# An investigation into the activity of the in situ ruthenium(III) chloride catalytic system for the metathesis of 1-octene

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## Abstract

A catalytic system consisting of RuCl$_3$·hydrate, a phosphine and an alkyne were investigated for the metathesis of 1-octene. Hydrogen was used during the reaction to obtain the highest yield of primary metathesis products. The influence of additives (oxygenates) was investigated and the reaction conditions optimized. Metathesis of 1-octene shows the best results at temperatures between 80 and 90 °C if acetic acid or ethanol was used as solvent and a PCy$_3$/Ru molar ratio of 1. It was also found that both internal and terminal alkynes could be used for the in situ activation of the metathesis precursor during metathesis reactions. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

A large number of homogeneous alkene metathesis catalyst systems are known to date [1]. Almost any metal capable of forming a metal carbene in situ or ex situ can be used. The most famous homogeneous catalyst systems are those based on the Schrock and Grubbs type metal carbene complexes. It was further found that the rate of ADMET, ROMP and acyclic metathesis reactions observed with these initiators were astonishing which led to a drive in finding faster initiators. Generally, these "so-called" fast initiators did not, however, keep up with functional group tolerance and it is frequently found that the faster the initiation, the more sensitive towards impurities, functional groups and polar solvents the catalyst become

[1]. The preformed RuCl$_2$(PCy$_3$)$_2$(=CHPh) complex is one of the catalysts that exhibit high metathesis initiation with exceptional high functional group tolerance [2]. It is, however, known that this complex undergoes deactivation during metathesis, as most initiators do and must be sacrificed during application.

It was only in the last number of years that ruthenium-based catalysts, such as the carbene complexes, developed by Grubbs and co-workers [2,3], showed promise because of its tolerance towards polar functional groups. Currently, it is mainly used in organic synthesis and for metathesis polymerization reactions. The most prominent and well studied of these systems are RuCl$_2$(=CHR)(PR$_3'$)$_2$ complexes [2]. They have the highest activity and selectivity when R′ = isopropyl or cyclohexyl [4].

From an industrial application perspective these catalysts are expensive (time and cost) to prepare and use. A more cost effective method seems to be the in situ catalytic system reported by Nubel and Hunt [5].

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They found that this catalytic system is very active for the metathesis of terminal alkenes with turnover rates of about $1000\,min^{-1}$ and turnover numbers of 50,000–100,000 after 2 h at 80–90 °C. Other in situ ruthenium-based catalytic systems with remarkable metathesis activity and functional group tolerance were also reported lately [6,7].

In our search [8,9] to find a catalytic system with a high metathesis activity towards longer chain terminal alkenes under moderate reaction conditions, and with a high tolerance against oxygen-containing additives (oxygenates), we decided to investigate the in situ $RuCl_3$·hydrate catalytic system. In this study, we investigated the metathesis activity and selectivity of this catalytic system towards 1-octene. Reaction conditions were optimized and it was found that the in situ system could be promoted with the use of both terminal and internal alkynes. The system was active in the presence of oxygenates with similar boiling points than 1-octene and also when it was subjected to a typical industrial feed stream.

## 2. Experimental

1-Octene (Aldrich) were passed through basic alumina and stored under nitrogen (very important!). Solvents such as ethanol, acetic acid and chlorobenzene (all from Merck) were dried and stored under a nitrogen atmosphere. The $RuCl_3$·hydrate and tricyclohexyl phosphine (Aldrich) were used as received. The oxygenates butanol, 2-pentanone, acetic acid and *n*-butyl acetate (all from Merck) were used as received. Water used was deionized using a Millipore water purification system. The alkynes 2-butyne-1,4-diol diacetate (BDD), 1-hexyne, 2-hexyne, 3-hexyne, 4-octyne, phenylacetylene and diphenylacetylene (all from Aldrich) were used as received. Glassware (20 ml round-bottom flask and cooler) were thoroughly cleaned, rinsed with acetone and dried in an oven at 100 °C. All liquids were transferred with Hamilton gastight syringes.

In a typical reaction, 1-octene (1 ml) was added to a 20 ml single-neck round-bottomed flask fitted with a cooler and an additional gas inlet port. The experimental setup was thoroughly purged with nitrogen before the rest of the reagents were added and kept under a nitrogen atmosphere. The phosphine ($1.24 \times 10^{-4}$ mol) dissolved in chlorobenzene

(5 ml) was then added to the alkene followed by the alkyne ($5 \times 10^{-4}$ mol). Finally, $RuCl_3$·hydrate ($5 \times 10^{-5}$ mol) dissolved in ethanol (concentration of mixture is $0.07\,mol\,dm^{-3}$) was added. The order of addition was found to be very important. If the ruthenium compound was added before the alkene no reaction took place. The reaction mixture was kept at the desired temperature for 2 h with stirring, while $H_2$ was simultaneously bubbled through the reaction mixture at a constant flow rate. In the experiments where the influence of oxygenates were investigated, the oxygenated component was added directly after the alkene in the sequence. Unless otherwise indicated, molar ratios and conditions used in the experiments were the following: alkyne/Ru = 10, alkene/Ru = 650, phosphine/Ru = 2.5 and reaction temperature = 80 °C.

