

Effect of alcohols and epoxides on the rate of ROMP of norbornene by a ruthenium trichloride catalyst

Andrew Mutch, Michel Leconte, Frédéric Lefebvre, Jean-Marie Basset *

Laboratoire de Chimie Organométallique de Surface, UMR CNRS-CPE 9986, 43 Bd du 11 Novembre 1918, 69616 Villeurbanne Cedex, France

Received 14 October 1997; accepted 8 December 1997

Abstract

$\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ has been used commercially in butanol as a solvent for several decades for the ring-opening metathesis polymerization (ROMP) of norbornene. Different alcohols have now been tested as solvents and the effect of added epoxides studied. The systems using benzyl alcohol or its derivatives with $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ are up to 50 times more active than $\text{RuCl}_3 \cdot x\text{H}_2\text{O}/n$ -butanol. It has been shown that benzyl alcohol reacts with RuCl_3 to yield quantitatively benzaldehyde and a ruthenium hydride, which, by reaction with the monomer leads to the ruthenium carbene initiating species. In the case of added epoxides or using tertiary alcohols as solvent, an increase in the rate of polymerization is observed which is attributed to the formation of a ruthenium carbene via an oxaruthenacycle intermediate. Such simple catalytic systems can be used with functionalized norbornenes. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Norbornene; Ring-opening metathesis polymerization; Ruthenium trichloride; Mechanism; Alcohol; Epoxides

1. Introduction

The ring-opening metathesis polymerization (ROMP) of cyclo-olefins is widely used for the synthesis of polymers containing double bonds which, in a second step, can be hydrogenated or transformed into other functionalities [1–3]. The catalysts are usually transition metal carbene complexes, obtained in situ or synthesized and characterized elsewhere. The metal is usually tungsten or molybdenum, and numerous carbene complexes of these metals were described and have high catalytic activity for the metathesis reaction [4–6]. Recently, the synthesis and

characterization of ruthenium carbene complexes was reported [7,8]. However, they display a smaller catalytic activity than the tungsten and molybdenum complexes for the metathesis of non-functional olefins but, in contrast to the latter, they are not sensitive to the oxygenate or nitrogen functions. This property allowed them to be used for the metathesis of functional olefins [9–11] and to realize the metathesis of olefins even in water [12]. In presence of cyclo-olefins, they lead, as the other carbene complexes, to polymers but their insensitivity towards the oxygen functions allows them to be used to catalyze the ROMP of functionalized monomers. Unfortunately, the cost of these catalysts prevents their use in the

* Corresponding author.

industry. Recently, an improvement has been made. Indeed, it has been shown that a simple procedure, consisting of the addition to the reaction mixture of $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$, tricyclohexylphosphine and a diazo compound, leads to in situ formation of a ruthenium carbene which has similar catalytic activity to the previously reported ruthenium carbenes [13,14]. However, this simple method has not been applied industrially. The only case where a ruthenium compound is used industrially is the synthesis of polynorbornene by CdF Chimie (now a part of Elf). The resulting material is sold under the tradename Norsorex[®] (Scheme 1). The catalyst is ruthenium trichloride, $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, in solution in *n*-butanol. The industrial plant, operating since 1976, has a capacity of 5000 tons per year and is located at Carling (France). The resulting polynorbornene has a very high molecular weight (higher than 3×10^6) and a very high *trans* content (at least 90%) [1]. It is used both for noise and vibration dampening and as a sponge for oil spills.

