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Isomerization of alkyl allyl and allyl silyl ethers catalyzed by ruthenium complexes

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Abstract

The results of double-bond migration in alkyl allyl and allyl silyl ethers catalyzed by ruthenium complexes [$RuClH(CO)(PPh_3)_3$] and in situ forming catalytic system {[$RuCl_2(cod)]_x$} with hydride and a phosphine) are presented. The conversion of allyl to 1-propenyl ethers is quantitative. The mechanism of double-bond migration has been investigated on deuterated reagents. It has been proved that the reaction is consistent with hydride mechanism, which encompasses addition and elimination of Ru–H and intermolecular exchange of hydrogen. We are presenting the first literature description of the direct recycling investigation of ruthenium catalyst for double-bond migration. The recycling has been investigated on model reaction of isomerization of 1,4-diallyloxybutane with [$RuClH(CO)(PPh_3)_3$]. It has been shown that fivefold recycle of the catalyst was successful. In the recycling investigation it has been found that the highest activity loss occurred after first use of the catalyst.

Keywords: Alkyl allyl ethers; Double-bond migration; Isomerization; Isomerization mechanism; 1-Propenyl ethers; Vinyl ethers

1. Introduction

Cationic photopolymerized 1-propenyl ethers are of increasing importance in many industrial fields, particularly in production of various protecting and decorative coatings, inks, adhesives [1–3]. Synthesis of 1-propenyl ethers might be easily achieved by isomerization of allyl ethers in the presence of bases [4,5] and various transition metal complexes [6–9]. Ruthenium hydride complexes belong to the most active catalysts in these reactions, what we have also shown by catalytic isomerization of allyl aryl ethers [10–12]. Moreover, application of ruthenium complexes is one of the most convenient and universal methods of synthesis 1-propenyl systems [13–15]. Source allyl ethers are commercially available or easy to synthesize. Also, double-bond migration catalyzed by simple ruthenium complexes is often applied in many syntheses [16,17] or as one of the steps of the tandem isomerization-RCM [18–23]. Here, we present our results of double-bond migration in alkyl allyl ethers catalyzed by [$RuClH(CO)(PPh_3)_3$]. We have successful results in isomerization of simple alkyl allyl and polyallyl ethers and allyl silyl ether. We have compared the reactivity of ethers in isomerization vs. structure of alkyl chain. Basing on reactions on deuterated species we have assigned the dominance of hydride mechanism. We were also trying to influence the stereoselectivity of isomerization of allyl *t*-butyldimethylsilyl ether. Finally, we present the results of the catalyst recycling.

2. Experimental

2.1. General procedures and starting materials

All reactions were performed under dry argon atmosphere. Solvents were dried with appropriate drying agents (molecular sieves, CaH_2 or Na) and distilled prior to use. NMR spectra were taken on a Varian Unity Inova 300 MHz (unless otherwise stated) spectrometer at room temperature. GC/MS analysis conditions: GC/MS system: GC trace with MS trace (THERMO FINNIGAN); injector: split/splitless injector with 4 mm deactivated glass liner, injector temperature 280 °C; autosampler: CombiPAL (CTC), sample volume: 0.5 μl; GC column: MDN

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5S (Supelco) 30 m × 0.25 mm × 0.25 μm; flow: constant pressure 100 kPa; temperature program: 40 °C for 1 min, 40–220 °C, 12 °C/min, 220 °C—8 min; transfer line: direct coupling to MS ion source, 250 °C constant; mass spectrometer: EI mode 70 eV ion source at 200 °C.

Ruthenium complexes were synthesized according to literature procedures: $[RuClH(CO)(PPh_3)_3]$ [41,42], $[RuCl_2(PPh_3)_3]$ [43], $\{[RuCl_2(cod)]_x\}$ [44].

The general procedure of the synthesis of alkyl allyl ethers: PTC catalysis in conditions enabling complete allylation of glycols [45–47]: powdered NaOH (2.5 mol per mole of hydroxyl group) and water (the same mass as NaOH) was placed in a round-bottomed flask equipped with a mechanic stirrer and condenser. During stirring, alcohol or glycol was added and the mixture was heated to 60 °C in water bath resulting in viscous slurry. Next, tetrabutylammonium hydrogensulfate (3% molar on each mole hydroxyl group) and allyl chloride (1.75 mol per mole of hydroxyl group) were introduced through the condenser. The mixture was kept under reflux and stirring for 5 h and left cold overnight. The formed two layers were separated, the aqueous layer was extracted with pentane. The organic layers were combined, dried over anhydrous $MgSO_4$ and the volatile residues were distilled off on a rotatory evaporator. The crude product was distilled giving at least 80% yield of pure ether (>98% based on GC).

All other reagents: CaH_2, $Li[AlH_4]$, deuterated reagents were purchased at Aldrich, Lancaster and Acros.

2.2. General procedure of isomerization

Isomerization has been carried out in screw-capped ampoules in scale 0.5–50 mmol. Substrate–alkyl allyl ether has been placed into the ampoule together with given amount of pre-catalyst and solvent, if necessary. The reaction mixture was purged with dry argon by bubbling through the solution for 1 min. After tight screwing, the ampoule was placed into a thermostated (±0.5 °C) oil bath, where it was kept for given period of time. Next, the ampoule was cooled down, solvent evaporated if necessary, and the residue was taken for NMR analysis. In order to remove majority of ruthenium complexes, the organic product was extracted with pentane or petroleum ether, while ruthenium complexes remained undissolved. The mixture was filtered and the traces of ruthenium complexes were removed by one of the following methods: (a) evaporation of solvent and distillation (for isomerization products of ethers 1, 2, 3, 4, 6 and 7); (b) adsorption of the catalyst on a functionalized siliceous foam [12] using 25 mg of the foam on each 1 mg of the initial amount of ruthenium pre-catalyst (for isomerization products of ether 5 and 11) then evaporation of solvent; (c) adsorption of the catalyst on charcoal using 50 mg of charcoal on each 1 mg of the initial amount of ruthenium pre-catalyst (for isomerization products of ether 20) then evaporation of solvent.

In a preparative scale (25–250 mmol) the reaction was carried out in round-bottom flask with argon flow and condenser. After similar treatment as described above, the crude product was distilled.

2.3. Competitive reactions method of comparison of isomerization rates of plain diallyl ethers

Allylbenzene (1.18–1.75 mmol), alkyl diallyl ether (equimolar amount as allylbenzene) together with $[RuClH(CO)(PPh_3)_3]$ (0.5% molar to the sum of ethers) were placed in dry THF (2 cm^3) in a screw-capped ampoule. The reaction mixture was purged with argon for 1 min. The screwed-capped ampoule was submerged in an oil bath (60 °C) for 0.5–2 h. Next, ^1H NMR spectrum was taken from the reaction mixture.

2.4. Typical procedure for [Ru]-catalyzed isomerization of 1,4-diallyloxybutane with recycling of catalyst

The process was carried out under argon atmosphere in a 100 ml reactor equipped with a dropping funnel and a magnetic stirrer. The allyl ether (0.24 mol, 40.86 g) and catalyst precursor (0.2 mol.%, 456.8 mg) were charged into the reactor and the reactants were stirred at 120 °C for 4 min. The quantitative yield of 1-propenyl compound was achieved. The main product was isolated from the post-reaction mixture by distillation above catalyst at reaction temperature of 120 °C under reduced pressure, usually 10 mmHg (Run 1). The ruthenium catalyst remained in the reactor during the distillation step. After complete distillation, a new portion of allyl substrate was directly introduced into the reaction vessel containing the catalyst and about 2% distillation residue and a new catalytic reaction was started. These operations, i.e. isomerization and distillation, were repeated several times. The reaction time of 2–5 Runs equals 60 min. Substrate conversions were quantitative.

2.5. Synthesis of allyl silyl ethers (9)–(12)

General procedure of the synthesis allyl silyl ethers: sonochemical reactions involving *O*-silylation of homoallyloxyalcohols with chlorosilanes (chlorotrimethylsilane or dichlorodimethylsilane) under ultrasound irradiation under an argon atmosphere [48].

2.6. Allyl triphenylmethyl ether (allyl trityl ether) (5)

In an Erlenmeyer flask allyl alcohol (5.0 g; 45.4 mmol), pyridine (50 cm^3) and trityl chloride (12.6 g; 45.4 mmol). were placed. The mixture was stirred until homogenization and then kept in room temperature without stirring for 5 days. The precipitate of pyridine hydrochloride was filtered off, volatile fractions were evaporated under vacuum and the crude product was recrystallized from hexane yielding in 13.3 g (83%) of pure allyl trityl ether. mp 69–71 °C ^1H NMR ($CDCl_3$): 3.61 (ddd, 2H, J = 5.1, 1.5, 1.5, O–CH_2), 5.16 (ddt, 1H, J = 10.5, 1.5, 1.5, (*E*) =CH_2), 5.42 (ddt, 1H, J = 15.6, 1.5, 1.5, (*Z*) =CH_2), 5.94 (ddt, 1H, J = 15.6, 10.5, 5.1, C<u>H</u>=CH_2), 7.19–7.50 (m, 15H, Ph). ^{13}C NMR ($CDCl_3$): 65.1 (O–CH_2), 86.8 (O–C), 115.3, 127.0, 127.8, 128.6, 135.1, 144.2 (–CH=CH_2 and Ph). MS (*m*/*q*, int (%)): 300 (2) M^+, 244 (25), 243 (31), 223 (14), 215 (28), 165 (32), 120 (31), 119 (33), 106 (12), 105 (100), 77 (52), 51 (11).

