



Novel co-catalytic activity of zinc metal with classical initiators for the ring opening polymerisation of norbornene

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Abstract

Zinc metal was shown to considerably increase the activity of the metal(III) chloride salts of ruthenium, iridium and osmium as metathesis initiators for the ROMP of norbornene. The stereochemistry of the polymers formed was determined by ^1H and ^{13}C NMR. Formation of the initial carbene species is not via the normally accepted vinyl hydride mechanism. An alternative mechanism involving a metallacyclopentane intermediate is postulated.

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Keywords: Ruthenium(III) chloride; Norbornene; ROMP; Zinc; Olefin metathesis

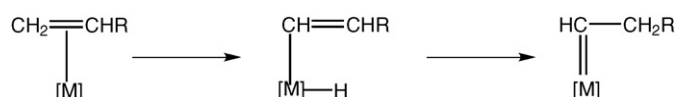
1. Introduction

The development of well-defined carbene metathesis initiators over the last decade has made alkene metathesis a useful tool for synthetic chemists [1–5]. The high activity shown by these initiators and excellent tolerance in particular of the ruthenium ones towards a variety of functional groups has facilitated numerous novel routes to many compounds via a variety of metathesis reactions. Despite these important developments classical initiators are still of interest [6–8]. This is especially true for ring opening metathesis polymerisation (ROMP) of highly active substrates such as norbornene (NBE) which may not justify the use of well-defined initiators. The metal(III) chloride salts of ruthenium, iridium and osmium are well known classical ROMP initiators. RuCl_3 is used in the industrial production of poly NBE [7,8]. These initiators have been used alone and in the presence of many different co-catalysts and their activity and the nature of the polymers they produce are well understood. It is well established that metathesis occurs via a metal carbene intermediate [9–12]. Whilst well-defined catalysts possess a carbene ligand to start with it is necessary for classical initiators to form an initial carbene species in order to perform metathesis. In most cases when unicomponent initiator systems

are employed formation of the initial carbene species is via the hydride mechanism (Scheme 1) [6]. When co-catalysts are used they can act in a number of ways usually as Lewis acids or by supplying an alkyl group to the metal that can rearrange to form a carbene. Here we present a simple initiator system based on RuCl_3 for the ROMP of NBE that utilises zinc metal as a co-catalyst. We setup these conditions in order to investigate how putting the $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ in a reducing environment altered its catalytic ability towards olefin metathesis. As highlighted in the work by Grubbs having a ruthenium(II) centre is a key to forming an active catalyst [13], while in the recent review by Katz it was emphasised that future research in the area of alkene metathesis should look again at the role of the oxidation states on the metal in the search for new initiators [14]. There are two literature precedents for the formation of an active catalytic system from a mixture of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ and zinc. McKinney and co-workers used this system to catalyse the dimerisation of acrylates [15], while recently it was used to catalyse the synthesis of unsymmetrical diorganyl selenides. Here we extend this catalytic system to olefin metathesis polymerisation [16].

Unusually the zinc co-catalyst promotes carbene formation in a manner more like that seen for unicomponent systems yet it does not proceed via the hydride mechanism that is normally associated with them. Recently, an alternative route to the formation of the propagating species involving the formation of a metallacyclopentane intermediate has been proposed [17].

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Scheme 1. The formation of the carbene initiator via a hydride transfer mechanism.

2. Experimental

2.1. Instrumentation

All NMR spectra were recorded on a Bruker Avance 300 at 25 °C. ¹H NMR spectra were recorded at 300 MHz, ¹³C spectra at 70 MHz and ³¹P at 123.6 MHz. Unless otherwise stated all samples were prepared in CDCl₃. All chemical shifts were recorded in parts per million (ppm) and referenced at 0 ppm against tetramethylsilane (TMS).

2.2. Polymerisation of NBE using groups 8 and 9 metal trihalide/metal dust systems

A typical polymerisation procedure is as follows. Metal dust (1 mmol) was added to a solution of ruthenium(III) chloride (0.032 g) in 2 ml of 1:1 ethanol:chlorobenzene in a pressure tube. Norbornene (0.5 g) was added and the tube was sealed. The mixture was stirred at 40 °C for 15 min. The polymer formed as one solid lump and separated from the reaction mixture. The polymer was chopped into smaller pieces and repeatedly washed with ethanol to remove the catalyst. It was then dissolved as much as possible in chloroform and precipitated with methanol. The polymer was dried under vacuum at 80 °C and analysed using NMR spectroscopy.