Reaction mixtures were analyzed using a Carlo Erba HRGC 4300 gas chromatograph equipped with an Alltech SE-30 capillary column ($30\,m \times 0.32\,mm \times 0.25\,\mu m$) and a flame ionization detector (FID). The following instrumental conditions were used: inlet temperature of 300 °C, injection volume of $0.2\,\mu l$, oven programmed from 70 to 250 °C at $10\,°C\,min^{-1}$, $N_2$ carrier gas with a flow rate of $2\,cm^3\,min^{-1}$ at 20 °C and FID temperature of 350 °C. A typical gas chromatogram is shown in Fig. 1. The internal standard method with 1,2-dichlorobenzene as standard was used to calculate the mole percentage of 1-alkene and metathesis products formed.

## 3. Results and discussion

Gas chromatographic analyses (see Fig. 1) of the reaction mixtures indicated the formation of primary metathesis product (PMP) and secondary metathesis product (SMP). Only the SMPs with a carbon chain length longer than the substrate and shorter than the high molecular mass PMP were seen on the chromatogram. The different metathesis products are formed as a consequence of the isomerization of 1-octene–2-octene and the following metathesis reactions [8]:

*Primary metathesis reaction*:

$$2CH_3(CH_2)_5CH=CH_2$$
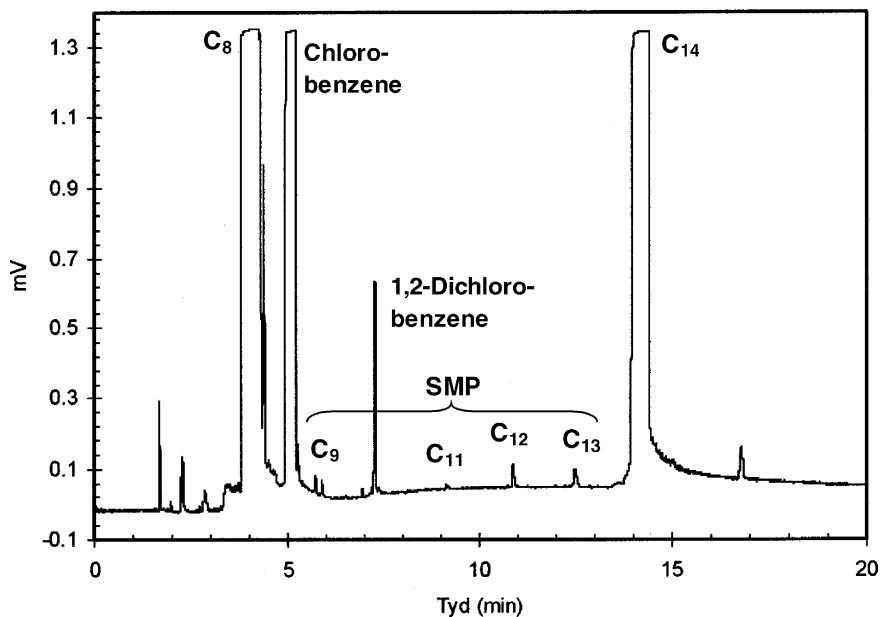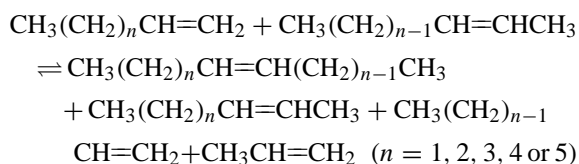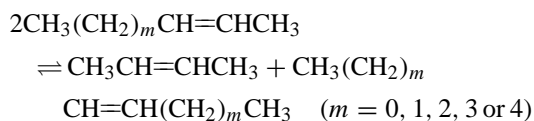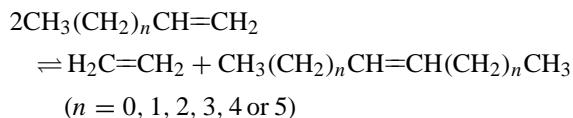$$\rightleftharpoons H_2C=CH_2 + CH_3(CH_2)_5CH=CH(CH_2)_5CH_3$$
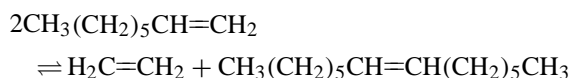
Fig. 1. A typical gas chromatogram of a metathesis reaction mixture of 1-octene.

