Available online at www.sciencedirect.com
ScienceDirect
Journal of Molecular Catalysis A: Chemical 280 (2008) 29–34
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Investigation of factors affecting ruthenium complexation in ROMP reactions of oxygen-containing norbornene derivatives using Grubbs first generation initiator

Izabela Czelusniak, Joseph D. Heywood, Alan M. Kenwright *, Ezat Khosravi *

Chemistry Department, Durham University, Durham DH1 3LE, United Kingdom

Received 31 May 2007; received in revised form 30 July 2007; accepted 15 October 2007
Available online 22 October 2007

Abstract

We report the synthesis and ring-opening metathesis polymerisation (ROMP) of a range of oxygen-containing norbornene derivatives using Grubbs first generation initiator. The ROMP reactions were followed by proton NMR and the identification of propagating species present was facilitated by the addition of excess tricyclohexyl phosphine and copper chloride (a phosphine scavenger), with the intention of further probing the structural, steric, and geometric factors determining the tendency for oxygen atoms in the monomers to complex to the ruthenium centre.

Keywords: NMR spectroscopy; Ring-opening metathesis polymerisation; Ruthenium complexes; Oxygen-containing norbornenes

1. Introduction

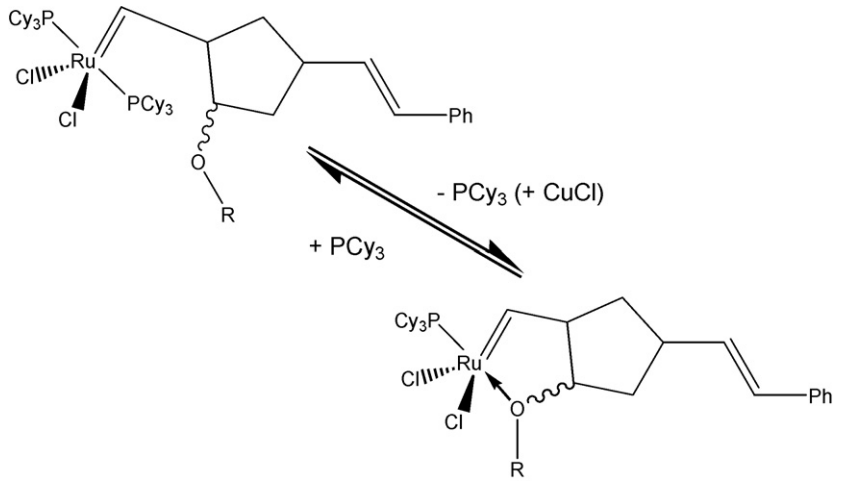
Ring-opening metathesis polymerisation (ROMP) has developed into an important method for the synthesis of custom polymers where the ability to control polymer architecture in the presence of a wide range of functional groups is of great importance. In this context, the functional group tolerance of the Grubbs ruthenium based initiators is a key factor, and has allowed the use of a much wider range of monomer species including those containing oxygen [1–3]. However, some reactions involving complexation of monomers containing oxygen to the ruthenium centre, particularly after inclusion of all the available free monomer into the living polymer chain is complete, have been observed previously in metathesis reactions [4–9]. In the case of ROMP reactions initiated using Grubbs first generation initiator, we previously reported the observation of oxygen-complexed species in solution and their identification by the addition of either excess tricyclohexyl phosphine or copper(I) chloride (a phosphine scavenger) by virtue of the type of equilibrium outlined in Scheme 1. In some cases the appearance of the oxygen-complexed species in solution accompanied the apparent regeneration of free initiator, which stimulated further investigation.