2.3. Synthesis of bis-(η^4 -dimethylmuconate)(trimethylphosphite)ruthenium(0) according to literature procedures [15]

2.3.1. Polymerisation of NBE using bis-(η^4 -dimethylmuconate)(trimethylphosphite)ruthenium(0)

This reaction was carried out using standard Schlenk techniques to exclude oxygen from the reaction vessel. A Schlenk tube was charged with bis-(η^4 -dimethylmuconate)-(trimethylphosphite)ruthenium(0) (0.06 g, 0.15 mmol) and degassed by three vacuum nitrogen cycles. Two milliliters of deoxygenated 1:1 ethanol:chlorobenzene was added via cannula under nitrogen. NBE (0.5 g) was added and the tube was sealed. The mixture was stirred at 40 °C for 2 h. The polymer was precipitated from the solution using ethanol and dried under vacuum at 80 °C. Yield 0.03 g (6%).

3. Results and discussion

Addition of zinc metal powder (100 mg) to a solution of RuCl₃·*n*H₂O (30 mg) and NBE (0.5 g) in 1:1 ethanol:chlorobenzene (2 ml), at 40 °C yielded 95% polyNBE after 2 h as opposed to 1.2% when no zinc was added (Eq. (1)) (Table 1). Furthermore, it was found that 70% polymerisa-

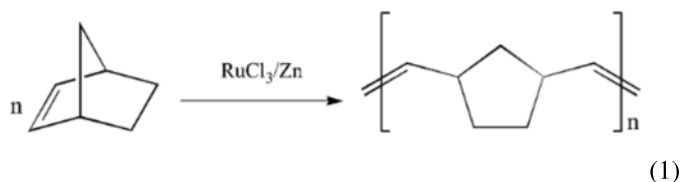
Table 1

The effect of zinc on ROMP of norbornene initiated by Group 8 and 9 trihalides

Metal chloride	Co-catalyst	Temperature (°C)	Time (min)	Polymer yield (%)
RuCl ₃	Zn	40	120	95
RuCl ₃	None	40	120	1.2
IrCl ₃	Zn	22	30	25
IrCl ₃	None	22	30	0
OsCl ₃	Zn	22	20	30
OsCl ₃	None	22	20	0
RhCl ₃	Zn	22	120	0
RhCl ₃	None	22	120	0

0.145 mmol of catalyst was used with a seven-fold excess of zinc in 1:1 ethanol:chlorobenzene.

tion was achieved after 15 min under these conditions. Similar increased activity was also observed for the analogous iridium and osmium systems whilst rhodium remained inactive (Table 1). The remainder of this work refers exclusively to the ruthenium-based system. Formation of the initiating species is the rate-limiting step in classical systems and it is believed that the increased activity is due to faster formation of the catalytic species aided by the presence of zinc metal.



Alcohols are believed to facilitate formation of the initial carbene species via the hydride mechanism [18]. The fact that the same increase in catalytic activity for the RuCl₃/Zn system was obtained in the aprotic solvent THF (Table 2) was the first indication that there was something unusual about this system and that the initial carbene species may not be formed by the accepted hydride mechanism. Further evidence against the hydride mechanism was provided when other conditions that should support it caused decreased activity and ones that should inhibit it resulted in increased activity. For example, performing the reaction under an atmosphere of H₂ resulted in slightly less polymer formation than under aerobic conditions (Table 2) and using sodium pieces, which should react with any hydride species, in place of zinc dust resulted in increased activity of the RuCl₃ catalyst (Table 3).