*Secondary metathesis reactions*:

$$2CH_3(CH_2)_nCH=CH_2$$
$$\rightleftharpoons H_2C=CH_2 + CH_3(CH_2)_nCH=CH(CH_2)_nCH_3$$
$$(n = 0, 1, 2, 3, 4 \text{ or } 5)$$

$$2CH_3(CH_2)_mCH=CHCH_3$$
$$\rightleftharpoons CH_3CH=CHCH_3 + CH_3(CH_2)_m$$
$$CH=CH(CH_2)_mCH_3 \quad (m = 0, 1, 2, 3 \text{ or } 4)$$

$$CH_3(CH_2)_nCH=CH_2 + CH_3(CH_2)_{n-1}CH=CHCH_3$$
$$\rightleftharpoons CH_3(CH_2)_nCH=CH(CH_2)_{n-1}CH_3$$
$$+ CH_3(CH_2)_nCH=CHCH_3 + CH_3(CH_2)_{n-1}$$
$$CH=CH_2 + CH_3CH=CH_2 \quad (n = 1, 2, 3, 4 \text{ or } 5)$$

In Fig. 2, the influence of the reaction temperature on the activity of the in situ catalytic system were investigated in the presence of different precatalyst solvents. The solvents used were ethanol and acetic acid [5]. $RuCl_3$·hydrate was dissolved in both solvents, respectively, and used in the reaction as described in Section 2. For the catalytic system $RuCl_3$·hydrate/ethanol/$PCy_3$/BDD, an optimum activity was obtained at a reaction temperature of about 80 °C. With a further increase in the reaction temperature, the activity of the catalytic system decreased drastically.

In the case where the precatalyst was dissolved in acetic acid, a steady increase in PMPs could be detected with an optimum activity at a temperature of 90 °C. This catalytic system was still very active at a temperature of 150 °C.

The influence of the BDD/Ru molar ratio on the metathesis activity of the $RuCl_3$·hydrate/EtOH catalytic system is illustrated in Fig. 3. PMPs of about 25% were detected at a BDD/Ru molar ratio of 0. Metathesis equilibrium was reached at a molar ratio of 1–2 with an optimum yield of about 50% PMPs. The SMPs varied between 2 and 4% over the whole BDD/Ru molar ratio range investigated. Thus, high selectivities were obtained during the reactions at different molar ratios, indicating very little double bond isomerization.

The influence of the BDD/Ru molar ratio on the metathesis activity of the $RuCl_3$·hydrate/MeCOOH catalytic system is illustrated in Fig. 4. Initially, a PMP yield of about 36% was obtained at a molar
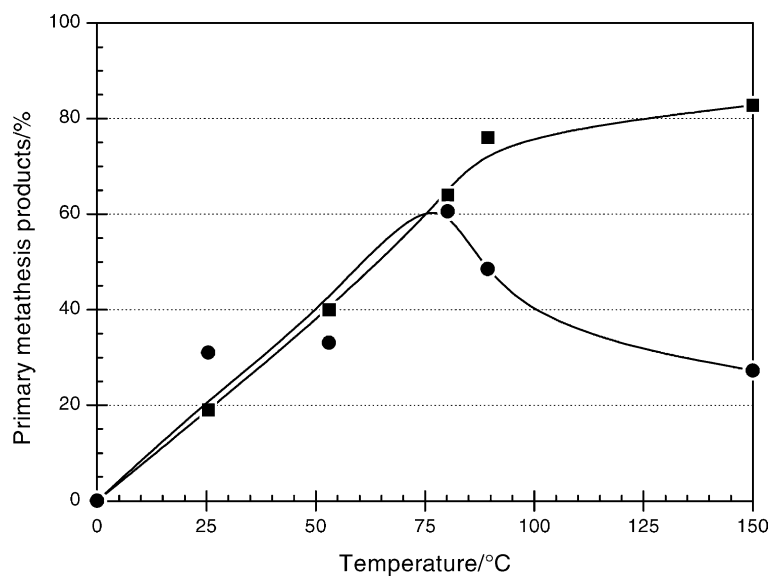
Fig. 2. Influence of different solvents of RuCl$_3$·hydrate at various reaction temperatures on the metathesis activity of the catalytic system towards 1-octene: (■) acetic acid; (●) ethanol.

ratio of 0. This is about 10% higher than was the case when ethanol was used as the solvent. An optimum yield of about 70% PMP and 1% SMP was obtained at a molar ratio of 10 and higher. Again, high

selectivities were obtained over the whole molar ratio range investigated.