We recently reported that when the Grubbs first generation initiator (**1**) (structures of initiator and monomers are given in Scheme 2) is used to initiate the polymerisation of 7-*t*-butoxynorbornadiene (**2**) using a monomer: initiator ratio ($[M]_0/[I]_0$) of 50, the reaction proceeds rapidly in $CDCl_3$ with almost complete consumption of initiator to form propagating ruthenium alkylidene species which are then converted slowly, but not completely, back to initiator, implying a secondary metathesis reaction. This is accompanied by the appearance of a small amount of another carbene species giving a broad signal at 17.44 ppm [4]. This has subsequently been shown to correspond to a species in which the oxygen attached to the 7-position of the norbornadiene complexes to the ruthenium centre, displacing one of the tricyclohexyl phosphine groups by forming a 5-membered ring. It was also shown to be a general reaction of norbornadienes having an oxygen atom directly attached to the 7-position [5].

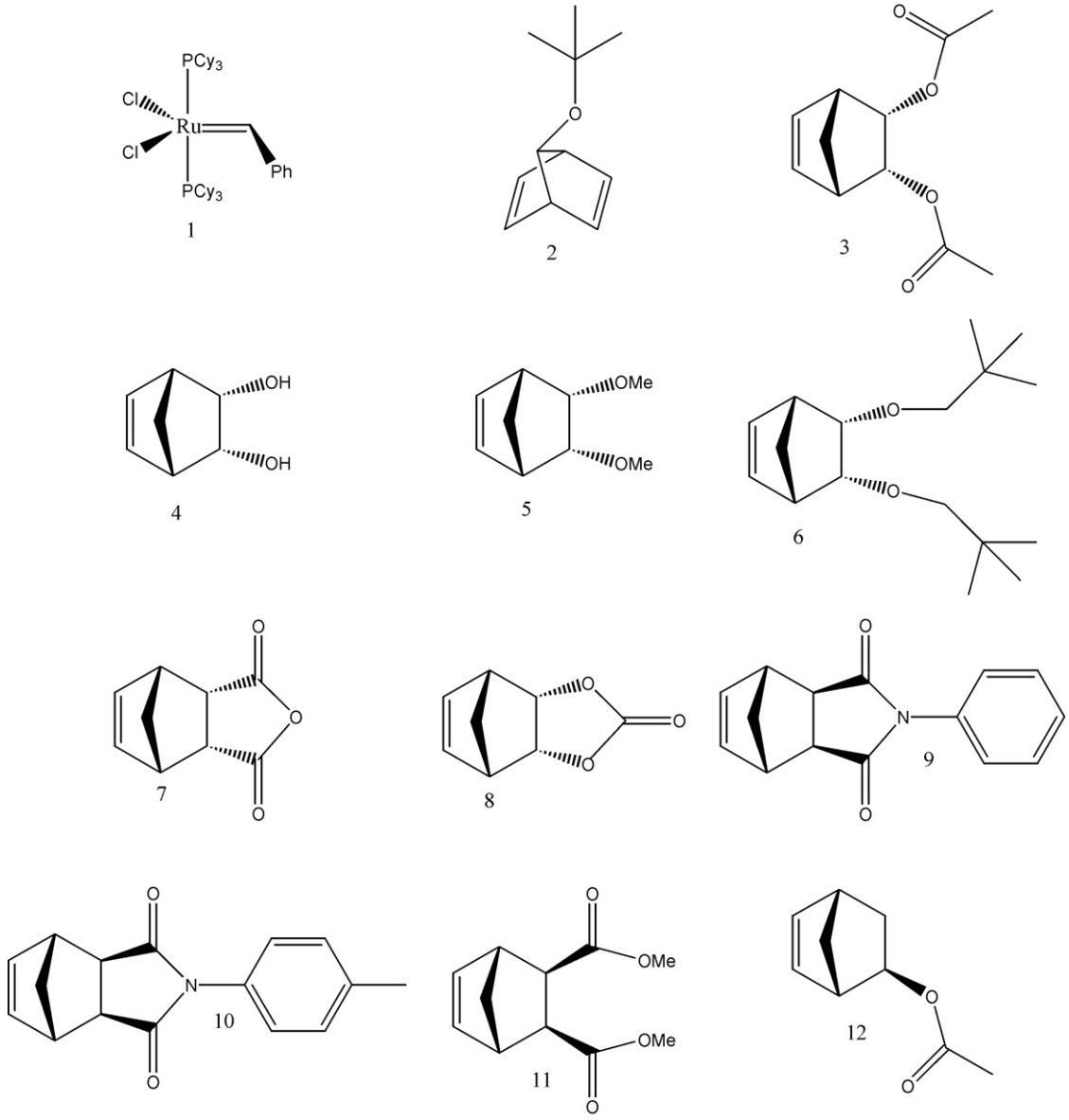
Similarly, species due to oxygen complexation were observed when some norbornene derivatives with oxygen-containing substituents at the 5 or 5 and 6 positions were polymerised [6]. Specifically, complexation was readily observed in monomers which had a carbonyl group directly attached to the 5-position, which would imply complexation via a 6-membered ring.