Co-catalysts in these systems are usually highly polar organometallic (generally main group) compounds. They act either as Lewis acids or by providing an organic moiety from which the initial carbene species is formed. As it has no organic

Table 2

Amount of poly(NBE) formed from Zn (1 mmol)/RuCl₃·*n*H₂O (0.145 mmol) after 15 min reaction at 40 °C using different reaction conditions

Solvent	Atmosphere	% polymer
1:1 ethanol:chlorobenzene	Air	70
1:1 ethanol:chlorobenzene	Hydrogen	60
1:1 ethanol:chlorobenzene	Nitrogen	60
THF	Air	70

Table 3
Ability of a range of metals with varying reduction potentials as co-catalysts for the polymerisation of NBE by RuCl₃

Metal	Reduction potential ^a (V)	% polymer ^b
Zinc	−0.8	70
Magnesium	−2.3	60
Iron	−0.4	35
Sodium ^c	−2.7	25
Silver	0.8	42
Copper	0.3	22
Aluminium	−1.7	0

^a Values taken from CRC Handbook, 59th ed., CRC Press, Cleveland.

^b Standard conditions as given in Section 2.2 were used throughout.

^c Not possible to directly compare the activity of this system to the others as reaction was performed in THF, and the metal was in small pieces instead of a fine powder.

groups it is clearly not possible for the zinc in this system to behave in this manner. It is believed that the active species in this system is a Ru(0) species with NBE ligands or ligands derived from it, the formation of which is facilitated by reduction of the RuCl₃ by zinc in the presence of NBE. Not surprisingly other metals brought about increased activity but only that of magnesium came close to zinc. Interestingly the order of activity brought about by the various metals showed no correlation with their reduction potentials (Table 3). This observation was also made by McKinney et al. when they used zinc to reduce RuCl₃ in a catalyst system for the dimerisation of acrylates [15]. Zinc probably works best as it has a high affinity for chloride ions. For this reason it has been used to abstract chlorides during the synthesis of ruthenium organometallic complexes [19].

It is often the case that an incubation period where the catalyst and co-catalyst are left together prior to addition of the monomer results in higher activity. This was not true for this system where incubation reduced activity and ruthenium metal was precipitated before any active complex could form. This would indicate that coordination of NBE ligands occurs simultaneously with or prior to reduction.

Attempts were made to test if the catalyst was substantially deactivated after 15 min reaction time. The polymerisation was carried out using RuCl₃ under the standard conditions outlined in Section 2.2. After 15 min the solid polymer was removed from the reaction and a further sample of norbornene (0.5 g) was added. The reaction was allowed to proceed for a further 15 min and the solid polymer was collected (15% yield). This finding would be consistent with the catalyst being substantially deactivated in the first 15 min of reaction. However, a significant amount of solid zinc was removed from the system upon removing the first sample of polymer, as it was stuck on the surface of the polymer. Therefore, it is also possible if the reaction is a heterogeneous one, that we are simply removing active catalyst from the system.

We were interested to know what oxidation state the zinc had reduced the ruthenium centre to. McKinney and co-workers had isolated a ruthenium(0) species using various phosphines (Fig. 1) from the system that carried out acrylate dimerisation [15], while Zhao et al. have speculated that a Ru(II) species is involved in the catalytic cycle to form unsymmetrical selenides

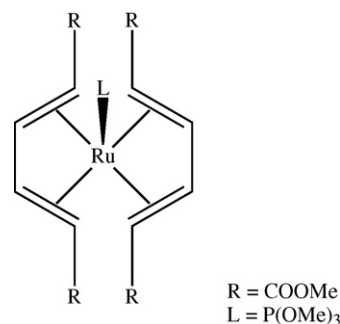


Fig. 1. Bis-(η^4 -dimethylmuconate)(trimethylphosphite)ruthenium(0).

[16]. Attempts were made to trap and isolate the active species in our system using phosphine ligands but with no success. This is often the case with classical initiator systems as only a small portion of the initiator used actually goes on to form active species. Therefore in order to investigate if the role of the zinc in facilitating the formation of the metathesis catalytic species was similar to that reported for the dimerisation system one of the complexes isolated by McKinney and co-workers bis-(η^4 -dimethylmuconate)(trimethylphosphite)ruthenium(0) (Fig. 1),

