

Communication

Ethenolysis of silicon containing cycloolefins

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Abstract

In this paper the ring-opening cross-metathesis of silicon substituted norbornenes with ethene is reported. Silicon containing norbornenes could be selectively ring-opened via a cross-metathesis with ethene employing Ru-based catalysts (RuCl₂(PCy₃)(=CHSiMe₃) (**3**) or RuCl₂(PCy₃)₂(=CHPh) (**4**)). It was also found that for the ethenolysis, the order of sequence of the individual reagents is of crucial importance. Under mild reaction conditions and by premixing of ethene and the catalyst before the silicon containing norbornene (C₁₃H₂₄O₃Si (**5**) or C₁₂H₂₄OSi₂ (**6**)) was added, it was possible to convert **5** and **6** into the desired silicon containing α,ω -diolefin quantitatively. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Ethenolysis; Ruthenium; Olefin metathesis; α,ω -Olefins; Ring-opening metathesis

1. Introduction

In 1967, Bradshaw et al. defined the cross-metathesis between ethene and internal olefins as ethenolysis [1]. Currently, ethenolysis processes are used to produce 1-alkenes, α,ω -diolefin, unsaturated fatty acid esters and fatty oils [2]. Examples of technical processes which use ethene for cross-metathesis are the Shell FEAST process (Further Exploitation of Advanced Shell Technology), Shell-Higher-Olefins-Process (SHOP) and the Phillips-Triolefin-Process [3]. Cross-metathesis with ethene yields compounds with terminal double bonds, having a broad range of applications. They can be used as cross-linking agents and starting materials in the production of specialty and fine chemicals [4]. These examples show the high potential of cross-metathesis for the synthesis of new compounds.

In the present study, we have investigated the ethenolysis of silicon substituted norbornenes using the Noels-type catalyst RuCl₂(PCy₃)(=CHSiMe₃) (**3**) and

the Grubbs-catalyst RuCl₂(PCy₃)₂(=CHPh) (**4**) as shown in Scheme 1 [5–7].

Furthermore, we demonstrate the importance of the sequence of addition of the compounds into the reaction mixture, namely the catalyst and the two monomers C₁₃H₂₄O₃Si (**5**) or C₁₂H₂₄OSi₂ (**6**) and ethene.