* Corresponding author. Fax: +44 191 384 4737.
E-mail address: a.m.kenwright@durham.ac.uk (A.M. Kenwright).

1381-1169/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2007.10.011



Scheme 1. Outline of oxygen complexation equilibrium experiments using PCy_3 and CuCl.



Scheme 2. Structures of Grubbs first generation initiator (**1**) and the oxygen-containing norbornene derivatives (**2**–**12**).

Similar complexation has been observed previously in the ROMP of norbornene amides [11]. Simple molecular modelling suggests that an oxygen atom directly attached to the 5-*endo* position of a norbornene monomer should have the same geometric relationship to the ruthenium centre of a propagating species as an oxygen attached to the 7-position of a norbornadiene monomer where the polymerisation is predominantly anti (the case for which we first observed complexation and regeneration of the initiator).

We therefore decided to synthesize a wider range of oxygen-containing norbornene monomers (shown in Scheme 2) and follow their behaviour in ROMP initiated by **1** with a view to further probing the factors determining oxygen complexation. In this investigation we were mainly interested in exploring the geometric factors affecting complexation, addressing the question of which geometric relationships between the ruthenium in the initiator and oxygen in the monomers lead to complexation. However, we were also interested in how the amount of oxygen complexation was related to the rate at which polymerisation took place. To that end we chose not only a range of monomer geometries, but also chose to look at some monomers which would be expected either to not be polymerised by Grubbs first generation initiator, or to polymerise very slowly. Although we did not carry out detailed kinetic studies of the polymerisation reactions, it was possible to derive estimates of the amount of monomer which had been consumed in a reaction under study by observation of the vinylic region (7–5 ppm) of the relevant proton NMR spectrum.

2. Results and discussions

The ^{1}H NMR spectrum in Fig. 1 shows the propagating species present when 5-*endo*,6-*endo*-norbornenediacetate (**3**) is reacted using initiator **1**. This monomer fulfils the criterion outlined above by having an oxygen in the 5-*endo* position which has the same geometric relationship to the ruthenium centre as the oxygen in 7-*t*-butoxynorbornadiene (**2**). The results show

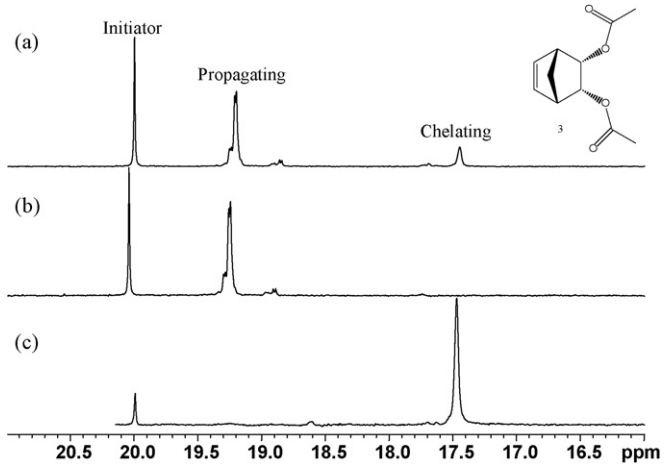


Fig. 1. The alkylidine region (21–16 ppm) of the ^{1}H NMR spectrum when (a) monomer **3** is subjected to ROMP by **1** using a ratio of $[M]_0/[I]_0 = 20$, $[I]_0 = 12$ mM at ambient temperature, (b) after the addition of 10 equiv. of PCy_3, and (c) after the addition of 10 equiv. of CuCl.