The process is straightforward. Norbornene and the catalyst ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ in *n*-butanol) are directly mixed in the extruder. It operates very simply in air. However, the rate of polymerization can vary by a large factor, due to the presence of small amounts of epoxynorbornane in the reaction mixture, formed by reaction of norbornene with atmosphere. Ivin et al. [15] also observed a drastic enhancement of the metathesis activity in the polymerization of norbornene catalyzed by $[\text{RuCl}_2(\text{PPh}_3)]^{4-}$ or $[\text{RuCl}_2(\text{py})_2(\text{PPh}_3)]^{2-}$ upon addition of molecular oxygen and attributed it to the formation of metallaoxacyclobutane intermediates which, by

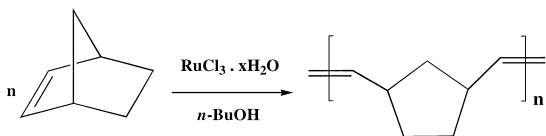
a concerted mechanism, gave the initiating metallocarbenes. However, the mechanism in absence of oxygen is not fully understood. We therefore decided to study more extensively the influence of the oxygenated molecules on the polymerization of norbornene. We began by looking at the influence of the alcohol alone so as to understand the reaction mechanism in the absence of epoxide. Then the effect of epoxides was studied. In this paper we will describe the results which relate to the initiation mechanism itself.

2. Experimental

Ruthenium trichloride, norbornene, alcohols and epoxides were purchased from Aldrich. When necessary, the products were purified by distillation, while the alcohols were treated beforehand by calcium hydride and then by sodium hydrogen sulfite. The functional norbornenes were also purchased from Aldrich and were always mixtures of *endo*- and *exo*-isomers (except for 5-norbornene-2,3-dicarboxylic which was purely *endo*).

2.1. Influence of alcohols on the rate of polymerization

A solution of 20 mg of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (0.02 mmol) in 5 ml of the desired alcohol was prepared in a Schlenk tube under argon and was heated to 60°C for 20 min. Meanwhile, a solution of norbornene (2 g, 21 mmol; norbornene/Ru = 500) in the same alcohol (15 ml) with an internal standard (octane, 0.5 ml) was prepared in another Schlenk tube equipped with a septum also maintained under an argon atmosphere. After heating the monomer solution to 100°C, the catalyst solution was introduced via the septum. The kinetics of the polymerization was followed by GPC analysis of samples of the solution taken at regular intervals and stored at -12°C .



Scheme 1.

2.2. Reaction of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ with alcohol

One milliliter of the desired alcohol was introduced in a Schlenk tube under argon and heated to 80°C. Ruthenium trichloride was then added (40 mg, 0.13 M) together with an internal standard (dioxane or octane). During the reaction, samples of the solution were analyzed by GPC after various reaction times.

2.3. Reaction of *cis*-2-butene

For the metathesis of *cis*-2-butene, the catalytic solution $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ /benzyl alcohol was prepared as above (interaction time 50 min) at 80°C. *cis*-2-Butene was then introduced (*cis*-2-butene/Ru = 200) and the system was heated at 100°C for 10 h.

2.4. Addition of epoxides to the reaction mixture

Norbornene (2 g, 0.021 mol) was dissolved in *n*-butanol (20 ml) in the presence of octane (0.5 ml) as an internal standard. The solution was heated, in a Schlenk tube, to 100°C under argon. Solid $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (20 mg, 0.07 mmol) and the epoxide were then quickly added to the Schlenk tube under vigorous stirring. Samples of the reaction mixture were analysed by GPC at regular time intervals.

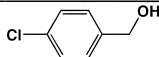
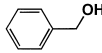
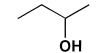
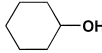
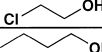
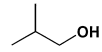
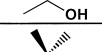
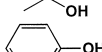
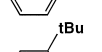
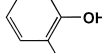
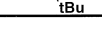
3. Results and discussion

3.1. Influence of the nature of alcohol on the conversion of norbornene

Depending on the nature of the alcohol used, wide variations in the induction period and the rate of polymerization were observed (Table 1). With phenols, no activity is observed in the ROMP of norbornene. This is probably due, at least in part, to the low solubility of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ in these media. Use of *t*-butanol led to a slightly more active system, comparable to that of the primary alcohols, such as *n*-butanol. Bet-