In their study, Nubel and Hunt [5] reported higher conversions of 1-tetradecene in the presence of
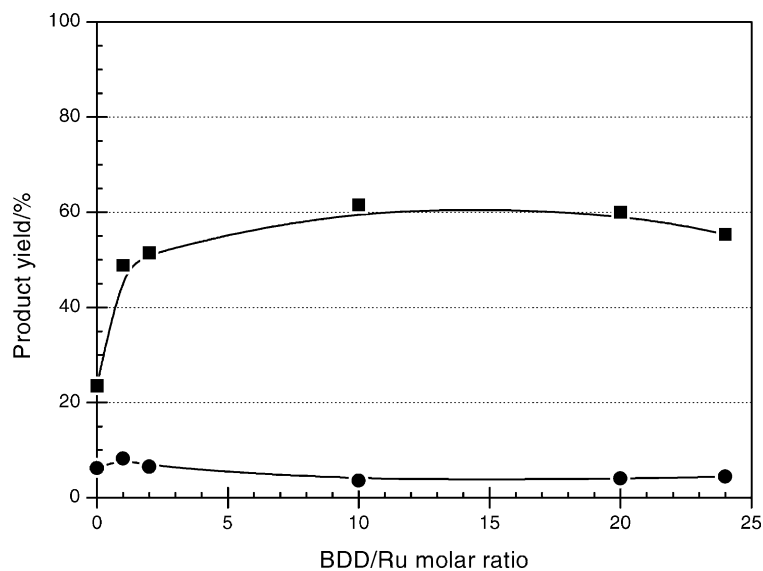


Fig. 3. Influence of the BDD/Ru molar ratio on the metathesis activity of the RuCl$_3$·hydrate/EtOH catalytic system towards 1-octene: (■) PMP; (●) SMP.
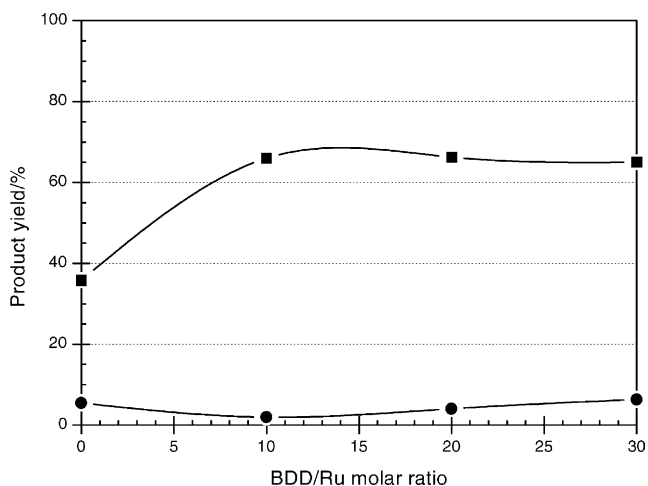
Fig. 4. Influence of the BDD/Ru molar ratio on the metathesis activity of the RuCl$_3$·hydrate/MeCOOH catalytic system towards 1-octene: (■) PMP; (●) SMP.

functionalized alkynes (BDD and propargyl acetate) than simple alkynes. We also investigated other aliphatic and aromatic alkynes to determine their influence on the metathesis of 1-octene. In Fig. 5, the influence of different alkynes on the metathesis activity of the RuCl$_3$·hydrate/EtOH catalytic system is given. The alkynes used were: BDD, diphenylacetylene,

phenylacetylene and 4-octyne. All the alkynes are symmetrical internal alkynes except phenylacetylene. All the alkynes gave similar yields, i.e. higher than 60% of PMPs and lower than 7% SMPs. In Fig. 6, the influence of the different alkynes on the metathesis activity of the RuCl$_3$·hydrate/MeCOOH catalytic system is given. All the alkynes gave a



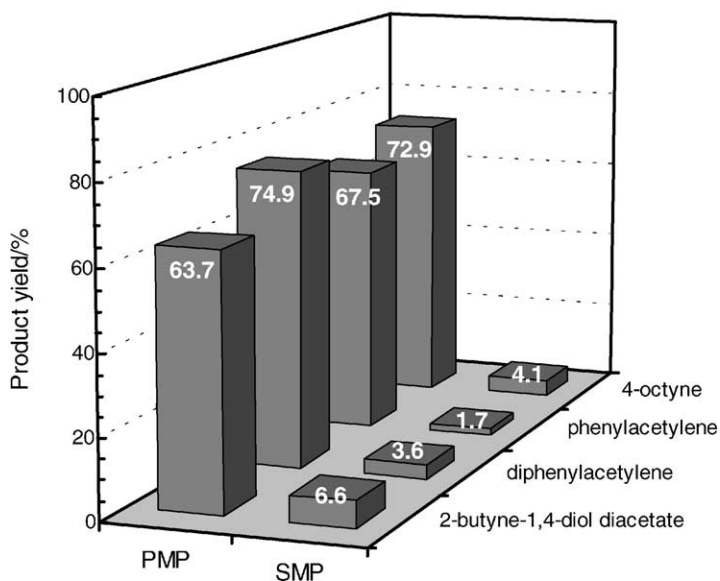Fig. 5. Influence of different alkynes on the metathesis activity of the RuCl$_3$·hydrate/EtOH catalytic system towards 1-octene.
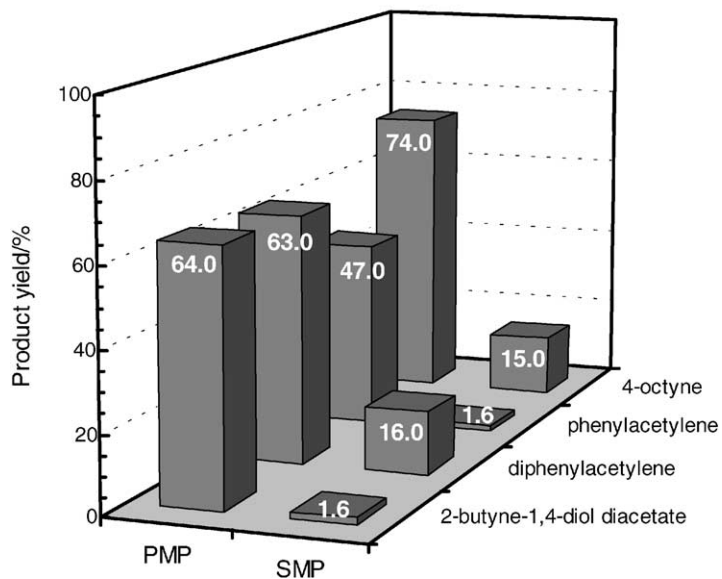
Fig. 6. Influence of different alkynes on the metathesis activity of the RuCl$_3$·hydrate/MeCOOH catalytic system with 1-octene.

