeded significantly slower than the one of *para*-isomer, and it could not be brought to an end. It was possible not before transformation of *o*-CHO group to an acetal system, i.e. *o*-$CH(OMe)_2$ group. Then the isomerisation occurred easily and quantitatively [44,50].

In the case of allyl alcohol (Q = HO), the reaction with [RuClH(CO)(PPh_3)$_3$] at 60–120 °C proceeds as it is shown in Scheme 9 [21,38].

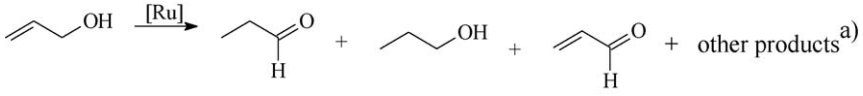
Analogous course of the reactions of allylic alcohols with ruthenium complexes was also observed by other authors [26,77]. In the first stage of the reaction, an oxidative addition of OH group from the alcohol molecule to the metal complex was observed. Then an intra- or intermolecular hydrogen transfer occurred [21,26,77].

However, 1-phenyl-2-propen-1-ol and 1-trimethylsililo-2-propen-1-ol (systems of Q–CH(R)CH=CH_2 type) isomerised easily and quantitatively to the corresponding ketones [21]. Also 5-hexen-1-ol and 9-decen-1-ol isomerised easily (96% conversion) to a mixture of hexenols or decenols already at 60 °C [21]. This means that the course of the reaction of unsaturated alcohols with the investigated ruthenium complexes is not so much determined by the presence of the OH group, as by its position in relation to the double bond. If the OH group is sufficiently far from the double bond, the migration proceeds without hindrance. An analogous situation takes place in the case of unsaturated chlorides and bromides, what is discussed later.

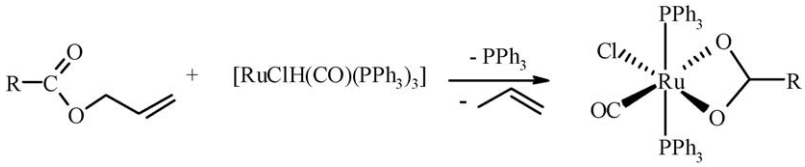
In the case of allyl *i*-propyl sulphide, allyl phenyl sulphone and allyl *t*-butyl sulphoxide, the isomerisation was probably accompanied by the same transformation as in the case of allyl phenyl sulphide (see Section 2.6.1), as we observed liberation of propene (however very slow). The isomerisation proceeded faster than Q-allyl bond cleavage. Therefore, it was possible to obtain Q-(1-propenyl) with high yields [42,50]. In our opinion, it is a result of the Q steric effect. *S*-allyl bond cleavage is favored by coordination of the metal atom via S atom, and this is hindered when Q is bulky.

In the reaction of allylic esters of RCOOallyl type (R = Me, Bu, MeO, Ph) with [RuClH(CO)(PPh_3)$_3$], products of the double bond migration were formed, i.e. 1-propenyl esters—Scheme 10 [21,37,50].

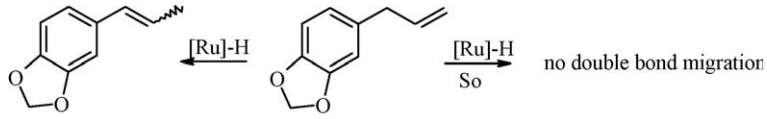
However, Q-allyl bond cleavage occurred in parallel, propene was liberated and catalytically inert carboxylate complexes were formed. In the case of reaction with allyl acetate, the complex was successfully isolated and its structure was defined—Scheme 11. It turned out that the structure is the same as in the case of the compound obtained earlier by Sanchez-Delgado et al. in the reaction of [RuClH(CO)(PPh_3)$_3$] with acetic acid [78]. One may assume that other esters react similarly as allyl acetate. Probably an analogous reaction as in Scheme 11 occurred also during heating of 3-butenoic acid (Q = COOH) with [RuClH(CO)(PPh_3)$_3$]. However, the double bond migration proceeded significantly faster, and we obtained a mixture of (*E*)- and (*Z*)-2-butenoic acids (98% conversion at 120 °C) [21].



Scheme 9. Reaction of allyl alcohol with [RuClH(CO)(PPh_3)$_3$] [21,38]. (a) Alkenes, water and polymers; analogous products were observed in the case of 3-buten-1-ol (Q = $HOCH_2$) and 3,3-dimethylallyl alcohol [21,38].



Scheme 11. Reaction of allylic carboxylates with $[RuClH(CO)(PPh_3)_3]$ [50]. R = Me, Bu, Ph.



Scheme 12. Solvent effect in the reaction of Q-allyl with $[RuClH(CO)(PPh_3)_3]$ (basing on [21]). [Ru]–H = $[RuClH(CO)(PPh_3)_3]$; So = EtSallyl or Et_2S, $allyl_3P$ or Bu_3P, $(allylO)_3P$ or $P(OMe)_3$, PhS(O)allyl or DMSO, PhNMe(allyl) or $PhNMe_2$, PhCH=Nallyl or Py.

We think that also for the same reasons, isomerisation of allyl *p*-carboxyphenyl ether (Q = *p*-$HOOCC_6H_4O$) could not be brought to an end, in spite of using high concentration of various [Ru]–H [21]. Meanwhile, allyl *p*-phenoxycarbonylphenyl ether (Q = *p*-$PhOOCC_6H_4O$) isomerised easily and quantitatively in the presence of $[RuClH(CO)(PPh_3)_3]$ already at 60 °C [21].