Table 1

Effect of the nature of the alcohol on the polymerization rate of norbornene by the $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ /alcohol system

Alcohol	Polymerization rate ($\text{mol} \cdot \text{min}^{-1} \cdot \text{mol}_{\text{Ru}}^{-1}$)	Induction period (min)
	225	0
	125	0
	24	3
	28	0
	30	0
	4	4
	4	22
	1	0
	3.5	23
	Reaction rate very low	
	No reaction	

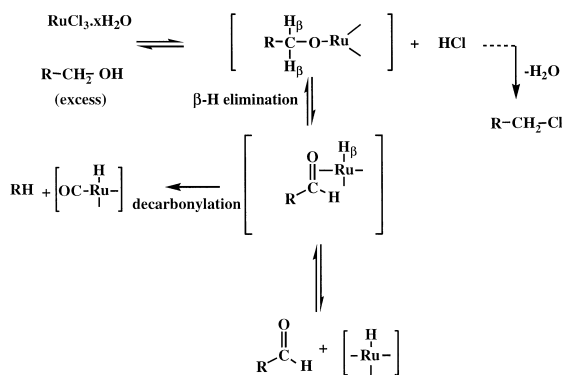
ter results were achieved with secondary alcohols where an increase of activity by a factor 8 could be observed. However, the best reaction media were obtained using benzyl and *p*-chloro-benzyl alcohols, for which the activity was more than 50 times greater compared to that using *n*-butanol.

The induction period probably corresponds to the build-up of a steady concentration of the initiating carbene during the initial stages of reaction.

3.2. The reaction of RuCl_3 with alcohols

In order to better understand these results, we studied the reaction mechanism via the determination of the reaction products of the alcohols with ruthenium trichloride.

We determined the evolved products formed during the interaction of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ with benzyl alcohol, *n*-butanol and *t*-butanol. For benzyl alcohol the formation of benzaldehyde



Scheme 2.

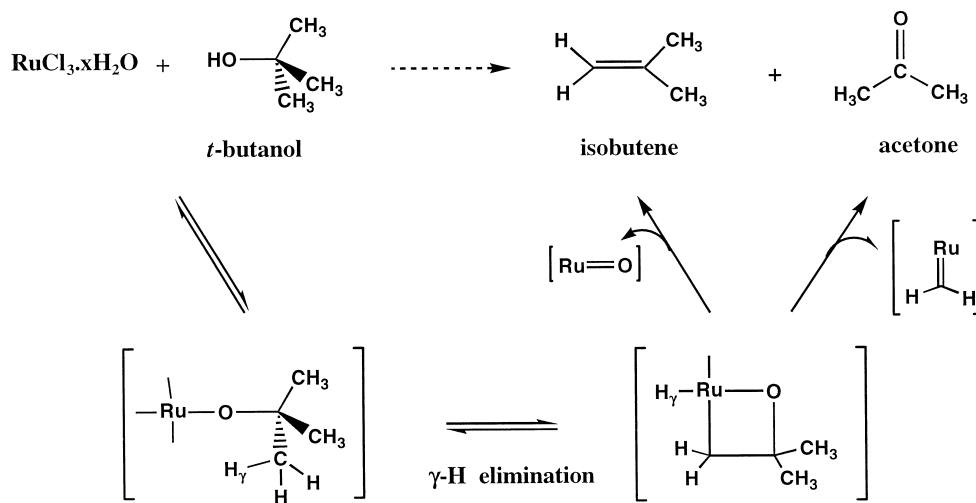
(0.7 eq. per Ru), benzyl chloride (approx. 0.1 eq. per Ru) and benzene (less than 0.05 eq. per Ru) was observed. When *n*-butanol was used, *n*-butanal (0.2 eq. per Ru), *n*-butyl chloride (0.08 eq. per Ru) and propane (0.002 eq. per Ru) were formed. In the case of *t*-butanol, only isobutene was detected in the gaseous phase together with acetone in the liquid phase. Their amounts were relatively small and difficult to measure precisely.