2.7. (1,1-d_2-Allyl) triphenylmethyl ether [(1,1-d_2-allyl) trityl ether]

mp 73–75 °C. ^{1}H NMR ($CDCl_3$): 5.16(dd, 1H, J = 10.5, 1.5, (*E*) =CH_2), 5.42 (dd, 1H, J = 15.6, 1.5, (*Z*) =CH_2), 5.94 (dd, 1H, J = 15.6, 10.5, C<u>H</u>=CH_2), 7.19–7.50 (m, 15H, Ph). ^{2}H NMR (THF): 3.02 (s, O–CD_2). ^{13}C NMR ($CDCl_3$): 65.1 (q, O–CD_2), 86.8 (O–C), 115.5 (=CH_2), 127.0, 127.8, 128.6, (Ph), 135.0 (CD_2–<u>C</u>=), 144.2 (C_1–Ar). MS (*m*/*q*, int (%)): 302 (2) M^+, 245 (24), 244 (17), 243 (48), 242 (18), 241 (25), 239 (16), 225 (17), 166 (15), 165 (41), 120 (10), 119 (10), 105 (100), 77 (34), 57 (15).

2.8. (1,1-d_2-Allyl)-alcohol

Synthesis of (1,1-d_2-allyl) alcohol is a modification of the method described in the literature [49]. A slurry of Li[AlD_4] (5 g, 0.13 mol) in dry ether (250 ml) was prepared under a nitrogen atmosphere. After cooling the stirred slurry in an ice bath a solution of acryloyl chloride (16.7 g, 0.21 mole) in ether (85 ml) was slowly added permitting the temperature to be maintained below 5 °C. The mixture was then stirred at room temperature for 2 h. After chilling the slurry in an ice bath water (6 ml), 15% NaOH (6 ml) and again water (6 ml) were added dropwise. The white precipitate was removed by filtration and then washed with ether. The combined filtrate was dried with anhydrous Na_2SO_4, concentrated by distillation and dried again with Na_2SO_4. After following distillation 3.4 g (88% yield) of allyl-1-d_2-alcohol was obtained, bp = 96–98 °C/760 mm. NMR and MS data are given in the literature [49,50].

2.9. (1,1-d_2-Allyl) benzyl ether

In a round-bottomed flask equipped with a condenser (1,1-d_2-allyl) alcohol (3.0 g, 50 mmole), benzene (30 ml), Bu_4NHSO_4 (0.7 g, 2.1 mmole) and 50% aq NaOH (12.8 g, 0.16 mol) were placed. Benzyl chloride (4.6 ml, 36 mmol) was then added dropwise within 0.5 h. Next, the mixture was heated in 60 °C for 3 h. After the mixture was cooled water (40 ml) was added and the product was extracted with pentane (40 ml). The organic layer was dried with anhydrous $MgSO_4$ and then decolorized with active coal. Solvents were evaporated and the product was purified by vacuum distillation (92–96 °C/8 mm).

^{1}H NMR ($CDCl_3$): 4.52 (s, 2H, –CH_2–), 5.21 (dd, 1H, J = 10.2, 1.5, (*Z*) =CH_2), 5.31 (dd, 1H, J = 17.4, 1.5, (*E*) =CH_2), 5.95 (dd, J = 17.4, 10.5, CH=C<u>H</u>$_2$), 7.21–7.38 (m, 5H, Ph). ^{2}H NMR (THF): 4.03 (s, O–CD_2). ^{13}C NMR ($CDCl_3$): 54.2 (q, O–CD_2), 72.2 (–CH_2–), 117.1 (=CH_2), 127.7, 127.8, 127.9, 128.5 (Ph), 135.0 (CD_2–<u>C</u>=), 138.5 (C_1–Ar). MS (40 eV, *m*/*q*, int (%)): 150 (2) M^+, 149 (6), 107 (27), 93 (51), 91 (100), 79 (32), 77 (28), 65 (28), 51 (7).

2.10. 1,2-Propandiol diallyl ether (18)

bp 168–171 °C. ^{1}H NMR ($CDCl_3$): 1.16 (d, 3H, J = 6.0, CH_3), 3.42 (d, 2H, J = 5.7, O–CH–C<u>H</u>$_2$–O), 3.66 (tq, 1H, J = 6.0, 5.7, O–C<u>H</u>–CH_2–O), 4.01 (dt, 2H, J = 4.2, 1.2, CH_2–O–C<u>H</u>$_2$–CH=CH_2), 4.07 (dt, 2H, J = 4.2, 1.2, CH–O–C<u>H</u>$_2$–CH=CH_2), 5.13(ddt, 2H, J = 7.2, 1.2, 1.2, (*E*)-CH_2–O–CH_2–CH=C<u>H</u>$_2$), 5.17 (ddt, 2H, J = 7.2, 1.2, 1.2, (*E*)-CH–O–CH_2–CH=C<u>H</u>$_2$), 5.25 (ddt, 2H, J = 17.1, 1.2, 1.2, (*Z*)-CH_2–O–CH_2–CH=C<u>H</u>$_2$), 5.25 (ddt,2H, J = 17.1, 1.2, 1.2, (*Z*)-CH–O–CH_2–CH=C<u>H</u>$_2$), 5.88 (ddt, 1H, J = 17.1, 7.2, 4.2, CH_2–O–CH_2–C<u>H</u>=CH_2), 5.94 (ddt, 1H, J = 17.1, 7.2, 4.2, CH_2–O–CH_2–C<u>H</u>=CH_2). ^{13}C NMR ($CDCl_3$): 17.3 (CH_3), 70.2 (O–CH–<u>C</u>H_2–O), 72.3 (O–<u>C</u>H–CH_2–O), 73.9 (CH_2–O–<u>C</u>H_2–CH=), 74.2 (CH–O–<u>C</u>H_2–CH=), 116.4 (CH_2–O–CH_2–CH=<u>C</u>H_2), 116.7 (CH–O–CH_2–CH=<u>C</u>H_2), 134.9 (CH_2–O–CH_2–<u>C</u>H=CH_2), 135.4 (CH–O–CH_2–<u>C</u>H=CH_2). MS (*m*/*q*, int (%)): 156 (5) M^+, 99 (12), 87 (37), 86 (13), 85 (100), 81 (15), 67 (16), 59 (20), 58 (16), 57 (98), 54 (20), 52 (22).

2.11. 2,3-Butandiol diallyl ether (19)

bp 93–95 °C/44 mmHg. ^{1}H NMR ($CDCl_3$): 1.11 (d, 6H, J = 6.3, CH_3), 3.50 (dq, 2H, J = 6.3, 4.5 O–CH–CH–O), 4.05 (ddd, 4H, J = 5.7, 1.5, 1.5 –O–C<u>H</u>$_2$–CH=), 5.13(ddt, 2H, J = 9.0, 1.5, 1.5, (*E*) =CH_2), 5.26 (ddt, 2H, J = 17.1, 1.5, 1.5, (*Z*) =CH_2), 5.90 (ddt, 2H, J = 17.1, 9.0, 5.7, –O–CH_2–C<u>H</u>=). ^{13}C NMR ($CDCl_3$): 14.9 (CH_3), 70.4 (O–CH–CH–O), 77.0 (–O–<u>C</u>H_2–CH=), 116.3 (=CH_2), 135.5 (–O–CH_2–<u>C</u>H=). MS (*m*/*q*, int (%)): 170 (1) M^+, 85 (32), 43 (55), 41 (100), 39 (18).

2.12. 1,2,3-Triallyloxypropane (20)

bp 102–103 °C/8 mmHg. ^{1}H NMR ($CDCl_3$): δ = 3.42–3.60 (m, 5H, C<u>H</u>$_2$–C<u>H</u>–C<u>H</u>$_2$), 4.01 (ddd, 4H, J = 6.0, 1.5, 1.5, CH_2–O–C<u>H</u>$_2$–CH=) 4.02 (ddd, 2H, J = 6.0, 1.5, 1.5, CH–O–C<u>H</u>$_2$–CH=), 5.17 (ddq, 1H, J = 10.2, 1.5, 1.5, (*E*) CH–O–CH_2–CH=C<u>H</u>$_2$), 5.19 (ddq, 2H, J = 10.2, 1.5, 1.5, (*E*) CH_2–O–CH_2–CH=C<u>H</u>$_2$), 5.27 (ddq, 2H, J = 17.4, 1.5, 1.5, (*Z*)-CH_2–O–CH_2–CH=C<u>H</u>$_2$), 5.28 (ddq, 1H, J = 17.4, 1.5, 1.5, (*Z*) CH–O–CH_2–CH=C<u>H</u>$_2$), 5.90 (ddq, 2H, J = 17.4, 10.2, 6.0, CH_2–O–CH_2–C<u>H</u>=), 5.91 (ddq, 1H, J = 17.4, 10.2, 6.0, CH–O–CH_2–C<u>H</u>=). ^{13}C NMR ($CDCl_3$): δ = 71.3, 72.3, 77.1, 77.9 (CH_2–CH–CH_2 and O–CH_2), 116.8, 116.9 (=CH_2), 134.8, 135.2 (CH_2–<u>C</u>H=). MS (*m*/*q*, int (%)): 213 (1) M^+, 83 (6), 81 (34), 79 (7), 73 (11), 57 (9), 55 (14), 43 (12), 42 (7), 41 (100), 39 (20).