yield of PMPs higher than 60% except for phenylacetylene with a yield of about 47%. The selectivity of BDD and phenylacetylene are very high with a yield lower than 5% SMPs. The yield of SMPs is about 16% for both diphenylacetylene and 4-octyne.

The influence of different solvents, acetic acid, ethanol and water, used to dissolve RuCl$_3$·hydrate is
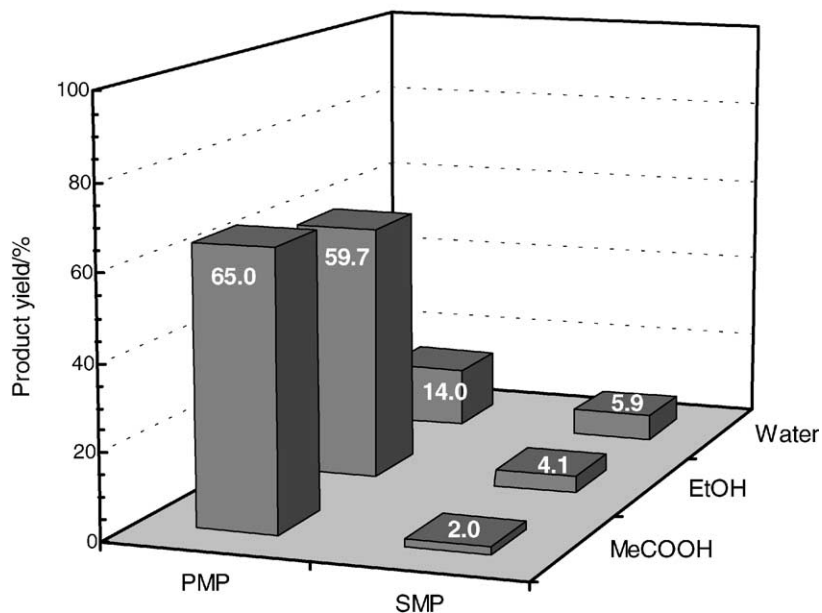


Fig. 7. Influence of different solvents on the metathesis activity of the RuCl$_3$·hydrate catalytic system with 1-octene.

Table 1
The influence of additives on the metathesis activity of the RuCl$_3$·hydrate/solvent/PCy$_3$/BDD/1-octene catalytic system

| Additive | Solvent | Additive/Ru molar ratio | PMP (%) | SMP (%) | Selectivity (%) |
|---|---|---|---|---|---|
| No additives | EtOH | 0 | 59.7 | 4.1 | 93.6 |
| | AcOH | 0 | 65.0 | 2.0 | 97.0 |
| Water | EtOH | 10 | 69.1 | 1.0 | 98.6 |
| | | 60 | 50.0 | 2.3 | 95.6 |
| | AcOH | 60 | 62.6 | 2.3 | 96.5 |
| 1-Butanol | EtOH | 10 | 65.1 | 1.5 | 97.8 |
| | | 60 | 61.0 | 0.5 | 98.9 |
| | AcOH | 60 | 49.8 | 1.1 | 97.9 |
| Acetic acid | EtOH | 10 | 71.4 | 1.0 | 98.7 |
| | | 60 | 58.9 | 0.7 | 97.4 |
| | AcOH | 60 | 64.6 | 4.5 | 93.5 |
| 2-Pentanone | EtOH | 10 | 73.4 | 1.0 | 98.7 |
| | | 60 | 59.8 | 2.2 | 96.5 |
| | AcOH | 60 | 77.7 | 1.5 | 98.0 |
| *n*-Butyl acetate | EtOH | 10 | 63.4 | 1.1 | 98.3 |
| | | 60 | 77.0 | 0.7 | 99.1 |
| | AcOH | 60 | 69.2 | 2.4 | 96.6 |

illustrated in Fig. 7. Acetic acid and ethanol have almost the same effect on the activity and selectivity of the RuCl$_3$·hydrate catalytic system. Low metathesis activity of the catalytic system was detected if water was used as the solvent. This behavior can best be explained in terms of phase separation between the organic and water phases.