It was interesting that in the case of allyl trifluoroacetate, the isomerisation product was not observed at all—only the products of Q-allyl bond cleavage, i.e. propene and carboxylate complex were detected, see Section 2.6.

$Ph_3Snallyl$ and $Bu_3Snallyl$ underwent mainly side reactions (~20% $R_3SnCH{=}CHCH_3$ was obtained; R = Bu or Ph)—probably as a result of oxidative addition to [Ru], with cleavage of weak C–Sn bond. Allyltin derivatives are known allylating agents [79] and substrates for synthesis of allylic complexes [80].

In the case of allylchlorosilanes ($Cl_3Siallyl$ or $ClMe_2Siallyl$), composition of the post-reaction mixture was complicated—the double bond migration products made up 10–20% of the mixture (with most products unidentified) [21]. The reactions were carried out in benzene at 60 °C, in the presence of 1 mol% $[RuClH(CO)(PPh_3)_3]$, $[RuCl_2(PPh_3)_3]$ or $[RuH_2(PPh_3)_4]$ [21].

2.6. Allylic systems not undergoing isomerisation

Many compounds of Q-allyl type, investigated by us, did not undergo isomerisation in the presence of $[RuClH(CO)(PPh_3)_3]$, $[RuCl_2(PPh_3)_3]$, $[RuH_2(PPh_3)_4]$, $\{[RuCl_2(1,5\text{-}COD)]_x\} + Li[AlH_4]$ or $\{[RuCl_2(1,5\text{-}COD)]_x\} + Li[AlH_4] + PPh_3$ at all.

Q-allyl → no double bond migration

Q = Cl, Br, $BrCH_2$, I, EtS, allylS, PhS, PhS(O), PhSe, CF_3COO, CF_3CFHCF_2O, $PhC(Me)_2OO$, Me_2N, $allyl_2N$, PhNMe, PhCH=N, 1-imidazolyl, O=C=N, S=C=N, Et_3N^+, Ph_3P^+, $allyl_2P$, Ph_2P, $(allylO)_2PO$, CHO.

In our opinion, the double bond migration did not occur in such systems mainly because of high complexing power of Q (or Q and the double bond simultaneously). Sometimes, isomerisation did not occur because of cleavage of the Q-allyl bond or another bond in Q moiety (occurring significantly faster than the double bond migration). The isomerisation was not observed also because of specific electron density distribution in Q-allyl. The causes of lack of these Q-allyls isomerisation are discussed more in detail below.

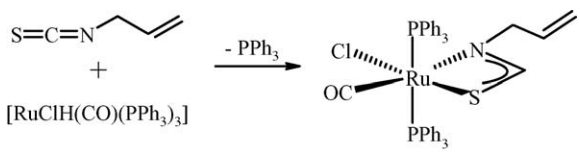
2.6.1. Q-allyl with high complexing power: Q = EtS, allylS, PhS, PhS(O), PhSe, Me_2N, $allyl_2N$, PhNMe, PhCH=N, 1-imidazolyl, O=C=N, S=C=N, $allyl_2P$, Ph_2P, $(allylO)_2PO$

There is no doubt that lack of the isomerisation in these cases results from strong coordination of Q, or Q and the double bond simultaneously, at the ruthenium atom. This leads to a transformation of the ruthenium precursor into complexes which are catalytically inert and stable in the reaction mixture. Solvent effects observed by us in safrole isomerisation reaction are a perfect confirmation of this thesis. Namely, an addition of any of the aforementioned strongly complexing Q-allyls or solvents with similar properties to the reaction mixture completely blocks safrole isomerisation—Scheme 12 [21].

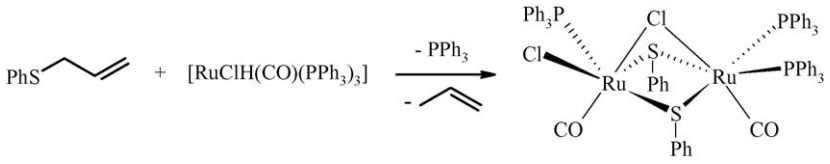
In the case of allyl isothiocyanate, allyl phenyl sulphide and allyl phenyl selenide, we managed to isolate the forming complexes and define their structure using X-ray analysis. In the reaction of allyl phenyl isothiocyanate with $[RuClH(CO)(PPh_3)_3]$, an irreversible addition of [Ru]–H to Q occurred, and allylic fragment did not participate in the coordination—Scheme 13. Obtained new complex was isolated and its structure was defined—see Section 4.5.

Then, in the case of PhSallyl and PhSeallyl, Q-allyl bond cleavage occurred, propene was liberated, and complexes were formed – a binuclear one (with PhSallyl [42,50]) or a tetranuclear one (from PhSeallyl [50]) – Schemes 14 and 15. In both these complexes with structures defined by us, Q were coordinated—in the form of a bridge.