2.13. (Z)-(1-Propenyl) triphenylmethyl ether, (Z)-[(1-propenyl) trityl ether]

^{1}H NMR ($CDCl_3$): δ = 1.28 (dd, 3H, J = 6.9, 1.8, (*E*) CH_3), 1.70 (dd, 3H, J = 6.9, 1.8, (*Z*) CH_3), 4.4 (dq, 1H, J = 6.9, 6.9, (*Z*) =C<u>H</u>–CH_3), 5.26 (dq, 1H, J = 12.0, 6.9, (*E*) =CH–CH_3), 6.13 (dq, 1H, J = 6.9, 1.8, (*Z*) O–CH=), 6.22 (dq, 1H, J = 12.0, 1.8, (*E*) O–CH=), 6.82–7.85 (m, 15H, Ph). ^{13}C NMR ($CDCl_3$): δ = 9.7 (CH_3), 88.3 (Ph_3<u>C</u>–), 101.9 (=<u>C</u>H–CH_3), 127.2, 127.8, 128.6 (Ph), 144.3 (O–<u>C</u>H=). MS (*m*/*q*, int (%)): 300 (5) M^+, 271 (100), 241 (10), 193 (8), 178 (28), 165 (42), 152 (14), 71 (7).

2.14. (E + Z) Cyclohexyl (1-propenyl) ether

^{1}H NMR ($CDCl_3$): δ = 1.14–1.95 (m, 11H, (*Z*) + (*E*) $C_{cyclohex}$-H), 1.53 (dd, 3H, *J* = 5.4, 1.5, (*E*) CH_3), 1.59 (dd, 3H, *J* = 5.4, 1.8, (*Z*) CH_3), 4.38 (dq, 1H, *J* = 5.4, 5.4, (*Z*) =C<u>H</u>–CH_3), 4.88 (dq, 1H, *J* = 12.2, 5.4, (*E*) =C<u>H</u>–CH_3), 6.99 (dq, 1H, *J* = 5.4, 1.8, (*Z*) O–C<u>H</u>=), 6.09 (dq, 1H, *J* = 12.2, 1.5, (*E*) O–C<u>H</u>=). ^{13}C NMR ($CDCl_3$): δ = 9.3 ((*Z*) CH_3), 12.5 ((*E*) CH_3), 23.7 ((*Z*) $C_{cyclohex}$-4), 23.8 ((*E*) $C_{cyclohex}$-4), 25.6 ((*Z*) $C_{cyclohex}$-3), 25.6 ((*E*) $C_{cyclohex}$-3), 32.2 ((*E*) $C_{cyclohex}$-2), 32.4 ((*Z*) $C_{cyclohex}$-2), 77.9 ((*Z*) + (*E*) $C_{cyclohex}$-1), 100.5 ((*E*) =<u>C</u>H–CH_3), 101.0 ((*Z*) =<u>C</u>H–CH_3), 144.2 ((*Z*) O–<u>C</u>H=), 145.2 ((*E*) O–<u>C</u>H=). MS (*m*/*q*, int (%)): (*Z*)-cyclohexyl(1-propenyl)ether: 140 (18) M^+, 83 (22), 82 (29), 81 (14), 67 (59), 58 (100), 56 (81), 54 (11); (*E*)-cyclohexyl (1-propenyl) ether: 140 (16) M^+, 83 (18), 82 (25), 81 (14), 67:57), 58 (100), 56 (78), 54 (10).

2.15. (E + Z) t-Butyldimethyl(1-propenyloxy)silane

^{1}H NMR ($CDCl_3$): δ = 0.0 (s, 6H, Me_2Si), 0.78–0.82 (m, 9H, *t*-BuSi), 1.38 (dd, 3H, *J* = 6.6, 1.5, (*E*) C<u>H</u>$_3$–CH=), 1.45 (dd, 3H, *J* = 6.6, 1.8, C<u>H</u>$_3$–CH=), 4.37 (dq, 1H, *J* = 6.6, 6.6, (*Z*) =C<u>H</u>–CH_3), 4.85 (dq, 1H, *J* = 12.0, 6.6, (*E*) =C<u>H</u>–CH_3), 6.06 (dq, 1H, *J* = 6.6, 1.5, (*Z*) O–C<u>H</u>=), 6.08 (dq, 1H, *J* = 12.0, 1.5, (*E*) O–C<u>H</u>=). ^{13}C NMR ($CDCl_3$): δ = −5.4 ((*Z*) Me_2Si), −5.2 ((*E*) Me_2Si), 8.9 ((*Z*) CH_3–CH=), 12.1 ((*E*) CH_3–CH=), 18.3 (Si<u>C</u>Me$_3$) 25.6 ((*Z*)SiC<u>Me</u>$_3$), 25.7 ((*E*) SiC<u>Me</u>$_3$), 104.8 ((*Z*) =<u>C</u>H–CH_3), 105.7 ((*E*) =<u>C</u>H–CH_3), 139.2 ((*Z*) O–<u>C</u>H=), 148.5 ((*E*) O–<u>C</u>H=). MS the same spectrum for each of the isomers (*m*/*q*, int (%)): 172 (18) M^+, 116 (14), 115 (100), 99 (14), 87 (15), 85 (54), 75 (33), 73 (13), 61 (8), 59(38).

2.16. (Z,Z)-, (Z,E)- and (E,E)-bis[4-(1-propenyloxy)butoxy] dimethylsilane

^{1}H NMR (400 Hz, $CDCl_3$): δ = 0.08 (s, 3H, –Si–CH_3), 1.52, 1.55 (dd, 3H, C<u>H</u>$_3$–CH=), 1.60–1.70 (m, 4H, –C<u>H</u>$_2$–C<u>H</u>$_2$–), 3.60–3.73 (m, 4H, –O–C<u>H</u>$_2$–CH_2–CH_2–C<u>H</u>$_2$–O–), 4.34 (dt, 1H, *J* = 6.6, (*Z*)-CH_3–C<u>H</u>=CH–), 4.73 (dt, 1H, *J* = 12.9, (*E*)-CH_3–C<u>H</u>=CH), 5.91 (dt, 1H, *J* = 6.2, (*Z*)-CH_3–CH=C<u>H</u>–), 6.18 (d, 1H, *J* = 12.6, (*E*)-CH_3–CH=C<u>H</u>–). ^{13}C NMR (100 Hz, $CDCl_3$): δ = −3.3 (–Si–CH_3), 9.2, 12.6 (<u>C</u>H$_3$–CH=), 25.8, 26.3 (=CH–O–CH_2–<u>C</u>H$_2$–), 28.9 (–<u>C</u>H$_2$–CH_2–O–Si–), 62.1 (–<u>C</u>H$_2$–O–Si–), 68.8, 71.7 (=CH–O–<u>C</u>H$_2$–), 98.3, 100.8 (CH_3–<u>C</u>H=CH), 145.5, 146.5 (CH_3–CH=<u>C</u>H–). MS (*m*/*q*, int (%)): (*Z,Z*)-bis[4-(1-propenyloxy)butoxy)]dimetylosilane: 316 (0.02) M^+, 145 (100), 75 (90), 115 (80), 101 (68), 55 (61), 32 (49), 59 (43), 71 (32), 57 (29). (*Z,E*)-bis[4-(1-propenyloxy)butoxy)]dimetylosilane: 316 (0.02) M^+, 145 (100), 75 (82), 115 (76), 101 (65), 55 (57), 32 (48), 41 (42), 59 (40). (*E,E*)-bis[4-(1-propenyloxy)butoxy)]dimetylosilane: 316 (0.02) M^+, 75 (100), 145 (99), 101 (80), 115 (80), 55 (77), 41 (70), 59 (53), 58 (50).

2.17. (Z,E)-Trimethyl-4-[(1-propenyloxy)butoxy]silane

^{1}H NMR (400 Hz, $CDCl_3$): δ = 0.11 (s, 9H, –Si–O–CH_3), 1.57, 1.54 (dd, 3H, (*Z*) and (*E*)-C<u>H</u>$_3$–CH=), 1.60–1.67 (m, 4H, –C<u>H</u>$_2$–C<u>H</u>$_2$–), 3.59–3.75 (m, 4H, –O–C<u>H</u>$_2$–CH_2–CH_2–C<u>H</u>$_2$–O–), 4.35 (dt, 1H, *J* = 6.5, (*Z*)-CH_3–C<u>H</u>=CH–), 4.74 (dt, 1H, *J* = 12.9, (*E*)-CH_3–C<u>H</u>=CH), 5.92 (dt, 1H, *J* = 6.2, (*Z*)-CH_3–CH=C<u>H</u>–), 6.21 (d, 1H, *J* = 12.0, (*E*)-CH_3–CH=C<u>H</u>–).