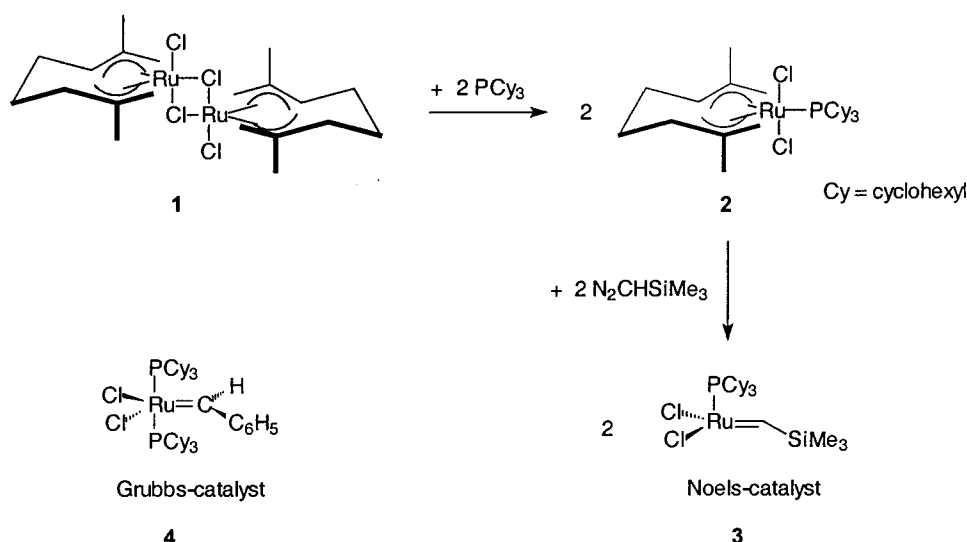
2. Results and discussion

The allylruthenium(IV) precursor [(η^3 : η^3 -C₁₀H₁₆)-Ru(η -Cl)Cl]₂ (**1**) was synthesized by reaction of ruthenium(III)chloride with isoprene in ethanol [5c,d]. Compound **1** was converted into complex **2** by addition of tricyclohexylphosphine (Scheme 1) [8]. Compound **2** was activated by addition of trimethylsilyldiazomethane (TMSD) resulting in **3**, which is stable in solution [8]. These catalysts, **3** and the Grubbs-catalyst (**4**) show different activity in ethenolysis of the silicon containing norbornenes **5** and **6** (Fig. 1).

In the absence of ethene the reaction of **5** and **6** with catalyst **2**, **3** and **4** yields polymers via ring-opening metathesis [5–7] (shown for **5** with catalyst **3** in Table 1).

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Scheme 1. Catalysts for the ethenolysis.

Premixing of ethene with **5** or **6** in toluene as a solvent, initiated by complex **3** (in situ generated from **2** and TMSD), yields some **7** or **8**. However, the polymer (**9** or **10**) is the main product. With increasing ethene concentration (pressure) the amount of polymer could be reduced, its molar mass became smaller but its formation could not be avoided (Tables 1 and 2).

Therefore, we have changed the sequence of addition of the reactants. At first, **2** was dissolved in toluene, then the solution was maintained under ethene pressure of 0.4 MPa. About 20 min later, the activator (TMSD) was added to form the active species **3**. Then the silicon containing norbornene (**5** or **6**) was introduced into the reaction mixture. In this case, no polymerization was observed and the yield of the desired monomers could be increased (Table 3).

The reaction conditions were relatively mild. However, it is quite obvious that the reaction parameters [cycloolefin], [ethene], [Ru] and temperature will influence these results and therefore these reactions need further optimization (Table 4).

The challenge in the cross-metathesis (pathway from **5/6** directly to **7/8**) is the prevention of polymerization of the cycloolefins (pathway from **5/6** to **9/10**) or from **7/8** to **9/10** and high yield of **7** or **8** (Scheme 2).

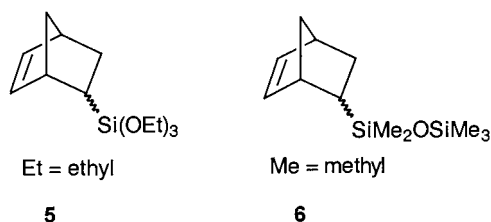


Fig. 1.

A breakthrough was the cross-metathesis of **5** and **6** with ethene catalyzed by **4**. It was again essential to premix the catalyst with ethene and add the cycloolefins **5** or **6** later. In this case it was possible, not only to present polymer formation, but also to convert the functionalized cycloolefins **5** and **6** via ethenolysis quantitatively into the corresponding cross-metathesis α,ω -dienes (**7** and **8**). These results can be explained as shown in Scheme 3:

The polymer formation can be avoided by premixing ethene with the catalyst. We assume that both, ethene and the catalyst (shown for **4** in Scheme 3), react via metallacyclobutane intermediate (**11a**) to the highly active species $L_nRu=CH_2$ (**11b**). $L_nRu=CH_2$ adds onto the norbornene derivatives (**5** or **6**) resulting in a monomer extended metallacyclobutane (**11c**). The reaction continues via intermediates **11d** and **11e**. Then **11e** splits into **7** (or **8**) and **11b**. The regenerated **11b** returns to the cycle until the ethenolysis is completed. The reaction of **11d** with **5** or **6** to oligomer or polymer is prevented under these experimental conditions.

Table 1
Ring-opening polymerization and ethenolysis of cycloolefins catalyzed by **3** (**2**+TMSD)^a

Cycloolefin	Ethene	Yield (%) ^b	M_n (kg mol ⁻¹) ^c	M_w/M_n ^{c,d}
6	Without	94	310	1.8
6	With ^e	89	5.6	1.7

^a Reaction condition: $T = 25^\circ\text{C}$; abs. toluene; [monomer]/[Ru] = 350/1; $t = 24$ h.