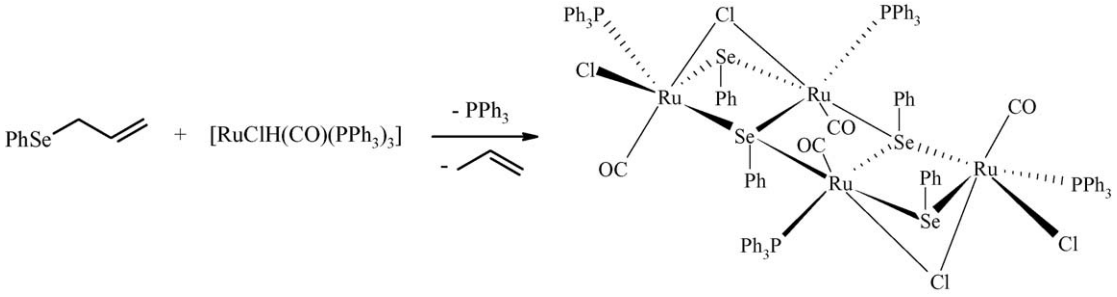
Then, in the reaction of *N*-allylimidazole with $[RuClH(CO)(PPh_3)_3]$ (in boiling benzene), a dark green



Scheme 13. Reaction of allyl isothiocyanate with $[RuClH(CO)(PPh_3)_3]$.



Scheme 14. Reaction of allyl phenyl sulphide with $[RuClH(CO)(PPh_3)_3]$ [42,50].



Scheme 15. Reaction of allyl phenyl selenide with $[RuClH(CO)(PPh_3)_3]$ [50]. Isolation of the product from the post-reaction mixture was described, and X-ray and NMR data of the product were presented in Section 4.5.

complex formed, and we did not succeed in defining its structure. The complex was decomposing during attempts to isolate and crystallize it. On the grounds of ^1H and ^{31}P NMR (in $CDCl_3$) spectra, it was ascertained that the complex did not contain hydride ligand, and it was symmetrical or contained only one molecule of coordinated triphenylphosphine.

Donor–acceptor abilities of solvents and, *per analogiam*, also of Q-allyl, may be estimated basing on donor or acceptor number [81,82]. These numbers have been used, e.g. in solvent selection for reactions with participation of cationic metal complexes [83]. Knowledge of solvent D_N and A_N has also been used in clarification of changes in the coordination sphere of metal complexes [83,84]. Donor and acceptor number of series of solvents, and qualitatively similar (in our opinion) Q-allyls, are presented in Table 3. The data of Table 3, together with the results of the solvent effect and Q-allyl effect on safrole isomerisation (Scheme 16), allow to form the following general conclusions.

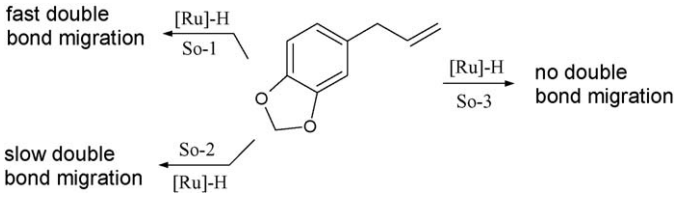
First, one can see that increase in D_N of the solvent (and qualitatively similar Q-allyl) leads to a decrease in the double bond migration rate, down to a complete lack of isomerisation.

However, it is not a simple dependence. For example Et_2O (and ROallyl, as we have assumed) has higher D_N value than MeCN (and most certainly also allylCN), and safrole isomerisation proceeds significantly faster in Et_2O than in MeCN [21]. Similarly, allyl ethers, diallyl ethers and acrolein's acetals isomerise easily and rapidly (most often at tempera-

Table 3
Donor–acceptor properties of selected solvents and allylic systems of Q-allyl type similar to the solvents

Solvent	Donor–acceptor properties			Q-allyl with similar donor–acceptor properties
	Quantitative criterion [81,82,85]		Qualitative criterion	
	D_N	A_N		
Benzene	0.1	8.2	Very weak donor, weak acceptor	1-Alkenes, allylcyclohexane, allylbenzene, 1,5-pentadiene, 1,5-cyclooctadiene[a], allylsilanes
Acetonitrile	14.1	18.9	Medium donor, medium acceptor	Allyl cyanide
Acetone	17.0	12.5	Medium donor, weak acceptor	Unsaturated ketones
Ethyl acetate	17.1		Weak donor	Allyl esters
Et_2O	19.2	3.9	Medium donor, very weak acceptor	Allyl ethers, di- and polyallyl ethers
DME	20.0	12.8	Medium donor, weak acceptor	Allyl ethers, di- and polyallyl ethers
THF	20.0	8.0	Medium donor, very weak acceptor	Cyclic ethers[a]
1,3-Dioxolane	21.2		Medium donor	Acrolein's acetals[b]
Sulpholane	14.8		Weak donor	Allyl sulphones
$P(OMe)_3$	23.0		Medium strong donor	Triallyloxyphosphine
DMF	26.6	16.0	Medium strong donor, weak acceptor	*N*-allylamides, *N*-allylimides
DMSO	29.8	19.3	Medium donor, medium acceptor	Allyl-phenyl sulphoxide
Et_2S	41.0	11.4	Medium strong donor, weak acceptor	Allyl sulphides
Pyridine	33.1	14.2	Medium strong donor, weak acceptor	*N*-allylimidazole, *N*-allylimines, allyl isocyanate
Et_3N	61		Very strong donor	*N*-allylamines

DME, dimethoxyethane.
[a] Systems of $QCH_2CH{=}CHR$ type.
[b] Systems of $QCH(R)CH{=}CH_2$ type.



Scheme 16. Solvent effect in the isomerisation of safrole catalysed by $[RuClH(CO)(PPh_3)_3]$ (basing on [21,60]). So-1 = benzene, toluene, acetone, THF, Et_2O, 1,4-dioxane; So-2 = DMF, MeCN, sulpholane, MeCN, Et_3N; So-3 = DMSO, allyl-phenyl sulphoxide, imidazole, *N*-allylimidazole, Et_2S, allyl ethyl sulphide.

tures of 60–80 °C), while allyl cyanide isomerises with difficulty (120 °C) [21,46,49,50].