^{13}C NMR (100 Hz, $CDCl_3$): δ = 0.0 (–Si–O–CH_3), 9.7, 13.1 (<u>C</u>H$_3$–CH=), 26.4, 26.9 (=CH–O–CH_2–<u>C</u>H$_2$–), 29.7 (–<u>C</u>H$_2$–CH_2–O–Si–), 62.7 (–<u>C</u>H$_2$–O–Si–), 69.3, 72.2 (=CH–O–<u>C</u>H$_2$–), 98.7, 101.3 (CH_3–<u>C</u>H=CH), 146.0, 147.1 (CH_3–CH=<u>C</u>H–). MS (*m*/*q*, int (%)):(*Z*)-trimethyl-4-[(1-propenyloxy)butoxy]silane: 202 (0.05) M^+, 73 (100), 145 (38), 103 (35), 75 (20), 55 (19), 115 (18), 45 (14), 59 (11), 41 (10), 101 (10), 43 (8). (*E*)-trimethyl-4-[(1-propenyloxy)butoxy]silane: 202 (0.12) M^+, 73 (100), 103 (30), 145 (26), 75 (23), 55 (22), 115 (16), 45 (16), 59 (15), 41 (12), 101 (11), 43 (10).

2.18. Trimethyl-4-[(1-propenyloxy)butenoxy]silane (mixture of all isomers)

^{1}H NMR (400 Hz, $CDCl_3$): δ = 0.17, 0.23 (s, 9H, –Si–O–C<u>H</u>$_3$), 1.51–1.70 (m, 3H, (*Z*) and (*E*)-C<u>H</u>$_3$–CH=), 2.18–2.49 (m, 2H, –=CH–C<u>H</u>$_2$–CH_2–O–), 3.58–3.76 (m, 2H, –CH_2–C<u>H</u>$_2$–O–), 4.42 (quintet, 1H, *J* = 6.6, (*Z*)-CH_3–C<u>H</u>=CH–), 4.82 (dt, 1H, *J* = 12.9, (*E*)-CH_3–C<u>H</u>=CH), 5.04–5.12, 4.56–4.67 (*m*, 1H, (*Z*) and (*E*)-O–CH=C<u>H</u>–CH_2–), 5.95–6.03 (*m*, 1H, (*Z*)-CH_3–CH=C<u>H</u>–), 6.15–6.36 (m, 1H, (*Z*) and (*E*)-O–C<u>H</u>=CH–), 6.37 (d, 1H, *J* = 12.5, (*E*)-CH_3–CH=C<u>H</u>–). ^{13}C NMR (100 Hz, $CDCl_3$): δ = 0.1, 2.5 (–Si–O–C<u>H</u>$_3$), 9.8, 12.9 (<u>C</u>H$_3$–CH=), 28.3, 31.5 (=CH–<u>C</u>H$_2$–CH_2–O–Si–), 62.7, 63.6 (–<u>C</u>H$_2$–O–Si–), 98.9, 101.3 (*Z,E*)-CH_3–<u>C</u>H=CH), 103.6, 105.1 ((*Z*) and (*E*)-O–CH=<u>C</u>H–), 140.1–147.1 ((*Z*) and (*E*)-CH_3–CH=<u>C</u>H–, (*Z*) and (*E*)-O–<u>C</u>H=CH–). MS (*m*/*q*, int (%)): 200 (12.3) M^+, 143 (44), 130 (14), 115 (12), 103 (41), 99 (13), 75 (20), 73 (100), 41 (8).

2.19. (Z,E)-Trimethyl-2-[(1-propenyloxy)ethoxy]silane

^{1}H NMR (400 Hz, $CDCl_3$):): δ = 0.06 (s, 9H, –Si–O–C(C<u>H</u>)$_3$), 1.47, 1.50 (dd, 3H, C<u>H</u>$_3$–), 3.62–3.74 (m, 4H, –C<u>H</u>$_2$–C<u>H</u>$_2$–), 4.29 (quintet, 1H, *J* = 6.6, (*Z*)-CH_3–C<u>H</u>=CH–), 4.69 (dt, 1H, *J* = 12.9, (*E*)-CH_3–C<u>H</u>=CH–), 5.89 (dt, 1H, *J* = 6.2, (*Z*)-CH_3–CH=C<u>H</u>–), 6.17 (d, 1H, *J* = 12.6, (*E*)-CH_3–CH=C<u>H</u>–). ^{13}C NMR (100 Hz, $CDCl_3$): δ = 0.0 (–Si–O–CH_3), 9.8, 13.1 (<u>C</u>H$_3$–CH=), 62.0, 62.5 (–<u>C</u>H$_2$–<u>C</u>H$_2$–), 70.7, 73.7 (=CH–O–<u>C</u>H$_2$–), 99.0, 101.3 (CH_3–<u>C</u>H=CH), 146.0, 147.1 (CH_3–CH=<u>C</u>H–).

2.20. 1,2-Bis(1-propenyloxy)propane (mixture of all isomers)

^{1}H NMR ($CDCl_3$): δ = 1.23 (d, 3H, *J* = 6.3, C<u>H</u>$_3$–CH_2), 1.52–1.59 (m, 6H, CH_3 1-propenyl groups) 3.58–4.00 (m, 3H, CH_2–CH), 4.39 (dq, *J* = 6.6, 6.6, CH_3–C<u>H</u>=), 4.40 (dq, *J* = 6.6, 6.6, CH_3–C<u>H</u>=), 4.76 (dq, *J* = 12.6, 6.6, CH_3–C<u>H</u>=), 4.77 (dq, *J* = 12.6, 6.6, CH_3–C<u>H</u>=), 5.98 (dq, *J* = 12.6, 1.2, =CH–O), 5.98 (dq, *J* = 12.6, 1.2, =CH–O), 6.11 (dq, *J* = 6.6, 1.2, =CH–O),

6.23 (dq, $J = 6.6$, 1.2, =CH–O). ^{13}C NMR ($CDCl_3$): $\delta = 9.2$, 9.3 ((*Z*) CH_3), 12.4, 12.5 ((*E*) CH_3), 16.9, 17.0, 17.3, 17.4 ($\underline{C}H_3$–CH–CH_2), 71.9, 72.3, 74.4, 74.9, 75.0, 75.1, 75.8, 76.3 ($\underline{C}H_2$–$\underline{C}H$–CH_3), 98.8, 101.0, 101.1, 101.3, 101.4, 101.7, 101.8 (=$\underline{C}H$–CH_3), 144.4, 144.5, 145.3, 145.5, 145.7, 145.8, 146.5, 146.6 (O–$\underline{C}H$=). MS (*m/q*, int (%)): 156 (1) M^+, 115 (9), 100 (31), 59 (100), 58 (15), 57 (35), 45 (15), 43 (67), 41 (82), 39 (34).

2.21. 2,3-Bis(1-propenyloxy)butane (mixture of all isomers)

^{1}H NMR ($CDCl_3$): $\delta = 1.15$ (d, $J = 6.0$, $C\underline{H}_3$–CH–CH–$C\underline{H}_3$), 1.17 (d, $J = 6.0$, $C\underline{H}_3$–CH–CH–$C\underline{H}_3$), 1.51 (dd, $J = 6.6$, 1.5 $C\underline{H}_3$–CH=), 1.55 (dd, $J = 6.6$, 1.5 $C\underline{H}_3$–CH=), 3.72–3.84 (m, 2H, CH_3–$C\underline{H}$–$C\underline{H}$–CH_3), 4.39 (dq, $J = 6.0$, 1.5, O–CH=$C\underline{H}$–), 4.87 (dq, $J = 12.3$, 1.5, O–CH=$C\underline{H}$–), 5.94 (dq, $J = 6.6$, 1.5, O–$C\underline{H}$=CH–), 5.96 (dq, $J = 6.6$, 1.5, O–$C\underline{H}$=CH–), 6.17 (dq, $J = 12.3$, 1.5, O–$C\underline{H}$=CH–). ^{13}C NMR ($CDCl_3$): $\delta = 9.1$, 9.2 ((*Z*) CH_3), 12.3 ((*E*) CH_3), 14.5, 14.8, 14.9 ($\underline{C}H_3$–CH–CH), 70.7, 70.8 (CH_3–$\underline{C}H$–$\underline{C}H$–CH_3), 100.6, 101.2, 101.3 (=$\underline{C}H$–CH_3), 144.3, 144.5, 144.6, 145.6 (O–$\underline{C}H$=). MS (*m/q*, int (%)): 170 (1) M^+, 115 (21), 114 (20), 85 (7), 73 (100), 58 (15), 57 (24), 56 (15), 55 (62), 45 (1), 43 (56), 41 (44), 39 (24).

2.22. 1,2,3-Tris(1-propenyloxy)propane (mixture of all isomers)

^{1}H NMR ($CDCl_3$): $\delta = 1.52$–1.60 (m, 3H, CH_3), 3.62–4.18 (m, 5H, CH_2–CH–CH_2), 4.44 and 4.72–5.02 (m, 3H, CH_3–$C\underline{H}$=), 5.96–5.99 (m), 6.01–6.08 (m), 6.14 (dq $J = 12.0$, 1.5) and 6.18–6.27 (m, 3H, =CH–O). ^{13}C NMR ($CDCl_3$): $\delta = 9.1$, 9.2, 9.3 ((*Z*) CH_3), 12.3, 12.4 ((*E*) CH_3), 62.4, 68.2, 69.2, 69.5, 69.7 71.0, 71.1, 72.6, 72.7, 78.8, 79.2, 80.6 (mixture of isomers CH_2–CH–CH_2), 99.1, 99.2, 99.3, 101.7, 101.7, 101.8, 101.9, 102.5, 102.6 (mixture of isomers =$\underline{C}H$–CH_3), 144.6, 144.7, 144.8, 145.6, 145.7, 145.8, 146.3, 146.4, 146.7 (mixture of isomers O–$\underline{C}H$=). MS (*m/q*, int (%)):212 (1) M^+, 156 (8), 97 (13), 71 (36), 69 (24), 57 (40), 55 (17), 43 (40), 41 (100), 39 (29).