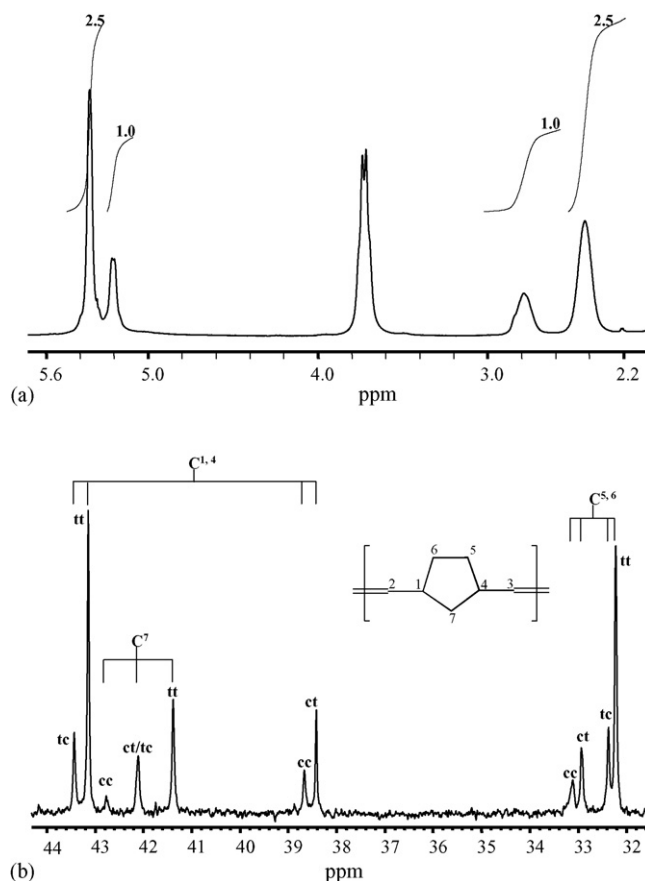


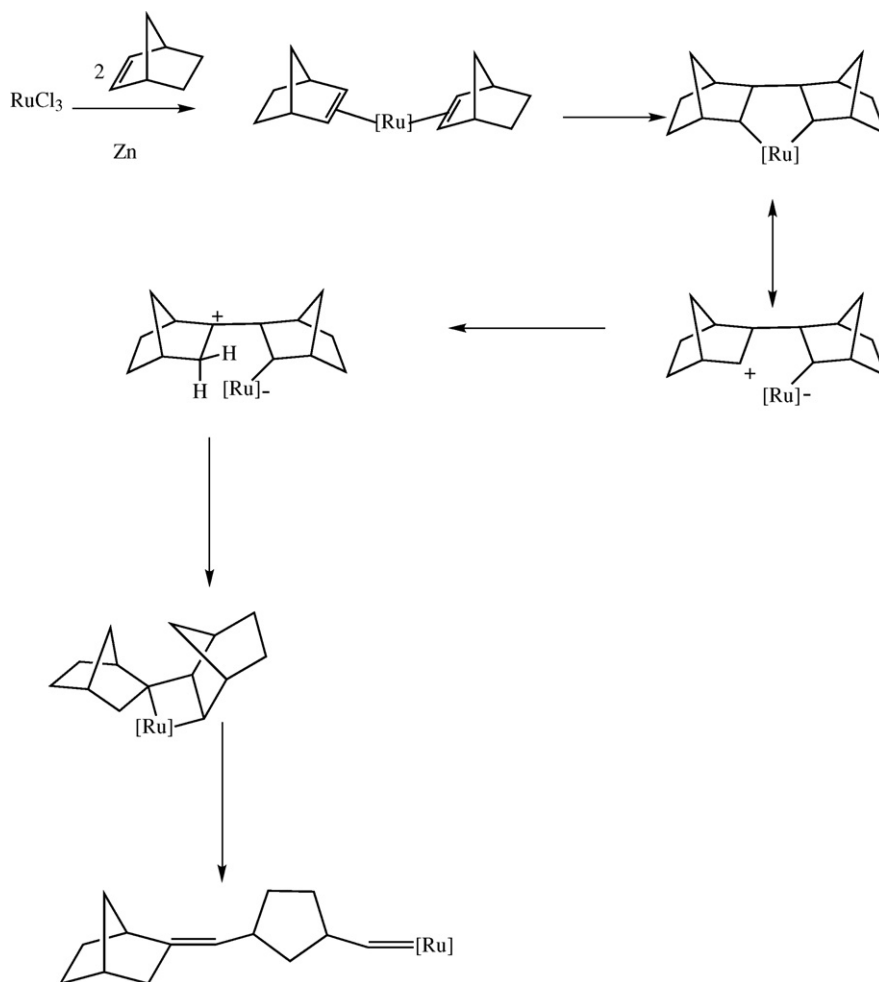
Fig. 2. (a) The ¹H NMR spectrum of polynorbornene initiated by the RuCl₃/zinc system. The olefinic protons appear as well resolved multiplets at 5.35 ppm (trans) and 5.21 ppm (cis) and those of the \square protons at 2.80 ppm (cis) and 2.45 ppm (trans). (b) The ¹³C NMR spectrum of polynorbornene prepared using RuCl₃/zinc showing the signals for the cyclopentane rings. The signals are assigned to the labelled carbons and to the dyad from which they arise.