Likewise, $P(OMe)_3$ has lower D_N value than DMF, meanwhile safrole and allyl phenyl ether isomerisation occurs in DMF, whereas it does not occur in phosphite [21]. *N*-allylamides similar to DMF isomerise easily, while $(allylO)_3P$ analogous with $P(OMe)_3$ does not isomerise at all (irrespective of the investigated ruthenium complexes, and even at temperature of 160 °C) [21]. This means that the influence of donor-acceptor abilities of Q-allyl and solvents on the course of the reaction between Q-allyl and [Ru], observed by us, cannot be described quantitatively. Application of A_N and D_N parameters does not lead to a sensible correlation. A similar lack of a simple dependence between the double bond migration rate in PhOallyl, and A_N and D_N of the solvents, was observed by us earlier in reactions catalysed by $[Ru(acac)_3]$ [33].

Pearson's concept of "hard" and "soft" acids and bases (HSAB) [86,87] is very useful for explanation of problems of coordination chemistry [87,88] and catalysis with participation of transition metal complexes [86,88–90]. It is clearly visible that hardness of metal atom and ligand (solvent or Q-allyl) has a great significance for course of the reaction between Q-allyl and ruthenium complexes. The effect of solvent or Q-allyl hardness can be seen particularly clearly while comparing the influence of pyridine and Et_3N on safrole isomerisation. The isomerisation occurs in Et_3N ($D_N = 61$), and it does not occur in pyridine ($D_N = 33.1$), however the last solvent is a weaker donor. Most evidently, medium-soft ruthenium atom is complexed more lastingly by medium-soft pyridine than by hard triethylamine.

Nevertheless, the steric effect of Q-allyl is also important. In our opinion, *t*-BuSallyl, $(i\text{-Pr})_2$Nallyl and $(Me_3Si)_2$Nallyl isomerisation occurs because of the fact that coordinating abilities of Q have been limited by the steric effect of *t*-Bu and Me_3Si, bounded with the donor atoms, i.e. sulphur and nitrogen. In EtSallyl and Me_2Nallyl, the substituents at the donor atoms are too small, and the isomerisation does not occur, or Q-allyl bond cleavage occurs (as a result of a strong coordination, weakening C–Q bond). In *i*-PrSallyl, the steric effect of Q is still insufficient, and isomerisation is accompanied by C–S bond cleavage [50]. However, in $(i\text{-Pr})_2$Nallyl the steric effect of two *i*-Pr group is sufficient. Nitrogen atom is shielded well enough to prevent strong coordination, and the double bond migration occurs practically quantitatively [45,46,60]. An important confirmation of the thesis concerning fundamental role of the complexing power of Q group in the reaction of Q-allyl with ruthenium complex, is found in reactivity of *S*-allylic systems. Namely, both allylic sulphide and allylic sulphoxide do not undergo isomerisation, while allyl phenyl sulphone and butadiene sulphone do undergo isomerisation to conjugated systems relatively easily [42,50]. Thus, when sulphur loses its complexing properties in relation to ruthenium, the double bond migration occurs. Probably because of the same reasons, allyl-phenyl ether does not undergo isomerisation in the presence of sulphides and allyl-phenyl sulphoxide. However, presence of allyl-phenyl sulphone or tetramethylenesulphone (sulpholane) does not hinder double bond migration in ether. An analogous effect was observed in RCM of *N*,*S*-allylic systems (e.g. *N*-allyl-2-*N*-(2-thioallylphenyl)-*p*-toluenosulphonoamide) [91]. Namely, only oxidation of sulphide sulphur to sulphone sulphur enabled RCM in the presence of Grubbs' second generation catalyst [91]. The decisive factor was probably the transformation of soft donor (sulphide or sulphoxide sulphur), strongly coordinated at the metal atom, into a hard donor (oxygen atoms in the sulphones), which was coordinated weakly.

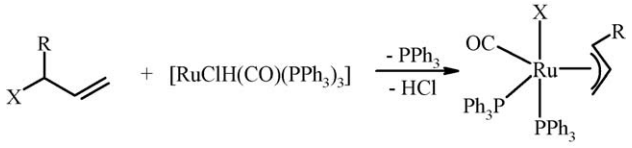
It was interesting that 3-allylthiophene (Q = 3-thienyl) [92] and *N*-allyl-2-thienylcarboamide (Q = (2-thienyl)-CO–NH) [40,60] easily underwent isomerisation to 1-propenyl derivatives (in the presence of 1 mol% $[RuClH(CO)(PPh_3)_3]$, at 80 °C). This means that "thiophene sulphur" and thiophene ring do not coordinate the ruthenium atom too strongly.

Sometimes, the coordination effects were rather subtle, they were manifesting itself only at low temperatures. That was the case for, e.g. isomerisation reactions of ethers of Y-C_6H_4Oallyl type and amides of Y-C_6H_4N(COMe)allyl type (Y = *o*-, *m*- or *p*-Cl, Br, Me, OMe, ...). Differences in the double bond migration rate in these systems, observed by us, were generally not big [21,41,44,50,60]. However, increasing the temperature of these reactions caused fast and quantitative isomerisation of all investigated ethers and amides (differences of rates of these reactions were practically fading).