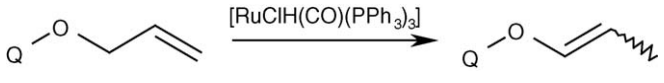
3. Discussion

3.1. Isomerization of alkyl monoallyl ethers

The reaction of double-bond migration has been the field of our research (Scheme 1).

The results of our reactions on alkyl allyl ethers are presented in Table 1.

Isomerization of plain alkyl allyl ethers occurred in moderate conditions, particularly in the presence of solvent. The solvent may accelerate the homogenization of the pre-catalyst. *Z* isomers dominated in the reaction mixture, what is in good agreement with thermodynamic stability of majority of 1-propenyl ethers [24]. Allyl trityl ether (5) isomerized to *Z* isomer almost exclusively. 2,5-Dihydrofurane (7) isomerized to the conjugated system—2,3-dihydrofuran with very low pre-catalyst concentration (0.1%) and in mild conditions. Attempts of isomerization of sililated ether with triple bond (12) failed. Most probably the addition of Ru–H to triple bond occurred, what is quite common for hydride ruthenium complexes [25,26]. Also the isomerization of allyl benzyl ether (4) was challenging—in most cases (changing temperature and reaction time) the conversion of allyl benzyl ether to 1-propenyl system was incomplete. In the meantime, precipitation of crystalline solid (yellow–orange) in the reaction mixture was observed (both allyl benzyl (4) and the product of its isomerization were liquid). It was the symptom of conversion of the catalyst with the ether to a new, inactive complex. The catalytic reaction practically ceased when the crystalline product had appeared. The difficulty of allyl benzyl ether (4) isomerization results from relatively weak C–O allyl bond, hence the alkyl (benzyl) fragment has very high stability. Nevertheless, isomerization of allyl benzyl ether was achieved by application of higher pre-catalyst concentration. The increase in the reaction temperature was not successful, due to higher contribution of side reaction—the destruction of the ether (C–O allyl bond cleavage). The later reaction has higher activation energy, thus it is more temperature sensitive.



Scheme 1.

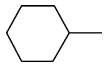
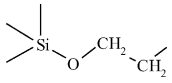
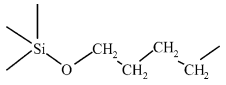
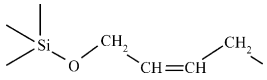
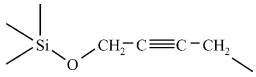
3.2. Isomerization of alkyl polyallyl ethers

We have also investigated the double-bond migration in di- and triallyl ethers (Table 2). The products of their isomerization might serve as interesting monomers for photopolymerization [27].

The double-bond migration in most of the di- and triallyl ethers occurred in mild conditions with the catalyst below 1%. Allyl (3-butenyl) ether (15) was the exception from this trend—it was necessary to add much more catalyst and apply more drastic conditions, probably due to the two-step reaction in this model: in the first step, the double-bond migration occurs to 2-butenyl system, and then to 1-butenyl—a homologue of 1-propenyl system. The post-reaction mixture consisted of all isomers of the di(1-propenyl) ethers (*Z,Z*; *E,E*; *Z,E* for symmetric ethers). The isomers were not separated, but the characteristic signals (with characteristic couplings) for *Z* and *E* 1-propenyl groups were observed on the NMR spectra. The GC analysis of the mixtures of symmetric di(1-propenyl)ethers was usually revealing three signals of approximate integrations (*Z,Z*; *E,E*; *Z,E* for symmetric ethers), and the MS spectra differed only in the intensity of fragmentation peaks.

As it has been shown, the double-bond migration of di- and triallyl ethers was an easy and convenient method of synthesis of di- and tri(1-propenyl) ethers for polymerization. The monomers are suitable for direct use in photoinitiated cationic polymerization without the necessity of removing the catalyst or further purification of the monomer; moreover Ru catalyst accelerates the polymerisation [28]. 1-Propenyl ethers have been purified mainly by distillation (under normal or reduced pressure). In

Table 1
Isomerization of alkyl monoallyl ethers (Q-O-allyl) with $[RuClH(CO)(PPh_3)_3]$

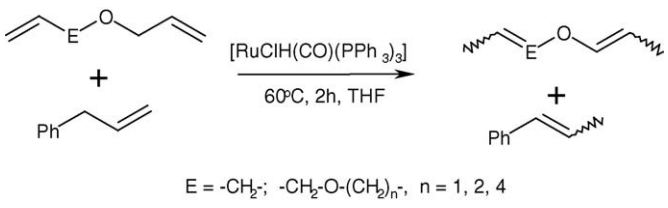
No.	*Q*	S/Ru	Solvent	*t*/τ	α; *E*/*Z*
1	Et—	200	CH_2Cl_2	60/1	100; 0.91
		200	–	80/6	100; 0.50
2	Bu—	200	THF	60/2	100; 0.34
		200	–	120/1	100; 0.67
3		200	THF	60/2	100; 0.42
4	$PhCH_2$—	80	THF	80/3	100; 0.37
5	Ph_3C—	100	THF	60/1	100; <0.014
6		400	–	80/2	100; 0.5
7		1000	–	60/1	100
8	*t*-$BuMe_2Si$—	500	THF	60/2	100; 0.34
9		200	–	80/3	100; 0.60
10		2000	–	80/2	100; 0.63
11		200	C_6H_6	60/2	100; 0.51
12		200	–	80/3	0
		200	–	120/6	11[a]

S/Ru—molar ratio: ether to pre-catalyst; *t*—reaction temperature (°C); τ—reaction time (h); α—conversion of allyl system (%); *E*/*Z*—molar ratio: *E* to *Z* isomers; a—polymerization of reaction mixture; compound (7)—2,5-dihydrofurane contains allyl system, but is not a Q group of Q-O-allyl.

the case of very high boiling point of the 1-propenyl ether (i.e. 21), the catalyst has been separated on functionalized siliceous foam, as it has been described for some aryl 1-propenyl ethers [12] and enamides [29]. In some cases, successful adsorption of catalyst has been achieved on charcoal.

For further applications, we have compared the relative rates of isomerization of diallyl ethers, where the allyloxy groups where separated by methylene chains of different length. Table 3. The competitive reaction method has been applied for that purpose Scheme 2.

The mixtures of diallyl ether and allylbenzene (molar ratio 1:1) were isomerized. The conversion of allylbenzene has been used as a reference—its parallel conversion was always very close to the conversion of the diallyl ether compared to the conversion of diallyl ether it was isomerized with (the deviation



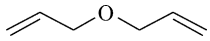
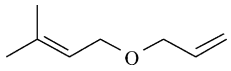
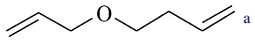
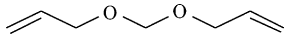
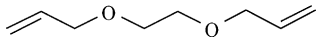
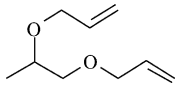
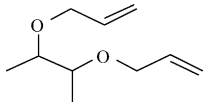
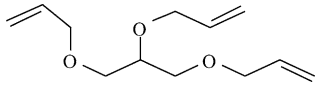
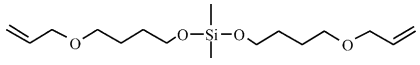
Scheme 2.

was always smaller than 10%). Basing on such a system we were able to assume that the catalytic activity of the ruthenium complex was a function of deactivating coordination (chelation) to diallyl ether. The comparison of conversion of diallyl ethers is presented in Table 3.

Diallyloxymethane underwent isomerization in the mildest conditions. Further spacing of allyloxygroups decreased the rate of isomerization. Also the conversion of isomerization of diallyl ether in the compared conditions (0.5 h) was worse than for diallyloxymethane. Diallyloxymethane shows the strongest tendency to isomerize to 1-propenyl ether, so diallyl ether is not consistent with the trend from diallyl ether to 1,4-diallyloksybutane. Most likely the ethers coordinate to metal center serving as chelating ligands and temporarily deactivating its catalytic activity Fig. 1. While diallyloxymethane (A), 1,2-diallyloxyethane (B) and 1,4-diallyloxybutane (C) might coordinate via oxygen atoms (what was also postulated by Pertici and for cyclic acetals [30] and for ethers by other researchers [31–33]).

The four-membered cycle of diallyloxymethane (A) seems to have the lowest stability, thus its formation has relatively low probability and this might explain the highest rate of its isomerization. On the other hand, five- and seven-member rings (B and C) should have similar stability, but the isomerization of 1,4-diallyloxybutane is the slowest process. The lack of two

Table 2
Isomerization of alkyl polyallyl ethers Q-(O-allyl)$_n$ with [RuClH(CO)(PPh$_3$)$_3$]

No.	Ether	S/Ru	Solvent	t/τ	α
13		127	–	100/3	100
		200	THF	60/3	100
14		100	–	80/3	100
15	 [a]	25	–	120/4	100
16	 [b]	500	THF	60/3	100
17		500	THF	60/1	100
18		500	CH_2Cl_2	60/1	100
19		200	CH_2Cl_2	60/2	100
20		100	CH_2Cl_2	60/2	100
21		200	–	80/2	100

[a] The reaction leads to the isomeric mixture of (2-butenyl) (1-propenyl) ethers with 96% selectivity.
[b] Acetal, here treated as diether; S/Ru—molar ratio: ether to pre-catalyst; t—reaction temperature (°C); τ—reaction time (h); α—conversion of allyl system (%).

oxygen atoms in diallyl ether might be the key to explain the deviation of the ether in the series. In the case of diallyl ether one should also take into account 3- or 4-dentate structures with simultaneous C=C and oxygen coordination. Perhaps quantum calculations of the stability of chelation of these ethers could help explaining the relative rates. Summarizing, we claim that the chelation in the systems is strong enough to decrease the rate of isomerization, and it limits the activity of the catalyst.