^b Yield is determined gravimetrically.

^c GPC in THF versus polystyrene standards.

^d $PDI = M_w/M_n$.

^e Ethene pressure from 0.4 up to 3.0 MPa.

Table 2

Ethenolysis of silicon functionalized norbornenes, **5** and **6** catalyzed by **3** (**2**+TMSD) — premixing of cycloolefin and ethene ^a

Cycloolefin	[Ru]/[cycloolefin]	[Ethene]/[cycloolefin]	[Ru]/[PCy ₃]	[TMSD]/[Ru]	Yield of α,ω -diolefin (%) ^b	Side product
5	1/600	2.5	1.5	1.5	24	Oligomer
5	1/600	2.5	3	1.5	20	Oligomer
6	1/400	3	1.5	1.5	6	Oligomer
6	1/200	2.5	1.5	1.5	5	Oligomer
6	1/400	16	6	3	10	Oligomer

^a Reaction conditions: $T = 20^\circ\text{C}$; $t = 4$ h; abs. toluene; $p = 0.4$ MPa; [ethene] saturation in toluene 0.58 mol l^{-1} [9].^b Yield based on GC-MS and ¹H-NMR-spectroscopy.

Table 3

Ethenolysis of silicon functionalized norbornenes, **5** and **6** catalyzed by **3** (**2**+TMSD) — premixing of ethene and catalyst ^a

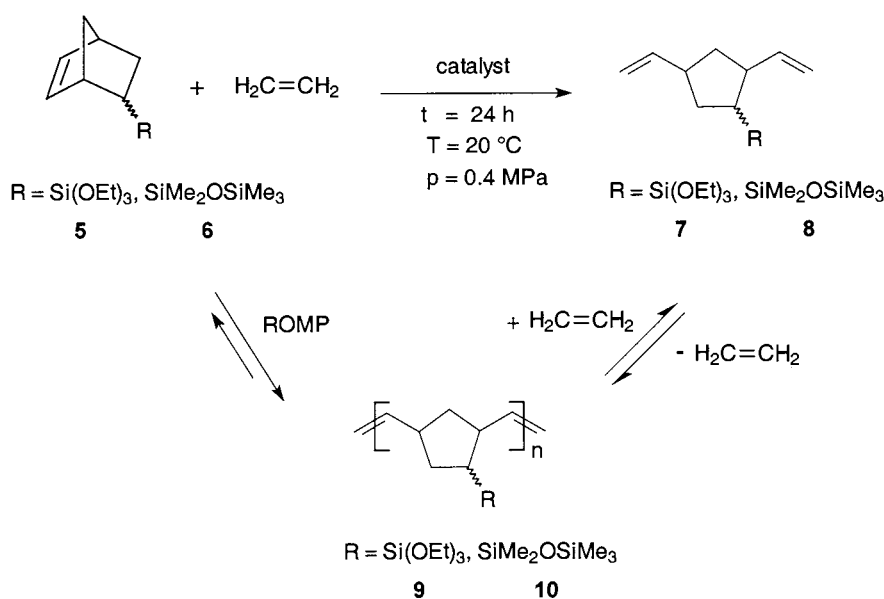
Cycloolefin	[Ru]/[cycloolefin]	[Ethene]/[cycloolefin]	[Ru]/[PCy ₃]	[TMSD]/[Ru]	Yield of α,ω -diolefin (%) ^b	Side product
5	1/700	4	1.5	1.5	25	–
5	1/950	10	2	1.5	32	–
6	1/600	10	1.5	1.5	20	–
6	1/700	10	3	2	31	–

^a Reaction conditions: $T = 20^\circ\text{C}$; $t = 24$ h; abs. toluene; $p = 0.4$ MPa; [ethene] saturation in toluene 0.58 mol l^{-1} [9].^b Yield based on GC-MS- and ¹H-NMR-spectroscopy.