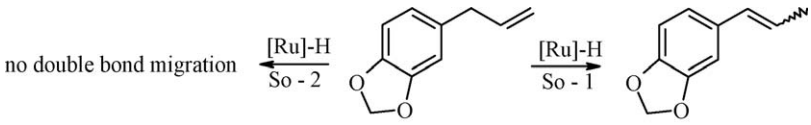
2.6.2. *Q functional group is a halogen (Cl, Br or I)*

When the functionalised alkene contains a halogen atom in the allylic (or benzylic) position, the double bond migration is not observed [21]. It applies to all investigated ruthenium complexes—hydride and non-hydride ones. An oxidative addition of Q-allyl (Q = Cl, Br or I) to a ruthenium complex (with C–Q bond cleavage), has been ascertained in the case of all investigated allylic halides [21]. Probable course of these reactions is shown in Scheme 17.

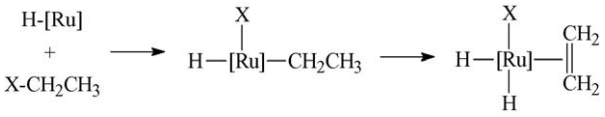
As one can see, halogen-π-allylic ruthenium complexes are products of these reactions. They are catalytically inert, as none



Scheme 17. Reaction of allyl halides with $[RuClH(CO)(PPh_3)_3]$ [21]. (a) X = Cl, Br, I; R = H and (b) X = Br; R = Ph.



Scheme 18. Solvent effect in the reaction of safrole with $[RuClH(CO)(PPh_3)_3]$ [21]. So-1 = CCl_4, $CHCl_3$, CH_2Cl_2, EtI, EtBr, CCl_2=CCl_2, PhCl and So-2 = allyl-X (X = Cl, Br, I), $PhCH_2Cl$, $PhCH_2Br$.



Scheme 19. Reaction of alkyl halides with ruthenium complexes—basing on [21,73].

of the investigated allylic halides has undergone isomerisation at temperatures of 40–100 °C. It is a somewhat surprising result, because isomerisation of alkenes catalysed by complexes of $[RuX(\eta^3\text{-}C_3H_5)(CO)_3]$ type (X = Br, Cl) has been described [93]. However, the complexes have not been very active, and they have been losing their activity quickly (isomerisation proceeding at 100 °C [93]).

Very important evidences confirming the proposed course of the reaction between ruthenium complexes and allyl halides were found in examination of solvent effect on safrole isomerisation—Scheme 18 [21].

Namely, safrole did not undergo isomerisation in the presence of allyl halides and benzyl bromide and chloride. However, alkyl halides (EtBr, EtI), and CCl_4, CH_2Cl_2, $CHCl_3$, Cl_2C=CCl_2 and chlorobenzene, do not hinder the double bond migration in safrole. On the contrary, they are good solvents for this and many other investigated by us isomerisation reactions of many allylic systems. The fact that alkyl halides are very good solvents, may result from formation of hydride π-olefin complexes, known of their high catalytic activity, in the reaction mixture [73]—Scheme 19.

It was also interesting that 4-bromo-1-butene did not undergo isomerisation in the presence of $[RuHCl(CO)(PPh_3)_3]$, whereas 6-bromo-1-hexene and 10-bromo-1-decene isomerised to a mixture of isomeric bromoalkenes (however allylic systems did not form) with 96% conversion—Scheme 20 [21].

This means that oxidative addition to [Ru], accompanied by C–halogen bond cleavage, occurs only in the case of allylic derivatives and it is significantly faster than the double bond migration. Considering this, in the case of 4-bromo-1-butene, the isomerisation had to occur first, but forming 1-bromo-2-butene (allylic halide) underwent a fast oxidative addition to [Ru]. In consequence, the active complex was quickly, quantitatively and irreversibly transformed into an inert halogen-π-allylic complex, and the isomerisation did not proceed further. It is also known that ruthenium complexes are catalysts of halogen atom exchange between various alkyl halides [94].

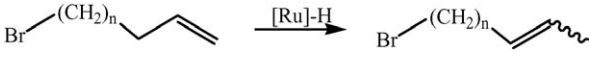
Key step of this reaction must consist in addition of halogen to [Ru], accompanied by C–halogen bond cleavage. As it is known, oxidative addition of allyl halides to transition metal complexes (including ruthenium) is a synthesis method for halogen-π-allylic complexes [73]. Synthesis of $[RuBr(\eta^3\text{-}C_3H_5)(CO)_3]$ in the reaction of $[Ru_3(CO)_{12}]$ with allyl bromide [95] may be an example. Oxidative addition of allyl bromide to $[RuCp(MeCN)(EPh_3)]PF_6$ (E = P, As or Sb), leading to allylic complexes of $[RuBrCp(\eta^3\text{-allyl})(EPh_3)]PF_6$ type, stable in the air and in solution, is also described [96].