that oxygen complexation takes place in the expected way, giving rise to a peak corresponding to the oxygen-complexed alkylidene at the same shift of 17.5 ppm [4,5]. Although the spectrum in Fig. 1(a) was recorded only some 30 min after the onset of reaction observation of the vinylic region shows that all the monomer present has been converted to polymer, and the ruthenium–alkylidene region (16–21 ppm) shows the presence of significant amounts of oxygen-complexed species. This suggests that an etheric (sp^3) oxygen in this position complexes to the ruthenium via a 5-membered ring. It has already been shown that a carbonyl group in the 5-*endo* position also complexes to the ruthenium via a 6-membered ring (giving an alkylidene signal at around 18.5 ppm) [6].

The identity of the oxygen-complexed species was confirmed by the subsequent addition of PCy_3 and CuCl as outlined in Scheme 1, and following the protocols reported previously [6]. It has previously been reported for a number of oxygen-containing systems that the rate at which the signal corresponding to the oxygen-complexed species appears is slow compared to the rate at which polymerisation occurs for favourable monomers [4–6], and that seems to be the case here also since at a point shortly after all the monomer has been consumed the intensity of the signal corresponding to the oxygen-complexed species is only about 10% of the intensity of the signal corresponding to the non-complexed propagating species. This corresponds substantially with the observation made originally in the polymerisation of **2** [10], although in the current case no regeneration of the initiator species was observed.

There does remain, however, in the case above, the possibility that complexation is taking place between the ruthenium and the carbonyl oxygen of **3** via a 7-membered ring. In order to try to rule out this possibility attempts were made to polymerise 5-*endo*,6-*endo*-dihydroxynorbornene (**4**) and 5-*endo*,6-*endo*-dimethoxynorbornene (**5**). In both cases, the polymerisations were problematic. In the case of **4**, the resulting polymer precipitated from the ($CDCl_3$) solution almost immediately on formation, while it was found that **5** was insoluble in $CDCl_3$ so it was necessary to carry out the reaction in d_8-THF (which may itself be a co-ordinating solvent). In both cases, the polymers formed precipitated immediately, effectively precluding investigation of the species present by the addition of tricyclohexyl phosphine and/or copper(I) chloride. Nevertheless, it was possible to record spectra of the reaction mixtures (for example see Fig. 2), which show the presence of the expected oxygen-complexed species.

Again, the extent of monomer conversion could be estimated from observation of the vinylic region of the spectrum. The polymerisation proceeds much more slowly than in the case of **3** discussed above. After about 15 min less than 5% of the monomer has been converted to "polymer" (more likely oligomer) and there is a significant amount of unreacted initiator remaining. No oxygen-complexed species is apparent at this stage. After 3 h all the initiator has reacted and about 15% of the monomer has been polymerised. The forming polymer has not begun to precipitate at this stage, presumably because it is still relatively low in molecular weight, but it is apparent that the major species present is the oxygen-complexed one. After