The influence of different oxygenates on the RuCl$_3$·hydrate/PCy$_3$/BDD/1-octene catalytic system with ethanol as solvent is illustrated in Table 1. These additives were selected to include a number of functionalized compounds having similar boiling points than 1-octene and which is generally found in industrial streams. No general tendency can be derived from these results. Generally, the addition of the additives resulted in an increase in the primary metathesis activity and a decrease in secondary products (a few exceptions do, however, exist). Selectivities remained high, above 90%.

In Fig. 8, the influence of different PCy$_3$/Ru molar ratios on the metathesis activity of the RuCl$_3$·hydrate/EtOH catalytic system with 1-octene was investigated. The catalytic system already reaches equilibrium at a PCy$_3$/Ru molar ratio of 1. A yield of about 64% PMPs and about 4% secondary metathesis were obtained with molar ratios ranging from 1 to 4.

In Table 2, the influence of different alkene/Ru molar ratios were investigated in the presence of the RuCl$_3$·hydrate/EtOH/PCy$_3$/BDD/1-octene catalytic system. This was done as a measure of the economic viability of this system in an industrial environment. A steady decline in PMPs were observed with an increase in the alkene/Ru molar ratio. At an alkene/Ru molar ratio of about 60,000 a yield of 40% PMPs and 4% SMPs were obtained. The selectivity of the system towards primary products decreased to 90%.

In an attempt to determine whether the position of the triple bond of the alkyne has an influence on the activity of the in situ catalytic system, activation by means of different hexynes, i.e. 1-hexyne, 2-hexyne and 3-hexyne, were investigated. The influence of

Table 2
The influence of the alkene/Ru molar ratio on the metathesis activity of the RuCl$_3$·hydrate/EtOH/PCy$_3$/BDD/1-octene catalytic system

| Alkene/Ru molar ratio | PMP (%) | SMP (%) | Selectivity (%) |
|---|---|---|---|
| 650 | 62.00 | 2.11 | 96.71 |
| 1000 | 65.63 | 2.10 | 96.89 |
| 10000 | 59.33 | 0.96 | 98.39 |
| 60000 | 40.03 | 4.39 | 90.12 |

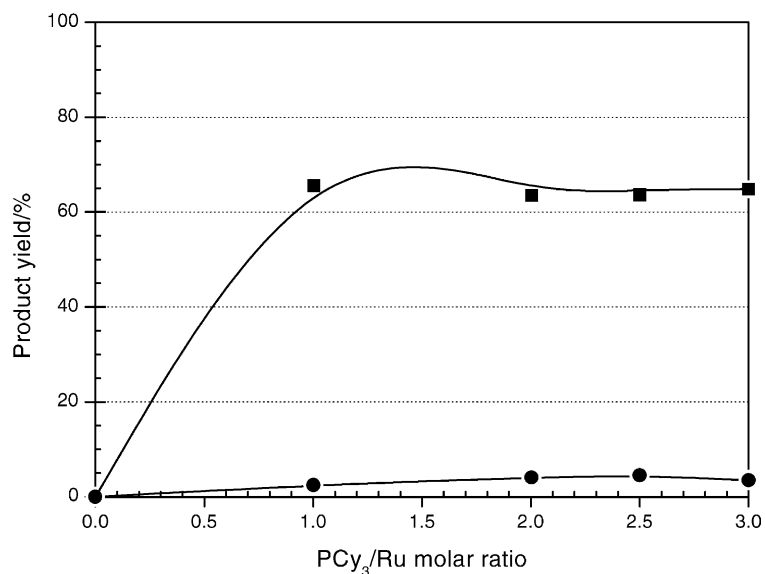Fig. 8. Influence of different PCy$_3$/Ru molar ratios on the metathesis activity of the RuCl$_3$·hydrate/EtOH catalytic system with 1-octene.

the hexynes on the metathesis activity of the RuCl$_3$·hydrate/EtOH/PCy$_3$/1-octene catalytic system is shown in Fig. 9. 1-Hexyne and 3-hexyne gives almost the same yield of PMPs, about 60%. 1-Hexyne gave a higher yield of SMPs, about 7%. The yield of