2.6.3. Et_3N^+ (Cl^- or Br^-) or Ph_3P^+ (Cl^- or Br^-) functional group

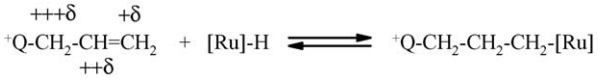
Allyl-phosphonium and allyl-ammonium salts did not undergo isomerisation in the presence of $[RuClH(CO)(PPh_3)_3]$, $[RuH_2(CO)(PPh_3)_3]$ or $[RuCl_2(PPh_3)_3]$ [21]. The reactions were carried out in THF, benzene or ethanol, at temperatures of 40–80 °C. Sometimes a transformation of the investigated salts was observed, but not to propenyl derivatives (probably the salts were slowly decomposing). It is not a result of equilibrium state in the Q-allyl—Q-(1-propenyl) systems, because isomerisation of similar systems ($[Ph_3M^+allyl]Br^-$ when M = P or As) in the presence of basic Al_2O_3 is known [97]. In our opinion, double bond migration does not occur, because [Ru]–H undergoes addition to allylic system solely formally without compliance with the Markovnikov rule. Such an orientation in the addition of [Ru]–H to double bond results from electron density distribution in $[Y\text{–}CH_2CH{=}CH_2]^+X^-$. Hydride ligand (to some degree—hydride ion) attaches itself reversibly, solely to more electropositive carbon atom—as it is shown below, in Scheme 21. It is a non-productive addition, since [Ru]–H elimination leads only to reproduction of the substrate (allylic system).

2.6.4. CF_3COO, $PhC(Me)_2OO$, CHO or CF_3CHFCF_2O functional group

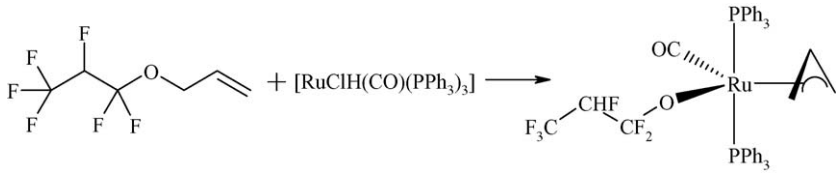
In the case of allyl trifluoroacetate, such as for other allyl esters, double bond migration competed with the Q-allyl bond cleavage. However, in the case of this ester, the cleavage was significantly faster. That is why, in our opinion, we did not observe 1-propenyl ester at all. Probably the reaction yielded the same



Scheme 20. Isomerisation of bromoalkenes catalysed by 1 mol%. $[RuClH(CO)(PPh_3)_3]$ (80 °C, 2 h, C_6D_6). When n = 0 no double bond was observed; when n = 3 or 7, 96% conversion to mixtures of internal bromoalkenes (80% of 2-alkenes) was observed (basing on [21]).



Scheme 21. Reaction of allyl ammonium or allyl phosphonium chloride or bromide with $[RuClH(CO)(PPh_3)_3]$—proposition. $^+Q = Et_3N^+$ or Ph_3P^+.



Scheme 22. Reaction of allyl hexafluoropropyl ether with $[RuClH(CO)(PPh_3)_3]$—proposition [50].

binuclear complex as the reaction of trifluoroacetic acid with $[RuClH(CO)(PPh_3)_3]$ [77].

Then, lack of the isomerisation in the case of allyl-cumyl peroxide (Q = $PhC(Me_2)OO$) is in our opinion caused by cleavage of weak O–O bond, catalysed by ruthenium complexes. Although the reactions were carried out at low temperatures (40–60 °C), in various solvents (benzene, THF, 1,4-dioxane), and using high concentrations of various precursors (10–20 mol% of $[RuClH(CO)(PPh_3)_3]$, $[RuCl_2(PPh_3)_3]$, $[RuH_2(PPh_3)_4]$), we never observed a product of double bond migration in the investigated peroxide. Addition of $PhC(Me)_2OO$allyl to the isomerisation medium of allylbenzene or allyl phenyl ether (catalysed by $[RuClH(CO)(PPh_3)_3]$, $[RuCl_2(PPh_3)_3]$ or $[RuH_2(PPh_3)_4]$) completely blocked the double bond migration in these very reactive Q-allyls. This means that active forms of [Ru], while reacting with peroxide, undergo a transformation to catalytically inert complexes.

Lack of the isomerisation in the case of 3-butenal (Q = CHO) results probably from decarbonylation of the aldehyde in the reaction with $[RuClH(CO)(PPh_3)_3]$ (or $[RuH_2(CO)(PPh_3)_3]$, or $[RuH_2(PPh_3)_4]$). It was confirmed that the forming complexes are catalytically inert [21]. It is noteworthy that the result of the reaction with 3-butenal corresponds well with the results obtained for allyl-benzyl ether. Benzaldehyde, which forms there, hinders further isomerisation of the ether. It was also proved that addition of 2-butenal, 2-propenal or benzaldehyde to the reaction mixture of, e.g. allylbenzene isomerisation completely blocks the double bond migration [21].

Among more than 60 examined allyl ethers, we found only one which did not undergo isomerisation in the presence of $[RuClH(CO)(PPh_3)_3]$, and it was allyl 1,1,2,3,3,3-hexafluoropropyl ether [50]. A yellow complex was the product of the reaction (in boiling benzene). Unfortunately we did not succeed in obtaining a crystal for X-ray analysis. Analysis of ^1H, ^{13}C and ^{31}P NMR spectra of the complex suggests that the reaction between the investigated ether and [Ru]–H proceeds as follows—Scheme 22.

Therefore, a cleavage of Q-allyl bond occurred, but propenyl fragment was coordinated, and not isolated in the form of propene, as in the case of the reaction of [Ru]–H with allyl phenyl sulphide or allyl phenyl selenide.