There is an interesting synthetic implication of the differences in the rates of isomerization—we have found such reaction conditions, which practically enable to isomerize diallyl ether and diallyloxymethane, whereas the other diallyl ethers (from Table 3 and probably even longer diallylethers) remained unreacted.

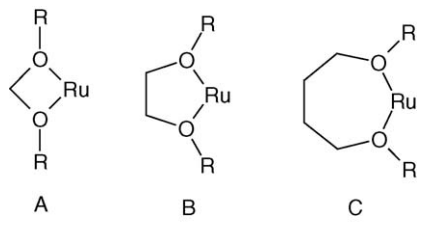


Fig. 1. R = allyl or l-propenyl.

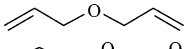
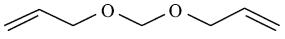
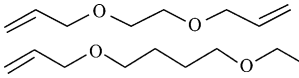
Also because of further applications for polymerization, we have compared the influence of additional methyl groups (branching) on the rate of isomerization of diallyl ethers (Table 4).

As expected, introduction of following methyl groups, thus branching the allyl system, decreased the isomerization rate. It is most likely the consequence of steric hindrance exerted on the metal center during the coordination of the allyl fragment.

3.3. Stereoselectivity of the double-bond migration

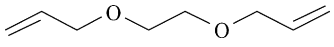
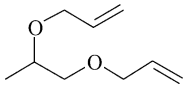
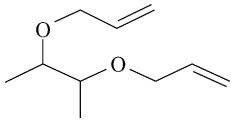
In all double-bond migration reactions (catalyzed by [RuClH(CO)(PPh$_3$)$_3$]) described herein, mixtures of *E*- and *Z*-

Table 3
Comparison of isomerization of plain diallyl ethers

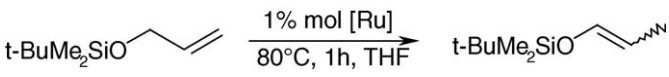
Diallyl ether	Conversion (%)		
	0.5 h	1.5 h	2 h
	35[a]	>98	–
	95	>98	
	12	17	33
	<1	3	5

Reaction conditions: 0.5% mol [RuClH(CO)(PPh$_3$)$_3$], t = 60 °C, THF.
[a] 0.25% mol of pre-catalyst was used.

Table 4
Comparison of isomerization of diallyl ethers

Diallyl ether	Conversion (%)
	100
	93
	60

Reaction conditions: 0.2% mol [RuClH(CO)(PPh_3)$_3$], $t = 60\,^{\circ}C$, $\tau = 1$ h, THF.



Scheme 3.

enol ethers have been obtained. The only exception was the isomerization of allyl trityl ether, where *Z*-enol ether formed almost exclusively (stereoselectivity >98%). Therefore, we tried to influence the stereoselectivity of double-bond migration in allyl ethers. We have examined the isomerization of allyl *t*-butyldimethylsilyl ether catalyzed by various hydride ruthenium complexes generated in situ from: [$RuCl_2(PPh_3)_3$] and Li[AlH_4], {[$RuCl_2$(1,5-cod)]$_x$} and Li[AlH_4], {[$RuCl_2$(1,5-cod)]$_x$} and PR_3 and Li[AlH_4] (see Scheme 3 and Table 5).

One of the best results (*E*/*Z* = 7.3) was obtained for [Ru]–H generated from {[$RuCl_2$(1,5-cod)]$_x$}, Li[AlH_4] and tris(2,4,6-trimethoxyphenyl)phosphine. Other phosphine ligands, such as PPh_3, P(*o*-tolyl)$_3$, P(OPh)$_3$, BINAP and PCy_3 were less effective for this catalytic system. The catalyst generated from {[$RuCl_2$(1,5-cod)]$_x$}, Li[AlH_4] and tris(2,4,6-trimethoxyphenyl)phosphine was also used in isomerization of allyl phenyl, allyl cyclohexyl, and allyl glycidyl ethers. Although conversion was always quantitative, we were unable to reach *E*/*Z* ratio higher than 1.2. This means that in order to get high *E*- or *Z*-stereoselectivity of double-bond migration not only the catalyst has to include a sterically demanding ligand, but also Q group in Q-allyl needs to be very bulky.

3.4. Recycling of the homogeneous ruthenium catalyst

Direct recycling of homogeneous ruthenium double-bond migration catalyst has not been described in the literature yet.

Table 5
Isomerization of allyl *t*-butyldimethylsilyl ether

[Ru]—H from [Ru]	*E*/*Z*
[RuClH(CO)(PPh_3)$_3$]	0.34
[$RuCl_2(PPh_3)_3$] + Li[AlH_4] (1:5)	0.36
{[$RuCl_2$(1,5-cod)]$_x$} + Li[AlH_4] (1:5)	0.35
{[$RuCl_2$(1,5-cod)]$_x$} + PPh_3 + Li[AlH_4] (1:1:5)	1.1
{[$RuCl_2$(1,5-cod)]$_x$} + P(2,4,6-$MeOC_6H_2$)$_3$ + Li[AlH_4] (1:1:5)	7.3

Reaction conditions: 1% mol [Ru], $t = 80\,^{\circ}C$, $\tau = 1$ h, THF; 100% conversion.

Table 6
The reaction time that was necessary to convert 1,4-diallyloxybutane to its di(1-propenyloxy) derivative

S/Ru	Reaction temperature (°C)		
	80	100	120
2000	120	90	60
1000	40	20	10
667	30	5	3
500	20	3	1

Reaction conditions: catalyst [RuClH(CO)(PPh_3)$_3$]; 100% conversion determined by GC; scale: 24 mmol of 1,4-diallyloxybutane; S/Ru—molar ratio: ether to pre-catalyst.

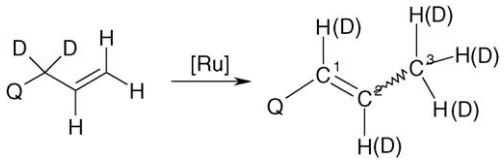
Only the works on enantioselective isomerization of allylamines deal with successful catalyst recycling [24]. We have been investigating the possibility of recycling the catalyst formed in situ (from the pre-catalyst [RuClH(CO)(PPh_3)$_3$]) in the model reaction of isomerization of 1,4-diallyloxybutane. In the preliminary experiment we were looking for reaction conditions (pre-catalyst concentration, reaction temperature and time) allowing to achieve quantitative conversion of the diallyl ether to its 1-propenyl derivative (>99.99%, GC–MS). The results are presented in Table 6.

The conditions: 120 °C and S/Ru = 500 were chosen for the catalyst recycling trials. The reactions of isomerization of 1,4-diallyloxybutane were carried out in a periodic reactor, as described in Section 2. We have found that the catalyst might be used at least five times. Each time the allyl to 1-propenyl conversion was practically quantitative and the yields of distilled products (isomers of di(1-propenyloxy)ethers) were always in the range 97–98%. After the first use of the catalyst, the reaction time was prolonged to 1 h. There are several pathways of transformation of allyl system, pre-catalyst, the real catalyst and other reagents in the reaction mixture. The reaction involves: ligand dissociation, Ru–H addition of double bonds in different orientations (anti-Markovnikov), chelation of dipropenyl ether, etc. The reaction of ruthenium complexes (pre- and real catalyst) with impurities present in the substrate (0.01% base on GC, but still high in comparison to the amount of the catalyst) should also be taken into account. However, we have not separated any product of permanent catalyst coordination, thus is it difficult to explain this dramatic deactivation of the catalyst after first use.

The results of catalyst recycling are very promising, especially in the synthesis of 1-propenyl ethers in larger scale. Due to the catalyst recycling, the costs of the precious catalyst are seriously reduced, so the catalyst costs are shifted to minority in the total costs.

3.5. Mechanism

There are two well-known pathways of double-bond migration catalyzed by transition metals [34]: the metal hydride addition–elimination (**I**) and the pathway which is based on π-allyl metal hydride transient complex (**II**). Mechanism (**I**) encompasses Markovnikov and anti-Markovnikov Ru–H addition to double bond both to the reactant and the product. As a



Scheme 4.

consequence, deuterium scattering is observed for isomerization of labeled allyl systems Scheme 4.

On the other hand, mechanism (**II**) involves formation of π-allyl metal hydride. Since the hydride ligand is taken from the position C^1 followed by its transfer to the terminal position C^3, it is regarded as a formal 1,3-hydrogen shift. Therefore, no deuterium should be found at position C^2 after isomerization of 1,1-d_2-allyl system according to mechanism (**II**). While isomerization of various allyl systems have been proved to occur via mechanism (**II**) [31,33,35], some typical non-hydride complexes may lead to the formation of π-allyl metal hydride as a transient step [31,36]—mechanism (**II**).