PMPs in the case of 2-hexyne is a little lower than the other two (it could also be attributed to experimental error). Generally, it is safe to say that there is no significant difference in the activation ability if the triple bond of the alkyne is internal or terminal.
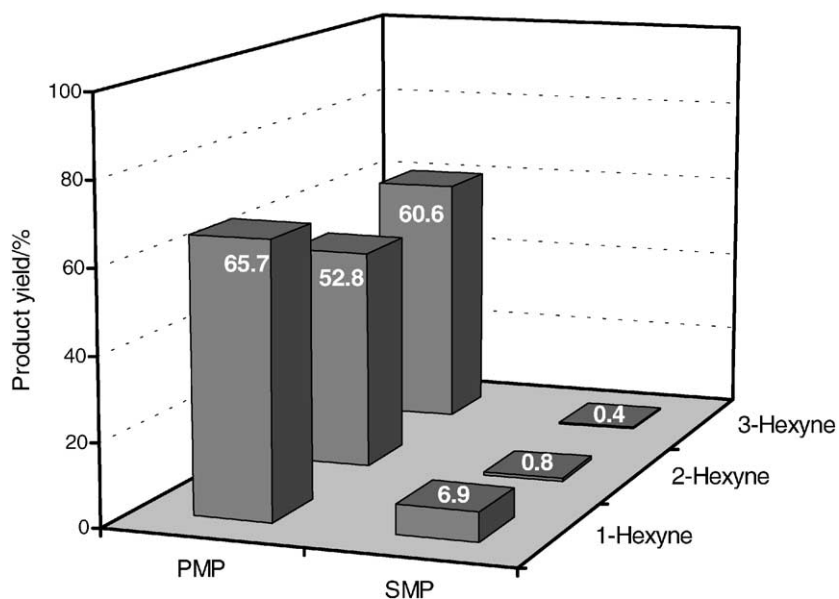


Fig. 9. The influence of hexynes on the metathesis activity of the RuCl$_3$·hydrate/EtOH/PCy$_3$/1-octene catalytic system.

## 4. Conclusions

In this study, we concentrated on the optimization of the reaction conditions of the in situ $RuCl_3 \cdot$hydrate catalytic system for the metathesis of 1-octene. The $RuCl_3 \cdot$hydrate/$PCy_3$/BDD gave an optimum metathesis activity at temperatures of about 80 °C (if EtOH was used as the solvent for the hydrate) and 90 °C (if MeCOOH was used as the solvent for the hydrate). If acetic acid was used as solvent, the catalytic system is still stable even at temperatures as high as 150 °C.

Both systems (EtOH and MeCOOH) gave an optimum activity at a BDD/Ru molar ratio of about 10. Metathesis activity is also possible without any alkynes present. Internal and terminal alkynes were used to determine the effect of the alkyne in activating the system. It is clear that the type of alkyne plays no obvious role. We used water, acetic acid and ethanol as the solvent for $RuCl_3 \cdot$hydrate. Acetic acid and $RuCl_3 \cdot$hydrate together are a more active catalytic system for terminal alkenes. Optimum metathesis activity was also observed at a $PCy_3$/Ru molar ratio of 1. This may indicate that only one phosphine ligand is necessary for an active catalyst.

The influence of different additives, such as $H_2O$, BuOH, MeCOOH, BuOAc and PrCOMe, on the activity of the $RuCl_3 \cdot$hydrate (EtOH or MeCOOH as the solvent)/$PCy_3$/BDD/1-octene catalytic system was also studied. No deactivation of the catalytic system was detected even with an additive/Ru molar ratio of 60. In the case where ethanol was used as the solvent for the hydrate, an increase in selectivity was detected when the additive/Ru molar ratio was increased.

The influence of the alkene/Ru molar ratio on the $RuCl_3 \cdot$hydrate/$PCy_3$/BDD/1-octene/EtOH catalytic system was investigated and if the alkene/Ru molar ratio was increased to 60,000, a yield of 40% PMPs were observed. The results obtained in the presence of the additives and the alkene/Ru molar ratio indicate that the in situ Ru system has great potential for application in an industrial environment.

In an attempt to find a satisfactory explanation for the formation of a metathesis initiator under these in situ conditions, we turned to literature.

In this study, the $RuCl_3 \cdot$hydrate was firstly dissolved in either ethanol or acetic acid. The role of the solvents may be to reduce the Ru(III) complex to a Ru(II) complex [10] or a metal hydride may be formed [11]. If $RuCl_3 \cdot$hydrate is dissolved in ethanol a ruthenium alkoxide complex forms via a β hydride elimination that subsequently decomposes to a ruthenium hydride [11]:
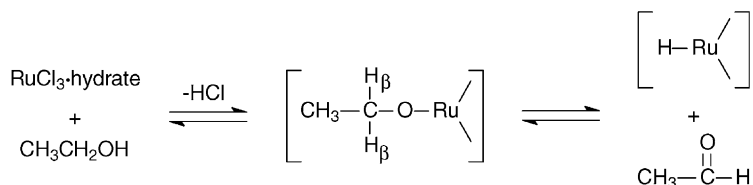