The formation of the products with benzyl alcohol and *n*-butanol is easily explained if an hydride mechanism such as that depicted in Scheme 2 is assumed.

This mechanism was proposed by Chatt et al. [16] and Chatt and Shaw [17] a long time ago

for the decarbonylation of alcohols. It leads to the formation of an hydride species which is necessary for initiating the ring-opening polymerization [1]. The first step of this mechanism is the coordination of the alcohol to the ruthenium, forming a ruthenium alkoxy complex, in agreement with the works of Tanielian et al. [18,19]. The evolution of hydrochloric acid, suggesting the loss of at least one chlorine ligand, can be easily evidenced by putting a pH paper at the top of the reactor flask. The unstable alkoxy complex decomposes rapidly by β -H elimination to give an hydrido-acyl complex which can be considered as the initiating species of the reaction. This complex can undergo a decarbonylation reaction, as proposed by Chatt et al. [16] and Chatt et al. [17] leading to the formation of small amounts of benzene and propane, which are the products of decomposition of benzyl alcohol and *n*-butanol, respectively. Nevertheless, under our experimental conditions, the decarbonylation pathway is not completed and the formation of benzaldehyde and *n*-butanal is preferred.

Scheme 2 shows how these oxidised products may be formed from hydride abstraction by the metal. Hence, the presence of oxidised products of the corresponding alcohol in active systems is associated with the formation of a ruthenium



Scheme 3.

hydride species. Measurements by chromatography showed that there are two to three times more benzaldehyde formed than *n*-butanal. The main difference in behaviour for the reactions in benzyl alcohol and *n*-butanol can be therefore explained in terms of greater quantities of ruthenium hydride species being rapidly formed in the first case, thus leading to a higher catalytic activity.

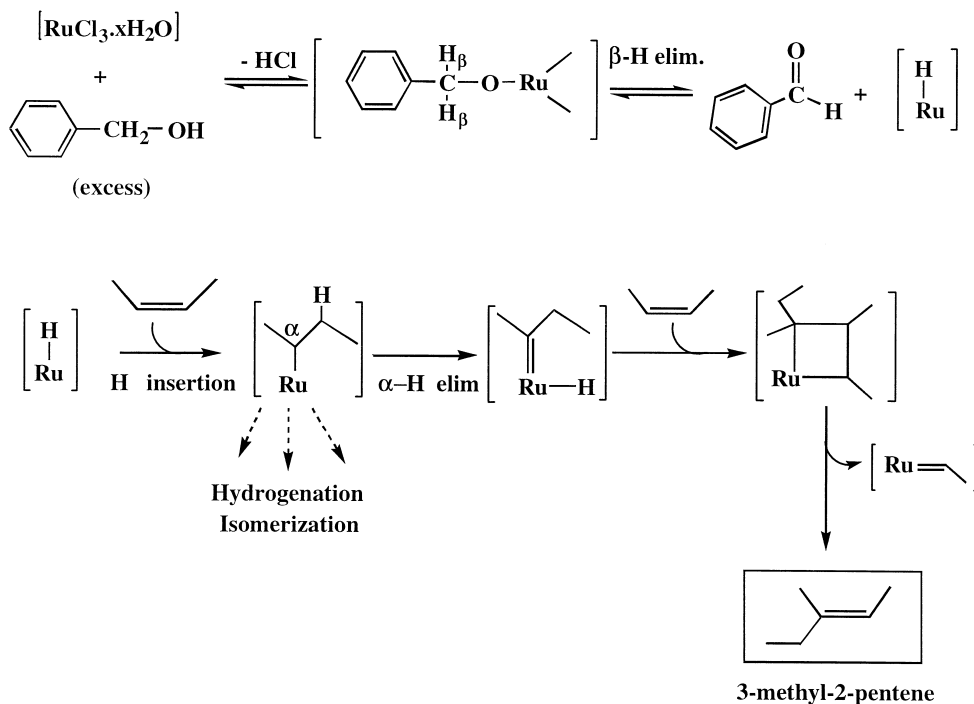
Note also that in this mechanism it is necessary to have a β -H elimination in order to form the metal–hydride species. This can also explain why the phenols are inactive, as they do not have hydrogen atoms in β -position.