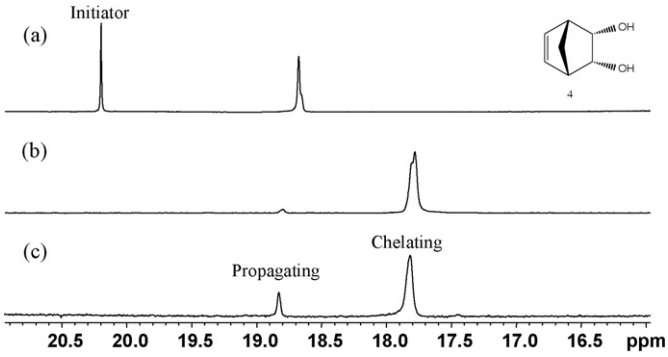


Fig. 2. The alkylidine region (21–16 ppm) of the ^{1}H NMR spectrum when monomer **4** is subjected to ROMP by **1** using a ratio of $[M]_0/[I]_0 = 20$, $[I]_0 = 12$ mM at ambient temperature (a) after 15 min (b) after 3 h, and (c) after 24 h.

24 h there is still residual monomer but overall about 50% of the monomer initially present has precipitated in the form of polymer (shown by integration of the vinylic region against TMS). There is an apparent increase in the ratio of propagating to chelating species, but the fact that precipitation of polymer chains removes the signals for some active species from the spectrum makes genuinely quantitative interpretation of this observation problematic.

In an effort to overcome the solubility problems associated with monomer **5** and its polymer an attempt was made to synthesize the 5-*endo*,6-*endo*-dineopentyl ether of norbornene (**6**) using the same methodology as for the preparation of the dimethoxy derivative (**5**), but this was unsuccessful, probably due to steric constraints.

Having established the nature of the complexation for *endo*-species where there is free rotation about the bonds joining the substituents to the norbornene we wished to extend the investigation to observe the effects of restricting the mobility of the substituents. We therefore investigated the ROMP of 5,6-*endo*-norbornenedicarboxylic anhydride (**7**) and 5,6-*endo*-norbornenecarbonate (**8**). The anhydride is not expected to polymerise rapidly, but after about 30 min the vinylic region of the spectrum shows around 10% monomer conversion and the alkylidine region (Fig. 3) clearly shows the presence of oxygen-complexed species between 19.0 and 18.5 ppm (the region expected for carbonyl complexation via a 6-membered ring). The fact that two distinct signals are observed may be due to the presence of *cis*- and *trans*- conformations for the adjacent double bond, but this is not proven.

In contrast the alkylidine region of the spectrum obtained when monomer **8** is polymerised shows that no complexation takes place (Fig. 4) even though the vinylic region shows around 30% monomer conversion at the time when the spectrum was recorded. Presumably, this is because the carbonate ring prevents oxygen attached to the 5-position from adopting the required conformation. This conclusion is supported by simple molecular modelling.

Having completed a survey of the complexation behaviour of *endo*- oxygen substituted norbornenes, we wanted to briefly compare the behaviour of *exo*- substituted norbornenes. The polymerisations of *exo*-*N*-phenyl-5,6-dicarboxyimidonorbornene (**9**) and *exo*-*N*-phenylmethyl-5,6-dicarboxyimidonorbornene (**10**) have already been reported [5] and show signals corresponding to carbonyl complexation via a 6-membered ring. The same is true of 5-*exo*,6-*exo*-dicarbomethoxynorbornene (**11**) [6].

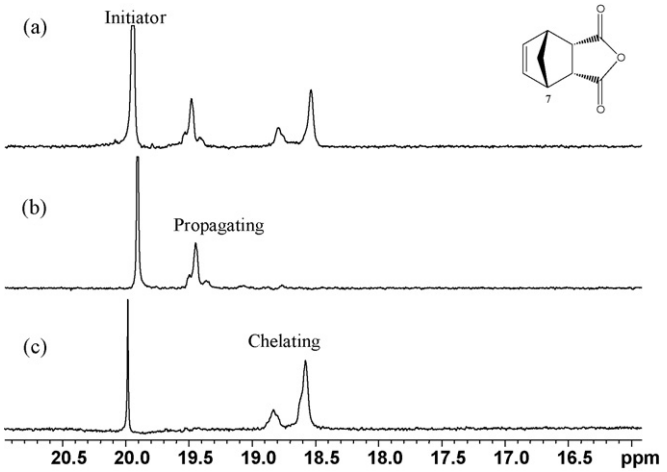


Fig. 3. The alkylidine region (21–16 ppm) of the ^{1}H NMR spectra when (a) monomer **7** is subjected to ROMP by **1** using a ratio of $[M]_0/[I]_0 = 20$, $[I]_0 = 12$ mM at ambient temperature, (b) after the addition of 10 equiv. of PCy_3, and (c) after the addition of 10 equiv. of CuCl.