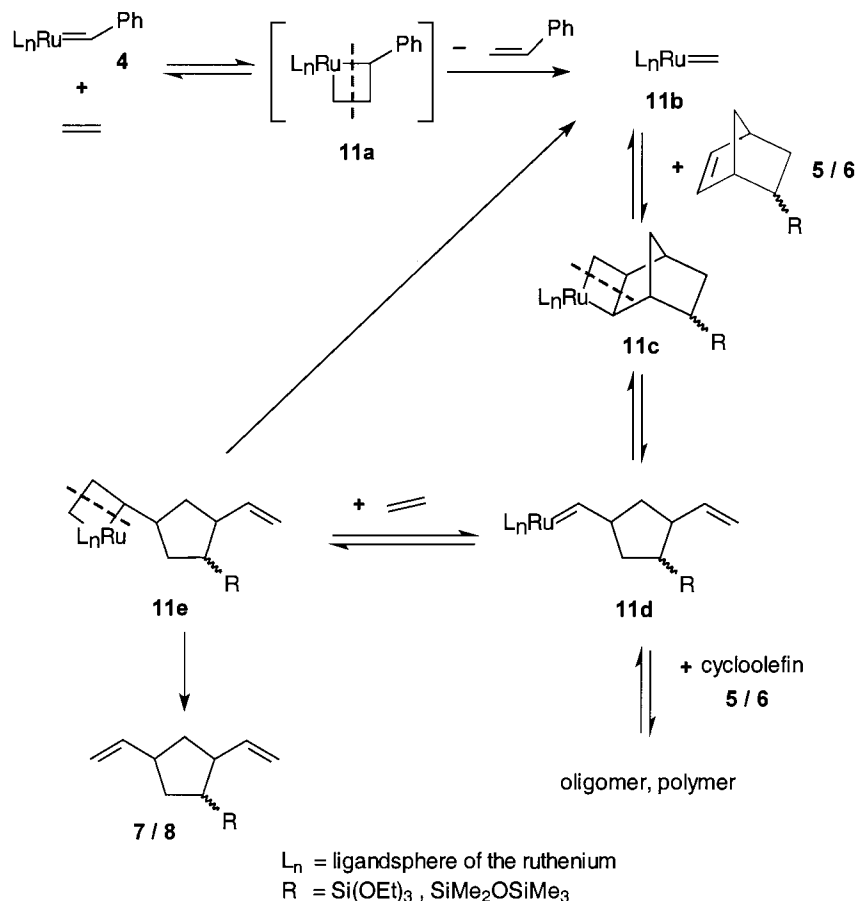
Table 4

Ethenolysis of silicon functionalized norbornenes, **5** and **6** catalyzed by **4** — premixing of cycloolefin and ethene ^a

Cycloolefin	[Ru]/[cycloolefin]	[Ethene]/[cycloolefin]	Yield of α,ω -diolefin (%) ^b	Side product
5	1/1000	23	99	–
5	1/4000	30	99	–
6	1/1000	14.5	99	–

^a Reaction conditions: $T = 20^\circ\text{C}$; $t = 24$ h; abs. toluene; $p = 0.4$ MPa; [ethene] saturation in toluene 0.58 mol l^{-1} [9].^b Yield based on GC-MS- and ¹H-NMR-spectroscopy.

Scheme 2. Ethenolysis and ring-opening polymerization of silicon containing cycloolefins.



Scheme 3. Supposed reaction mechanism.

3. Conclusions

The cross-metathesis of silicon substituted norbornene derivatives **5** and **6** with ethene catalyzed by the Noels-type catalyst (**3**) and the Grubbs-catalyst (**4**) yields the desired α,ω -diolefins **7** (or **8**) under mild conditions (room temperature, low ethene pressure and low catalyst concentration). ROMP of **5** and **6** could be avoided completely, when ethene and catalyst were mixed before **5** or **6** were added to the reaction mixture. With catalyst **3**, the yield of **7** (or **8**) was rather low. An almost quantitative yield was observed when **4** was applied as catalyst.

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