was prepared and used as a ROMP initiator, forming polymer in a low yield (6%) with the reaction conditions used here. However, the activity is higher than using solely $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ as the initiator under similar conditions, excluding the possibility that it is a small amount of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ impurity that is active in this system. It is worth noting that the initiation of olefin ROMP using a ruthenium(0) species with no co-catalyst is highly unusual. ^1H and ^{13}C NMR analyses showed the microstructure of the polymers formed using this complex and the RuCl_3/Zn system to be very similar [20]. For both cases the percentage of *cis* double bonds (σ_c), as determined from the ^1H NMR spectra (Fig. 2a), was found to be 0.29. Analysis of the ^{13}C NMR spectra of the polymers gives information on how the *cis* and trans double bonds are distributed throughout the polymer. Signals for the four possible dyads tt, tc, cc and ct can be identified (Fig. 2b). As would be expected for both polymers the tt dyad is the most common. For both polymers the distribution of the *cis* double bonds was random as the $r_c r_t = \text{tt cc/tc ct}$ values determined for both polymers were approximately 1. It has previously been shown that the nature of the ligands on metathesis initiators affects polymer stereochemistry [21], this provides strong evidence for similar ligand environments in both of these systems. These findings lend weight to the proposal that the active species in the RuCl_3/Zn system is also a ruthenium(0) species

but we cannot completely exclude the possibility that it has the more conventional ruthenium(II) centre.

A mechanism (Scheme 2) is proposed for the olefin metathesis reaction using the Zn/RuCl_3 initiator system which does not involve the formation of a Ru-H bond and as in the case of the acrylate dimerisation catalyst involves the coordination of at least 2 alkene ligands (in this case NBE) to a ruthenium(0) centre. These rearrange to form a metallacyclopentane. This ring contracts to form a metallacyclobutane via a 1,2 H^- shift in a transient metallacarbenium ion species. This mechanism was recently proposed by Rooney et al. for metathesis initiated by methylaluminiumoxane (MAO) and other systems where the hydride mechanism does not occur [17].

Although well-known co-catalysts, it is unusual for main group metal compounds to act alone as metathesis initiators. However the activity of the aluminium system mentioned above [17] and previously, that shown by magnesium [22] based initiators indicates that zinc itself may be active in our system. Running the experiment without using RuCl_3 eliminated this possibility. Even in the presence of species previously shown to be capable of forming zinc carbenoid species such as Motherwell [23] and Simmons-Smith [24] cyclopropanating reagents no activity was observed without ruthenium. The zinc carbenoid species were also tested as co-catalysts with RuCl_3



Scheme 2. Proposed mechanism for the formation of the active carbene catalyst using the RuCl_3/Zn system.

for the polymerisation of NBE on the premise that they may aid carbene formation however this study indicated that zinc is the only important co-catalyst component.

4. Conclusions

Zinc facilitates the formation of the initial carbene species in a novel initiator system for ROMP of NBE by reduction of the Group 8 and 9 metal(III) species. This results in significantly increased activity over that observed for ROMP using the metal(III) halide alone. The study indicates that the hydride mechanism normally associated with the formation of the active carbene is not occurring in these systems. The results also give evidence that it is possible to catalyse the polymerisation of NBE using a ruthenium(0) system with no addition of a co-catalyst.

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