The situation is more complicated for *t*-butanol as (i) it does not have hydrogen atoms in β -position and (ii) it leads to very different products (isobutene and acetone). This can be rationalized as depicted in Scheme 3. As previously, the initial coordination of *t*-butanol to ruthenium leads to an alkoxy derivative. How-

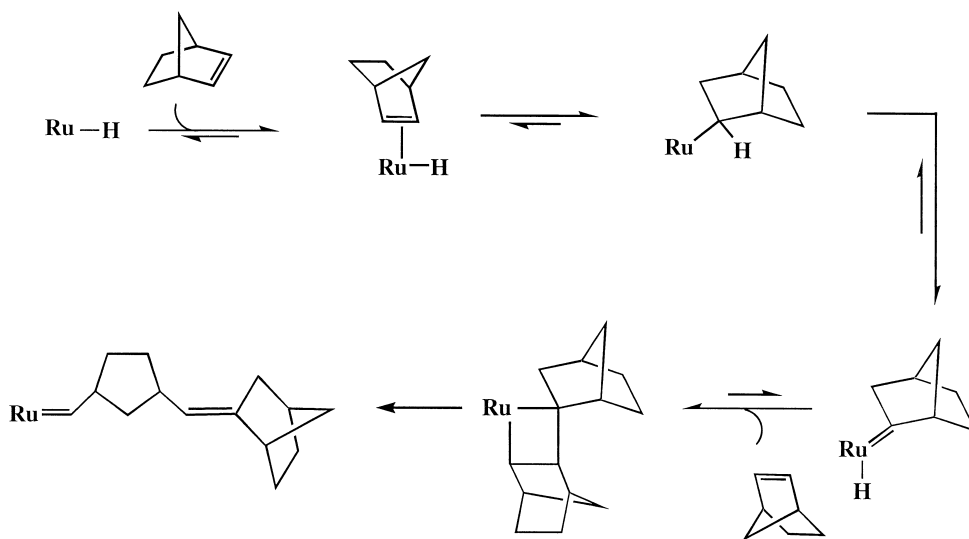
ever, the absence of hydrogen atoms in the β -position favours decomposition of the unstable alkoxy species by γ -H elimination to form an oxametallacycle. Metathesis of the oxaruthenacyclic intermediate thus leads to isobutene and a ruthenium-oxo species, or, to acetone and a ruthenium-methylidene carbene which can directly initiate the polymerization of norbornene.

3.3. The $\text{RuCl}_3/\text{PhCH}_2\text{OH}/\text{cis-2-butene}$ system

In order to obtain further proof of the hydride mechanism, we carried out the metathesis of *cis*-2-butene with the more active ruthenium trichloride/benzyl alcohol system. *cis*-2-Butene was introduced into the reactor and heated to 100°C. The gaseous phase was periodically analyzed. After a few minutes, butane, 1-butene



Scheme 4.



Scheme 5.

and *trans*-2-butene were evolved and small amounts of 3-methyl-2-pentene detected.

The formation of all these products can again be easily explained by assuming an hydride mechanism (Scheme 4). *cis*-2-Butene reacts firstly with the ruthenium hydride to give a ruthenium butyl complex. Several reactions are then possible. β -H elimination of this alkyl complex would give either *cis*- or *trans*-2-butene while 1-butene could be obtained by isomerization. Hydrogenolysis of the Ru-alkyl moiety can also lead to butane. However, this ruthenium alkyl complex can also undergo an α -H elimination to form a ruthenium-alkylidene species. This carbene complex can then undergo metathesis with a second molecule of *cis*-2-butene to give the observed 3-methyl-2-pentene. The fact that only small amounts of the metathesis product are detected confirms that compared to α -H abstraction, the β -H elimination step is strongly favoured.