3. Summary

It has been shown in the paper that Q functional group in $Q–CH_2CH{=}CH_2$ has in many cases an essential influence on course of the reaction between Q-allyl and $[RuClH(CO)(PPh_3)_3]$, and other hydride ruthenium complexes. Complexing and steric properties of the group and strength of C–Q bond have decisive significance. Inclination of Q-allyl for the oxidative addition to [Ru] is also of importance. In order the double bond migration catalysed by $[RuClH(CO)(PPh_3)_3]$ to occur without hindrance (without side products), Q-allyl may not contain the following structural elements:

- chlorine, bromine or iodine atom in the allylic fragment of the molecule (in allylic position);
- allylic, primary OH group;
- SH and NH_2 not protected with bulky substituents;
- aliphatic aldehyde group;
- $SiCl_3$, $SiMeCl_2$, $SiMe_2Cl$ groups;
- $[NR_3]^+$ or $[PR_3]^+$ group in allylic position;
- peroxo (O–O), SnR_3 and other groups containing weak C–heteroatom bonds or weak heteroatom–heteroatom bonds;
- nitrogen, sulphur, selenium, phosphorus atoms (and other atoms and atom groups of high complexing power) which are not shielded with bulky substituents, hindering complexing of the ruthenium atom.

If the above requirements are met, Q-allyl isomerisation in the presence of hydride ruthenium complexes is a very convenient synthesis method for very numerous systems of Q-(1-propenyl) type, such as: 1-propenyl arenes, trialkyl or triaryl (1-propenyl) silanes, alkyl, aryl or trimethylsilyl (1-propenyl) ethers, enamines, enamides, *N*-(1-propenyl) imides, some B-, P- or S-(1-propenyl) systems.

4. Experimental

Solvents used in the isomerisation reactions were purified in a standard way (drying using molecular sieves 3 or 4 Å, $Li[AlH_4]$, CaH_2 or metallic sodium, then distillation). All isomerised compounds (both commercial and synthesized) were purified (dried using molecular sieves 3 or 4 Å, or CaH_2, then distilled or crystallized) before the reaction with ruthenium complexes.

^1H, ^2H, ^{13}C and ^{31}P NMR, GC–MS and HPLC-MS measurements were described in our previous papers [40–46,48–50,60]. All measurements of diffraction intensities were performed on a KUMA KM4 four-circle diffractometer, Zr foil filtered MoKα radiation, $\omega/2\Theta$ scan mode [98]. The structures were solved by direct methods using the program SHELXS-97 [99] and refined by full-matrix least-squares with the aid of the program

SHELXL97 [100]. Tables of bond distances and angles, atomic coordinates, and anisotropic thermal parameters for carbonylchloro(*N*-allyliminomethylmethanethiolato-κ-*N*,*S*)bis(triphenylphosphine)ruthenium(II) and di(μ-chloro)di-chloro-bis-(μ$_3$-phenylselenolato)-bis(μ-phenylselenolato)-tetracarbonyltetrakis(triphenylphosphine)tetraruthenium(II) have been deposited with the Cambridge Crystallographic Data Centre [101].

4.1. Allylic compounds

Both commercial Q-allyls (Sigma–Aldrich, Merck or Lancaster) and Q-allyls synthesized by us were used in the research. Syntheses of Q-allyl compounds (using literature methods or methods developed by us) were described in our previous papers [21,40–46]. Allyl-cumyl peroxide has been obtained from Prof. S. Baj (Silesian University of Technology), who we hereby thank.

4.2. Ruthenium complexes

[$RuCl_3 \cdot 3H_2O$] from Johnson Matthey was used in our investigations. The following ruthenium complexes were obtained according to the literature methods: [$RuCl_2(PPh_3)_3$] [102–104], [$RuHCl(CO)(PPh_3)_3$] [104–106], [$RuHCl(PPh_3)_3$] [106], [$RuH_2(CO)(PPh_3)_3$] [105], [$RuH_2(PPh_3)_4$] [107,108], $\{[RuCl_2(1,5\text{-COD})]_x\}$ [109,110], $\{[RuCl_2(NBD)]_x\}$ [109,110], and $\{[RuCl_2(benzene)]_2\}$ [111].

4.3. Methodology of the isomerisation reactions

Methods of carrying out the reactions of allylic systems with ruthenium complexes, and methods of analysis of post-reaction mixtures' composition were described in our previous papers [21,40–50,60].

4.4. Isolation of the isomerisation products from the post-reaction mixture

Isomerisation products (1-propenyl compounds or acetals—cyclisation products) were isolated using: (a) distillation from above the catalyst under normal or reduced pressure [21,40–50,60]; (b) sublimation from above the catalyst—after distilling off the solvent on a vacuum evaporator [21]; (c) precipitation of the catalyst using hexane or petroleum ether, then adsorption of the catalyst residue on diatomite [21,71,72], activated carbon [21,41,50,60] or functionalised mesoporous siliceous foams [44,50,60]; (d) a column with silica gel (hexane as an eluent) [21,44]. For instance, for a quantitative separation of [Ru] from 10 g 1,2-di(1-propenyloxy)benzenes, obtained in isomerisation of 1,2-diallyloxybenzene (in the presence of 250 mg [$RuClH(CO)(PPh_3)_3$]), it is enough to use 10 g of silica gel (100–200 mesh) [44,50]. Ru contents was lower than 1 ppm (estimated using atom absorption). A detailed description of separation of the isomerisation products, and their properties (NMR, MS and others) were provided in our earlier papers [21,40–50,60,70–72].