Although mechanisms (**I**) and (**II**) are alternative ones, the double-bond migration in allyl systems might be the superposition of both of them (as parallel reactions) with their appropriate impacts to the overall reaction. While the presence of deuterium at C^2 proves multiple hydride addition–elimination (mechanism (**I**)), it does not eliminate any contribution of π-allyl mechanism (**II**). Only sole 1,3-hydride shift is the proof of π-allyl mechanism (**II**) and the absence of mechanism (**I**). The reverse possibility may not be proven.

In order to put some light on the double-bond migration of allyl ethers catalyzed by various ruthenium complexes, we have synthesized (1,1-d_2-allyl) benzyl ether (**4a**) and (1,1-d_2-allyl) trityl ether (**5a**). They were isomerized by $[RuClH(CO)(PPh_3)_3]$ or $\{[RuCl_2(cod)]_x\} + PR_3$ (+$Li[AlH_4]$). During the course of the reaction and/or after its completion, ^2H NMR spectra have been taken in order to determine the deuterium distribution in the propenyl chain (Scheme 5 and Table 7).

The isomerization of (4a) led to both (*E*) and (*Z*) isomers. Deuterium distribution in both isomers is similar within the measurement error (2%). When isomerization is not complete (distribution after shorter time 3 and 2.5 h, respectively) and the isomeric product composition is controlled by kinetics, one of the deuterium atom remains at the initial position C^1, while the other is scattered between the remaining positions C^2 and C^3.

Table 7
Deuterium distribution (%)

Reaction conditions	τ (h)	C^1	C^2	C^3
[Ru]: $[RuClH(CO)(PPh_3)_3]$	3[a]	50	32	17
[H] = none; *t*: 80 °C	6	30	25	45
[Ru]: $\{[RuCl_2(cod)]_x\}$	2.5[b]	50	30	16
[H] = $Li[AlH_4]$; *t*: 120 °C	12	28	25	47

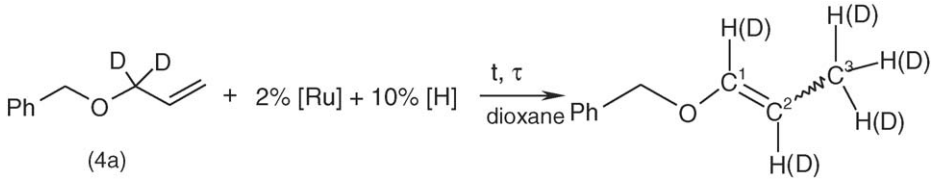
Reaction conditions: 2% mol [Ru], 10% [H], 1,4-dioxane; 100% conversion.
[a] Conversion 95%.
[b] Conversion 90%.

It may be surprising to find the dominance of deuterium at C^2 over C^3 after shorter reaction time. It might be explained by intermolecular deuterium transfer (Ru–D) from the isomerized molecule to another allyl system followed by Ru–D addition with anti-Markovnikov orientation leading to non-productive reaction. As Cramer estimated [37], the ratio of anti-Markovnikov over Markovnikov addition of M–H to double bond might be even 15:1. Other researchers claim that despite steric factors Markovnikov M–H addition occurs in majority (65% and more) [38,39].

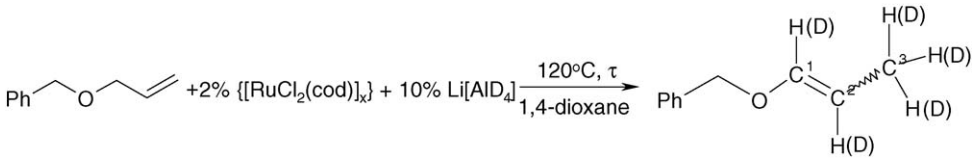
Relatively high part of deuterium at position C^2 proves the presence of addition–elimination mechanism (**I**). As mentioned above, while π-allyl metal hydride (**II**) may not be excluded, the relative high part of deuterium at position C^2 in respect to C^3 proves that mechanism (**I**) is dominant or/and there is a parallel addition–elimination reaction with relatively high rate.

Another experiment was designed in order to find deuterium scattering among propenyl positions from the external source of deuterium, $Li[AlD_4]$ (Scheme 6 and Table 8). Such a reaction would prove that $Li[AlH_4]$ is the source of active hydride ligand for $\{[RuCl_2(cod)]_x\}$ in this new catalytic system.

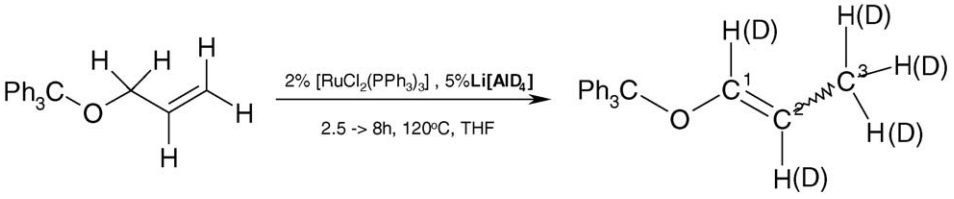
The isomerization was complete after 2.5 h (from ^1H NMR), at this time some hydride (at ^2H NMR −6.95 ppm) was observed, thus it might have been the inorganic $Li[AlD_4]$ or some Ru–D. Again, we also observed here the results of high-rated Ru–D addition–elimination leading presumably to double-bond



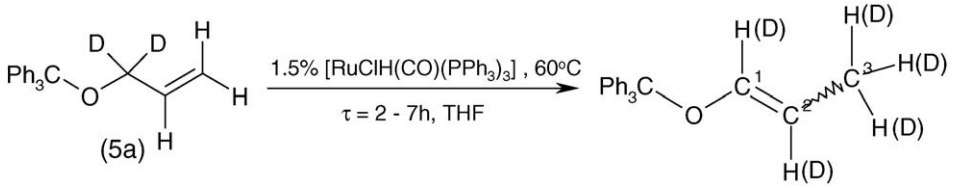
Scheme 5.



Scheme 6.



Scheme 7.



Scheme 8.

migration. However, the high part of deuterium at C^2 and its increase over the other positions with prolongation of reaction time proves the dominance of the non-productive Markovnikov addition. It was also important to exclude the direct transfer of deuterium from $Li[AlD_4]$ to C=C. We have carried out reaction of allyl ethers with $Li[AlH_4]$ and other hydrides (i.e. CaH_2 and $Na[BH_4]$) without ruthenium complexes, but no double-bond migration product was observed. Therefore, we assume that deuterium is not able to transfer from $Li[AlD_4]$ to propenyl without ruthenium contribution.

It is interesting to find 1/5 of deuterium substituted at propenyl chain aimed to C^1 position. Its presence there proves that Ru–D addition also occurs in the case of the 1-propenyl system and this reaction should not be neglected in the description of the mechanism.

Applying an external source of deuterium, the formation of Ru–D species from the non-hydride and pre-catalyst is forced. There are 40 deuterium atoms potentially available for each propenyl system (molar ratio: allyl ether/$Li[AlD_4]$ = 1:10). Thus, we use a catalyst which in fact should be present in analogical system: deuterated ether and $Li[AlH_4]$, where Ru–D is taken from the ether. In this way, we mimic the intermolecular deuterium transfer in the latter system. We have prepared a similar experiment (Scheme 6), but after the reaction, internal reference (DMSO-d_6) was added to the sample in order to evaluate the amount of deuterium shifted to 1-propenyl system. In Table 8, there is given the percentage of deuterium which was found at appropriate 1-propenyl positions. It was assumed that all of deuterium atoms at $Li[AlD_4]$ were available to serve as d_1-hydride ligands and transfer to the propenyl chain.

Table 8
Deuterium distribution (%)

τ (h)	C^1	C^2	C^3
2.5	19	41	40
12	21	46	33

Reaction conditions: 2% mol $\{[RuCl_2(cod)]_x\}$, 10% $Li[AlD_4]$, t = 120 °C; 1,4-dioxane.

Such a high concentration of deuterium in the propenyl system in the above reaction (Scheme 7) and the similarity of deuterium distribution among all positions support our suspicion that intermolecular transfer of deuterium should not be neglected. Moreover, mechanism (**I**) is undoubtedly proven even for such a non-hydride precursor like $\{[RuCl_2(cod)]_x\}$. The bridging chloride ligands in this complex are most likely cleaved and replaced by hydride ligands in the course of the reaction. As one can notice from these results (Table 9), almost half of the deuterium from $Li[AlD_4]$ has been transferred to the propenyl chain after 8 h.

Although *ortho*-metalation of phosphine to hydride ruthenium complexes is known [40], it has been excluded on the base of the reaction of allyl benzyl ether isomerization catalyzed by $\{RuClH(CO)[P(Ph\text{-}d_5)_3]_3\}$ or by the system $\{[RuCl_2(cod)]_x\} + P(Ph\text{-}d_5)_3$. No incorporation of deuterium from phosphine to propenyl chain was observed.

Isomerization of allyl trityl ether is an interesting example of selective reaction towards only one isomer—*Z*. It was interesting to compare the mechanistic studies on such a stereoselective reaction to non-stereoselective isomerization of allyl benzyl ether. Thus (1,1-d_2-allyl)trityl ether was isomerized by $[RuClH(CO)(PPh_3)_3]$ as shown in Scheme 8.

Distribution of deuterium was monitored by ^2H NMR and its relative abundance is presented in Table 10.