The mechanism of the norbornene polymerization can now be proposed on the same basis as for *cis*-2-butene (Scheme 5). Norbornene reacts with the ruthenium hydride, leading to the corresponding norbornyl derivative. This compound can undergo, as *cis*-2-butene, a β -H elimination, restoring the starting products,

or a α -H elimination, leading to the initial propagating carbene.

3.4. Effect of epoxides on the reaction rate

Small amounts of epoxynorbornane, detected in the industrial reactor, were shown by the plant engineers to increase the rate of polymerization. We therefore studied the effect of the molar ratio epoxide/Ru on the norbornene polymerization rate. As the purpose of these experiments was to understand the industrial results, the catalytic system used here was RuCl_3/n -butanol. Fig. 1 shows that for a norbornene/Ru ratio of 300 addition of epoxynor-

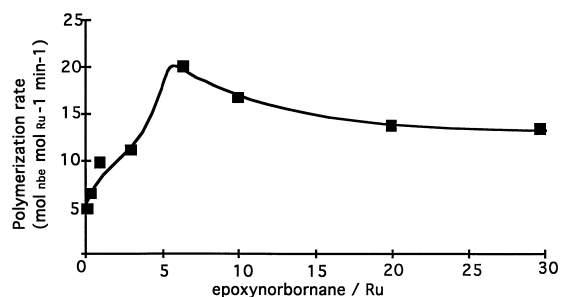


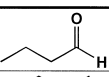
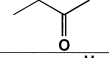
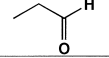
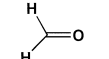
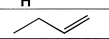
Fig. 1. Norbornene polymerization rate by the $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ /epoxynorbornane system as a function of the epoxynorbornane/Ru ratio.

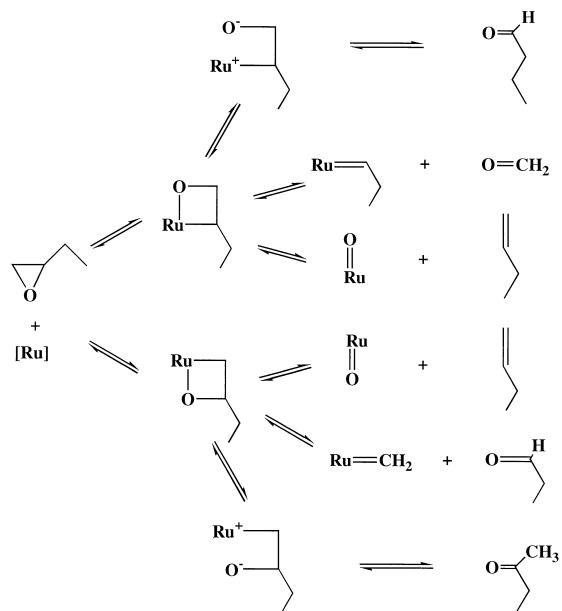
bornane increases the rate of norbornene polymerization by a factor up to 4. There is in fact an optimum ratio epoxide/ruthenium, near epoxide/Ru = 6. When another epoxide is used, the kinetic behaviour is qualitatively the same but the highest polymerization rate is obtained at a different epoxide/Ru ratio (for example ca. 1.0 for epoxyoctane). The epoxide thus promotes the reaction. This observation is in agreement with the results of Ivin et al. [15]; however, in our case, addition of molecular oxygen did not increase significantly the polymerization rate, showing that the formation of the epoxide from molecular oxygen and norbornene was very slow.