4.5. Synthesis, isolation and properties (NMR, X-ray) of complexes obtained in the reaction of allyl isothiocyanate and ally phenyl selenide with [$RuClH(CO)(PPh_3)_3$]

4.5.1. Carbonylchloro(N-allyliminomethylmethanethiolato-κ-N,S)bis(triphenylphosphine)ruthe-nium(II)

Allyl isothiocyanate (1 mmol) and [$RuClH(CO)(PPh_3)_3$] (0.2 mmol) were heated in benzene (8 cm^3) at temperature of 60 °C. During the reaction, little orange crystals were being formed on the vessel walls. After 3 h, the reaction mixture was cooled and the solutions was decanted from above the crystals. After rinsing with hexane–chloroform mixture and then crystallizing from $CHCl_3$–hexane mixture (1:1), 100 mg of clear orange crystals of the complex was obtained.

4.5.2. Crystal data for the ruthenium complex with thioisocyanate

The crystal chosen for X-ray analysis was a clear orange plate with the approximate dimensions 0.2 mm × 0.5 mm × 0.6 mm. $C_{41}H_{30}ClNOP_2RuS$ (783.18 g mol^{-1}) crystallizes in the monoclinic system, space group $P2_1$, with $a = 11.795(2)$ Å, $b = 25.672(5)$ Å, $c = 12.683(3)$ Å, $\beta = 106.13(3)^\circ$, $V = 3689.1(13)$ $Å^3$, $Z = 4$, μ(Mo Kα) = 0.67 mm^{-1}, and $D_{calcd} = 1.410$ g cm^{-3}. The e.s.d. unit cell parameters were determined by least-squares refinement using 32 centered reflections within $4.2^\circ < \Theta < 28.2^\circ$. A total of 6918 reflections were collected to $2\Theta_{max} = 50.11^\circ$ (h, $-12 \rightarrow 13$; k, $0 \rightarrow 30$; l, $0 \rightarrow 15$), of which 6591 were unique. In refinements, weights were used according to the scheme $w = 1/[\sigma^2(F_o^2) + (0.10P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. The refinement of 865 parameters converged to the final agreement factors $R = 0.0754$, $R_w = 0.2112$, and $S = 1.758$ for all observed reflections with $F > 4\sigma(F_o)$. The electron density of the largest difference peak was found to be −3.12 Einstein $Å^{-3}$, while that of the largest difference hole was 1.62 Einstein $Å^{-3}$.

4.5.3. Di(μ-chloro)dichloro-bis(μ$_3$-phenylselenolato)-bis(μ-phenylselenolato)-tetracarbonyltetrakis(triphenylphosphine)tetraruthenium(II)

Allyl phenyl selenide (5 mmol) and [$RuClH(CO)(PPh_3)_3$] (0.5 mmol) were heated in boiling benzene (10 cm^3) for 3 h. The solvent was evaporated on a vacuum rotary evaporator, then the excess of selenide and other soluble compounds were removed from the residue using repeated extraction with hexane. Yellow-orange solid residue (450 mg) was dissolved in benzene–dichloromethane mixture and separated on a chromatographic column filled with silica gel (100–200 mesh, 10 g). 240 mg of complex was obtained (eluent: benzene–dichloromethane, 1:1), and then crystallized from benzene–heptane mixture.

^{1}H NMR ($CDCl_3$): $\delta = 6.90$–7.75 (60H, m, C_6H_5). ^{13}C NMR: ($CDCl_3$): $\delta = 120.4$ (s, C_{Ar}), 120.8 (s, C_{Ar}), 127.8 (t, $J_{P-C} = 5.0$, C_{Ar}), 129.7 (s, C_{Ar}), 131.8 (s, C_{Ar}), 133.4 (t, $J_{P-C} = 21.6$, C_{Ar}), 134.6 (t, $J_{P-C} = 5.0$, C_{Ar}), 177.2 (t, $J_{P-C} = 4.0$, Ru–CO). ^{31}P NMR: ($CDCl_3$) $\delta = 26.1$ (2P, d, $J = 18.1$), 49.9 (1P, d, $J = 18.1$).

4.5.4. Crystal data for the ruthenium complex with allyl phenyl selenide

The crystal chosen for X-ray analysis was a clear orange block with the approximate dimensions 0.3 mm × 0.4 mm × 0.5 mm. $C_{51}H_{40}Cl_4O_2P_2Ru_2Se_2$ (1248.63 g mol^{-1}) crystallizes in the monoclinic system, space group $P2_1/c$, with a = 12.052(2) Å, b = 24.448(5) Å, c = 16.378(3) Å, β = 105.38(3)°, V = 105.38(3) Å^3, Z = 4, μ(Mo Kα) = 2.44 mm^{-1}, and D_{calcd} = 1.783 g cm^{-3}. The e.s.d. unit cell parameters were determined by least-squares refinement using 44 centered reflections within $2^\circ < \Theta < 16^\circ$. A total of 8505 reflections were collected to $2\Theta_{max} = 50.12^\circ$ (h, $-13 \rightarrow 13$; k, $0 \rightarrow 29$; l, $0 \rightarrow 19$), of which 7969 were unique. The intensity decay of the reference reflections was 40.9%. In refinements, weights were used according to the scheme $w = 1/[\sigma^2(F_o^2) + (0.10\ P)^2]$, where $P = (F_o^2 + 2\ F_c^2)/3$. The refinement of 553 parameters has led to the final agreement factors R = 0.0820, R_w = 0.2351, and S = 1.155 for 3469 observed reflections with $F > 4\sigma(F_o)$;. The electron density of the largest difference peak was found to be 1.69 Einstein Å^{-3}, while that of the largest difference hole was −2.20 Einstein Å^{-3}.

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