The metal hydride route is supported by a study of Wolf et al. [12]. In this study, a metal hydride complex was isolated when $RuCl_2(COD)_2$ was dissolved in 2-butanol and reacted with $P(i\text{-}Pr_3)_3$ and $H_2$ at 80 °C:
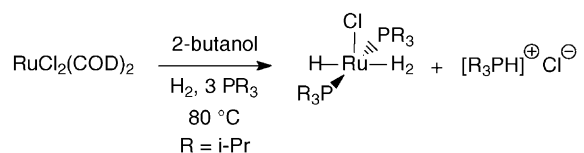


It is also known that $RuCl_3$ can react with $PCy_3$ to form $RuHClL_2$ under reducing conditions. The role of $H_2$ in the reaction could therefore be: (a) to reduce the metal and (b) to stabilize the organometallic compound through an oxidative addition reaction [12]:
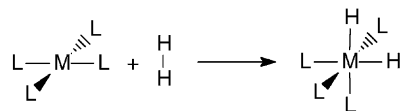


Because $RuCl_3 \cdot$hydrate, ethanol (or acetic acid), $PCy_3$, $H_2$ and 80 °C were used in this study we assume that a similar metal hydride species, i.e. $RuHCl(H_2)(PCy_3)_2$, was formed.
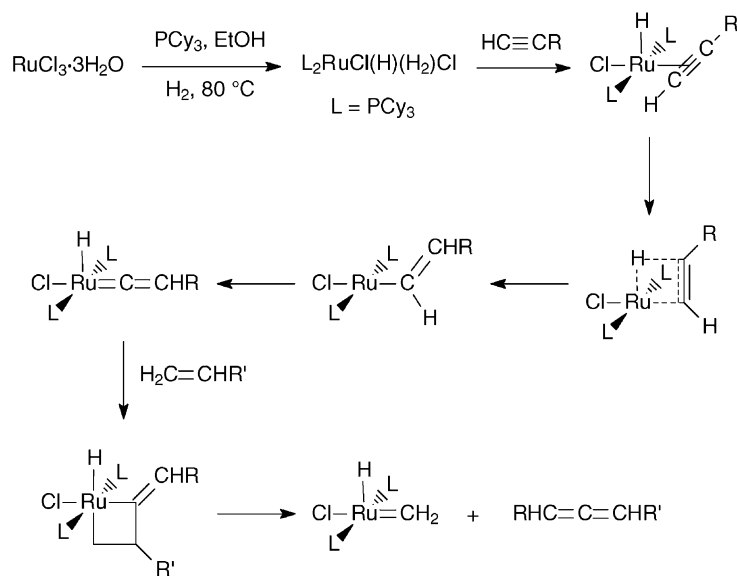
The next step in the in situ metathesis reaction is the addition of an alkyne. According to the experimental data in this study, it is clear that the $RuCl_3 \cdot$hydrate catalytic system is highly active in the presence of a terminal or internal alkyne. Wolf et al. [12] postulated the formation of a metal carbene (**1**, **2**) when an alkyne

reacts with the RuHCl(H$_2$)L$_2$ complex in the presence of [HPCy$_3$]Cl:
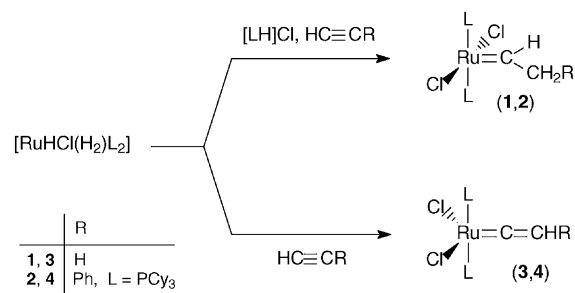


to a metallacyclobutane complex in the presence of a terminal alkene, which subsequently leads to a ruthenium carbene complex. This may explain why we found that the in situ catalytic system is active in the absence of an alkyne. It appears that the presence of an alkyne causes the route to the active carbene via the vinylidene species to be much faster and that the alkene can thus act as a proton source.

A possible mechanism for the formation of the active metal carbene in the in situ ruthenium system using a terminal alkyne can thus be visualized as follows:



This is not the only viable route to a metal carbene under the reaction conditions used in this investigation. Further investigations using inter-alia spectroscopic methods need to be done to understand the mechanism.

In the absence of the phosphine salt the hydrido vinylidene complexes **3** and **4** are formed. The vinylidene complexes can react with [HPCy$_3$]Cl to form the carbene complexes. HCl (or MgCl$_2$ and H$_2$O) can also be used as a proton source to convert **3** (or **4**) to **1** (or **2**) [12]. Synthetic procedures for the generation of Ru carbenes from dihydrogen complexes exist in the literature [13,14].

An alkene can also act as a proton source to form a metal carbene. According to Mutch et al. [11] the ruthenium hydride complex can be converted

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