Ivin et al. proposed a mechanism involving the formation of metallaoxacyclobutanes by reaction of the epoxide with the ruthenium complex. By using epoxynorbornane or epoxyoctane, we were unable to observe evidence for such a mechanism, probably due to difficulties in analysis of the reaction products. We studied then the reaction of 1,2-epoxybutane with $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ both at 30 and 65°C. At the two temperatures, the same products evolved: butanone, *n*-butanal, 1-butene, propanal and formaldehyde. Their relative amounts are given in Table 2.

The formation of all these compounds can be explained easily by assuming that the reaction

Table 2
Products formed by interaction of epoxybutane with $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ at various temperatures

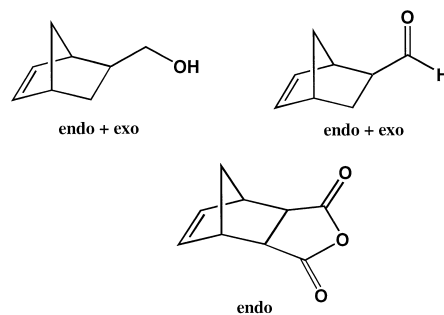
Products	Amount (10^6 per mol of ruthenium)	
	30 °C	65 °C
	15.0	3.7
	3.4	23
	6.8	9.0
	traces	traces
	2.2	traces



Scheme 6.

passes through the formation of metallaoxacyclobutanes (Scheme 6).

Depending on which C–O bond of the epoxide is broken, two metallaoxacyclobutanes can be formed. By metathetic opening, these cyclobutanes lead to formaldehyde, 1-butene and propanal and to the initiating ruthenium carbenes. However, the most important pathway (for this epoxide) seems to be a β -H elimination which leads to butanone or *n*-butanal. Even if most of these products could be formed via other mechanisms, these results are consistent



Scheme 7.

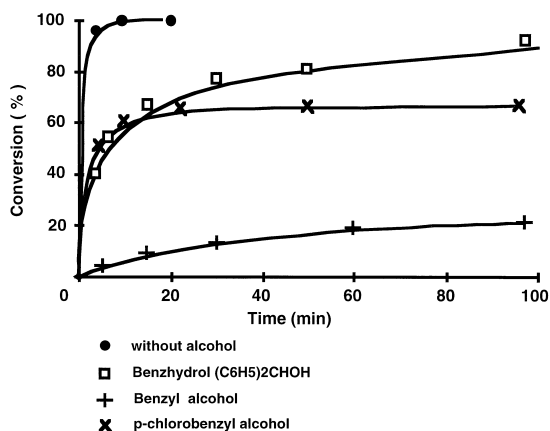


Fig. 2. Polymerization of 5-norbornene-2-methanol by RuCl_3 in the presence of various alcohols.

with a mechanism passing through metallaoxacyclobutanes.

3.5. Application to the polymerization of functionalized norbornenes

The polymerization of various functionalized norbornenes by $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ was studied (Scheme 7). The best results were obtained with 5-norbornene-2-methanol and 5-norbornene-2-carboxaldehyde. However, in presence of alcohols, the reaction was very slow, and not quantitative. As an example Fig. 2 gives the conversion of 5-norbornene-2-methanol as a function of time with various alcohols. 5-Norbornene-2-carboxaldehyde gives similar results. In contrast, in absence of alcohol the polymerization is very rapid and quantitative. This shows that the alcohol and aldehyde functions can react directly with the metallic center, leading directly to the active species.

Polymerization of 5-norbornene-2,3-dicarboxylic anhydride is more difficult, probably due to the presence of protons formed during the reaction of the alcohol with ruthenium trichloride. Indeed, the anhydrides decompose into carboxylic acids in acidic media. However, a relatively slow polymerization is observed with the $\text{RuCl}_3 \cdot x\text{H}_2\text{O}/p$ -chlorobenzyl alcohol system.