In contradiction to (1,1-d_2-allyl)benzyl ether, one of deuterium atoms always remains in the position C^1 even with prolongation of the reaction time. The presence of deuterium in the position C^3 might result from intermolecular deuterium

Table 9
Deuterium distribution (%)

Reaction time (h)	1-Propenyl positions			Sum
	C^1 (%)	C^2 (%)	C^3 (%)	
2.5	2.1	6.8	9.2	18.1
8	6.7	11.6	27.3	45.6

Reaction conditions: 2% mol $\{[RuCl_2(cod)]_x\}$, 5% $Li[AlD_4]$, t = 120 °C; THF; Sum—percentage of deuterium.

Table 10
Deuterium distribution (%)

Reaction time (h)	1-Propenyl positions		
	C^1 (%)	C^2 (%)	C^3 (%)
2	52.4	20.0	27.6
7	52.3	20.9	26.8

Reaction conditions: 1.5% mol $[RuClH(CO)(PPh_3)_3]$, $t = 60\,^{\circ}C$; THF.

transfer followed by Markovnikov Ru–D addition to allyl system—hydride mechanism. Finally, deuterium at the position C^2 comes from the anti-Markovnikov Ru–D addition to the double bond of allyl system, which is thermodynamically more favored.

The mechanism investigations led us to conclusion that a the classical hydride mechanism is dominant for isomerization of alkyl allyl ethers catalyzed by $[RuClH(CO)(PPh_3)_3]$ and also by the in situ forming catalyst $\{[RuCl_2(cod)]_x\}$ + hydride. The latter system consists of active hydride ligand, which is transferred among propenyl fragments intermolecularlly. Also, it was found that many unproductive Ru–H additions to allyl (substrate) and 1-propenyl occur. *Ortho*-metalation as a source of hydride ligand was eliminated from the mechanistic considerations basing on the lack of deuterium transfer from phosphine ligand to propenyl fragment. Also the stereoselective reactions are the result of the hydride mechanism. The bulkiness of the stereoselectively isomerizing ethers forces the anti-Markovnikov addition of Ru–H to allyl fragments (substrate).

4. Conclusion

Isomerization of alkyl allyl and allyl silyl ethers is a convenient and effective method of synthesis of 1-propenyl ethers. Ruthenium hydride complex—$[RuClH(CO)(PPh_3)_3]$ is sufficiently active in the reaction. We have shown that the catalyst might be recovered and used again. However, the highest activity loss was observed after first use of the catalyst.

We have proved that hydride mechanism is dominant in isomerization, although existence of parallel mechanisms in minority may not be ruled out. The same mechanism occurs for the catalyst formed in situ from $\{[RuCl_2(cod)]_x\}$ and hydride, i.e. $Li[AlH_4]$, thus an inorganic hydride serves as hydride donor for the polymeric complex.

Acknowledgments

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References

[1] J.V. Crivello, Radiat. Phys. Chem. 63 (2002) 21.
[2] M. Sangermano, G. Malucelli, R. Bongiovanni, A. Pirola, U. Annby, N. Rehnberg, Eur. Polym. J. 38 (2002) 655.
[3] W.G. Kim, H.K. Ahn, H.W. Lee, S.H. Kim, J.V. Crivello, Opt. Mater. 21 (2002) 343.
[4] E. Taskinen, J. Chem. Soc., Perkin Trans. 2 (2001) 1824.
[5] H.B. Mereyala, S.R. Gurrala, S.K. Mohan, Tetrahedron 55 (1999) 11331.
[6] H.B. Mereyala, S.R. Lingannagaru, Tetrahedron 53 (1997) 17501.
[7] A. Wille, S. Tomm, H. Frauenrath, Synthesis (1998) 305.
[8] N.L. Bauld, J. Yang, Tetrahedron Lett. 40 (1999) 8519.
[9] G.-J. Boons, S. Isles, Tetrahedron Lett. 35 (1994) 3593.
[10] M. Urbala, N. Kuźnik, S. Krompiec, J. Rzepa, Synlett (2004) 1203.
[11] S. Krompiec, N. Kuźnik, T. Bieg, B. Adamus, J. Majnusz, M. Grymel, Pol. J. Chem. 74 (2000) 1197.
[12] S. Krompiec, N. Kuźnik, R. Penczek, J. Rzepa, J. Mrowiec-Białoń, J. Mol. Catal. A: Chem. 219 (2004) 29.
[13] S. Krompiec, M. Pigulla, M. Krompiec, S. Baj, J. Mrowiec-Białoń, J. Kasperczyk, Tetrahedron Lett. 45 (2004) 5257.
[14] S. Krompiec, M. Pigulla, W. Szczepankiewicz, T. Bieg, N. Kuźnik, K. Leszczyńska-Sejda, M. Kubicki, T. Borowiak, Tetrahedron Lett. 42 (2001) 7095.
[15] N. Kuźnik, S. Krompiec, T. Bieg, S. Baj, K. Skutil, J. Organomet. Chem. 665 (2003) 167.
[16] H. Wakamatsu, M. Nishida, N. Adachi, M. Mori, J. Org. Chem. 65 (2000) 3966.
[17] R. Beugelmans, S. Bourdet, A. Bigot, J. Zhu, Tetrahedron Lett. 35 (1994) 4349.
[18] V. Tuyen Nguyen, S. Debenedetti, N. De Kimpe, Tetrahedron Lett. 44 (2003) 4199.
[19] V. Tuyen Nguyen, N. De Kimpe, Tetrahedron Lett. 45 (2004) 3443.
[20] W.A.L. van Otterlo, E.L. Ngidi, S. Kuzvidza, G.L. Morgans, S.S. Moleele, C.B. de Koning, Tetrahedron 61 (2005) 9996.
[21] W.A.L. van Otterlo, G.L. Morgans, L.G. Madeley, S. Kuzvidza, S.S. Moleele, N. Thornton, C.B. de Koning, Tetrahedron 61 (2005) 7746.
[22] W.A.L. van Otterlo, G.L. Morgans, S.D. Khanye, B.A.A. Aderibigbe, J.P. Michael, D.G. Billing, Tetrahedron Lett. 45 (2004) 9171.
[23] W.A.L. van Otterlo, E.L. Ngidi, C.B. de Koning, Tetrahedron Lett. 44 (2003) 6483.
[24] S. Krompiec, Zeszyty Nauk. Pol. Śl. Chem. Z. 136 (1997).
[25] A.F. Hill, C.T. Ho, J.D.E.T. Wilton-Ely, J. Chem. Soc., Chem. Comm. (1997) 2208.
[26] M.R. Torres, A. Vegas, A. Santos, J. Organomet. Chem. 309 (1986) 169.
[27] J.V. Crivello, K.D. Jo, J. Polym. Sci., Part A: Polym. Chem. 31 (1993) 1483.
[28] D. Martysz, M. Antoszczyszyn, M. Urbala, S. Krompiec, E. Fabrycy, Prog. Org. Coat. 46 (2003) 302.
[29] S. Krompiec, M. Pigulla, N. Kuźnik, M. Krompiec, B. Marciniec, D. Chadyniak, J. Kasperczyk, J. Mol. Catal. A: Chem. 225 (2005) 91.
[30] P. Pertici, C. Malanga, A. Guintoli, G. Vitulli, G. Martra, Gazz. Chim. Ital. 126 (1996) 587.
[31] H.C. Clark, H. Kurosawa, Inorg. Chem. 12 (1973) 1566.
[32] A.J. Hubert, A. Georis, R. Warin, P. Teyssié, Chem. Soc., Perkin Trans. 2 (1972) 366.
[33] D.V. McGrath, R.H. Grubbs, Organometallics 13 (1994) 224.
[34] G.W. Parshall, S.D. Ittel, Homogeneous Catalysis, Wiley-Interscience, New York, 1992.
[35] F.G. Cowherd, J.L. von Rosenberg, J. Am. Chem. Soc. 91 (1969) 2157.
[36] S.H. Bergens, B. Bosnich, J. Am. Chem. Soc. 113 (1991) 958.
[37] R. Cramer, J. Am. Chem. Soc. 88 (1966) 2272.
[38] W.T. Hendrix, J.L. von Rosenberg, J. Am. Chem. Soc. 98 (1976) 4850.
[39] P. Taylor, M. Orchin, J. Am. Chem. Soc. 93 (1971) 6504.
[40] Houben-Weyl, in: Methoden der Organischen Chemie, Thieme Verlag, Stuttgart, 1986, Vol. Band 13, Teil 9a.
[41] J.J. Levison, S.D. Robinson, J. Chem. Soc. A (1970) 2947.
[42] N. Ahmad, J.J. Levison, S.D. Robinson, M.F. Uttley, Inorg. Synth. 15 (1974) 45.

[43] T.A. Stephenson, G. Wilkinson, J. Chem. Soc. A (1968) 2660.
[44] E.W. Abel, M.A. Bennett, G. Wilkinson, J. Chem. Soc. A (1959) 3178.
[45] M. Urbala, Politechnika Szczecińska (2001).
[46] M. Antoszczyszyn, D. Brenk, Przem. Chem. 75 (1996) 443.
[47] E. Janus, M. Antoszczyszyn, M. Urbala, Polish J. Appl. Chem. 43 (1999) 77.
[48] M. Urbala, M. Antoszczyszyn, Ultrason. Sonochem. 11 (2004) 409.
[49] R.D. Schuetz, F.W. Millard, J. Org. Chem. 24 (1959) 297.
[50] R.J. Anderson, S. Ashwell, I. Garnett, B.T. Golding, J. Chem. Soc., Perkin Trans. 1 (2000) 4488.