4. Conclusion

We have shown that the nature of the alcohol has a great influence on the catalytic performances of the $\text{RuCl}_3 \cdot x\text{H}_2\text{O}/\text{alcohol}$ system in the polymerization of norbornene. The best results were achieved with benzyl or *p*-chlorobenzyl alcohols: the resulting systems are up to 50 times more active than the original $\text{RuCl}_3 \cdot x\text{H}_2\text{O}/n$ -butanol catalyst, used industrially. The reaction mechanism involves the formation of a ruthenium alkoxide which decomposes into a hydrido-acyl complex via a β -H elimination reaction. In the last step this complex transforms into the active ruthenium hydride species by loss of an aldehyde molecule. In the presence of epoxides or tertiary alcohols, the reaction mechanism is completely different and passes through metallaoxacyclobutanes, which, by metathetic opening, give directly the ruthenium carbene complexes.

The polymerization of oxygen-containing functionalized norbornenes (alcohol or aldehyde functions) occurs very rapidly in presence of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ alone.

References

- [1] K.J. Ivin, J.C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, London, 1997.
- [2] V. Dragutan, A.T. Balaban, M. Dimonie, *Olefin Metathesis and Ring-Opening Polymerization of Cyclo-Olefins*, Wiley, New York, 1985.
- [3] R. Streck, in: Y. Imamoglu, B. Zümreoglu, A.J. Amass (Eds.), *Olefin Metathesis and Polymerization Catalysts*, NATO ASI Series 326 (1990), p. 489.
- [4] J. Feldman, R.R. Schrock, *Prog. Inorg. Chem.* 39 (1991) 1.
- [5] J. Wengrovius, R.R. Schrock, M.R. Churchill, J.R. Missert, W.J. Young, *J. Am. Chem. Soc.* 102 (1980) 4515.
- [6] F. Lefebvre, M. Leconte, S. Pagano, A. Mutch, J.M. Basset, *Polyhedron* 14 (1995) 3209.
- [7] R.H. Grubbs, S.J. Miller, G.C. Fu, *Acc. Chem. Res.* 28 (1995) 446.
- [8] S.T. Nguyen, L.K. Johnson, R.H. Grubbs, J.W. Ziller, *J. Am. Chem. Soc.* 114 (1992) 3974.
- [9] S.J. Miller, S.H. Kim, Z.R. Chen, R.H. Grubbs, *J. Am. Chem. Soc.* 117 (1995) 2108.
- [10] S.H. Kim, N. Bowden, R.H. Grubbs, *J. Am. Chem. Soc.* 116 (1994) 10801.

- [11] G.C. Fu, R.H. Grubbs, *J. Am. Chem. Soc.* 114 (1992) 5426.
- [12] D.M. Lynn, S. Kanaoka, R.H. Grubbs, *J. Am. Chem. Soc.* 118 (1996) 784.
- [13] A. Demonceau, A.F. Noels, E. Saive, A.J. Hubert, *J. Mol. Catal.* 76 (1992) 123.
- [14] A.F. Noels, A. Demonceau, E. Coulier, A.J. Hubert, R.L. Marquez-Silva, R. Sanchez-Delgado, *J. Chem. Soc., Chem. Commun.* (1988) 783.
- [15] K.J. Ivin, B.S.R. Boreddy, J.J. Rooney, *J. Chem. Soc., Chem. Commun.* (1981) 1062.
- [16] J. Chatt, B.L. Shaw, A.E. Field, *J. Chem. Soc.* (1964) 466.
- [17] J. Chatt, B.L. Shaw, *Chem. Ind.* (1961) 290.
- [18] C. Tanielian, A. Kiennemann, T. Ösparucu, *Can. J. Chem.* 57 (1979) 2022.
- [19] C. Tanielian, A. Kiennemann, T. Ösparucu, *Can. J. Chem.* 58 (1980) 2813.