Ideally, we would have liked to synthesize a norbornene monomer having *exo*-oxygens directly attached to both the 5- and 6-positions of the norbornene (to avoid head/tail effects in the NMR spectrum) but this proved to be synthetically challenging, so we decided to look instead at the synthetically simpler 5-*exo*-norbornene acetate (**12**) which was polymerised using **1**. After the polymerisation had finished (complete conversion of the monomer), two peaks were observed at 18.88 and 18.75 ppm. A third, broader peak was also observed at 18.92 ppm. In this case 10 equiv. of PCy_3 were added to the solution first and a ^{1}H NMR spectrum was recorded showing that the broad peak at 18.92 ppm disappeared. Subsequently, 20 equiv. of CuCl were added to the solution and another ^{1}H NMR spectrum was recorded which showed that the broad peak at 18.92 ppm did not reappear. The PCy_3 was added first because the CuCl tends to make the ruthenium initiator less stable [6]. These additions indicate that the peak at 18.92 ppm is not a chelation peak. It could be a first insertion product (a species that consists of the initiator with one monomer unit attached) or a side product of the initiator in the solution that is quenched when the free PCy_3 coordinates with the ruthenium.

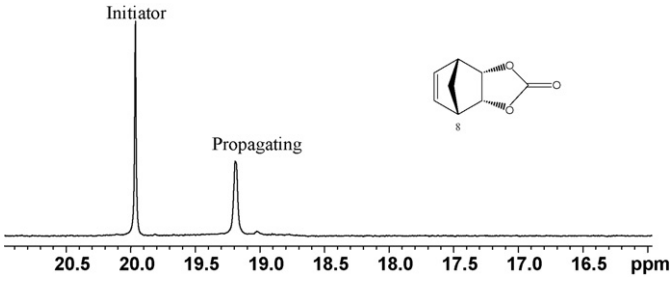


Fig. 4. The alkylidine region (21–16 ppm) of the ^{1}H NMR spectra when monomer **8** is subjected to ROMP by **1** using a ratio of $[M]_0/[I]_0 = 20$, $[I]_0 = 12$ mM at ambient temperature.

The two peaks at 18.88 and 18.75 ppm are not affected by the addition of free phosphine or the phosphine sponge (CuCl), indicating that they are propagation peaks and not chelation products. The alkylidine region of the NMR spectrum of the polymerisation reaction shows effects due to head/tail placement of the monomer, but shows no effects due to chelation.

3. Conclusions

Our investigations have shown that oxygen-complexation plays an important role in the ROMP of oxygen-containing norbornene monomers initiated by Grubbs first generation initiator. In this work we have extended the work reported in previous publications [5,6] by looking at monomers having (etheric) oxygen atoms directly attached at the 5/6 positions or having carbonyl groups at the 5/6 positions. Our conclusions are that complexation occurs via a 6-membered ring for carbonyl groups at the 5/6 position regardless of whether the substituents are *endo*- or *exo*- and equally regardless of whether there is free rotation of the substituents or the carbonyl is constrained in a ring such as an anhydride or an imide. In contrast, for monomers having (etheric) oxygen atoms directly attached at the 5/6 positions, complexation occurs via a 5-membered ring only if the substituents are *endo*- and even then complexation does not occur if rotation of the oxygen is constrained by its inclusion in, for example, a cyclic carbonate.

Our experiments with tricyclohexyl phosphine and copper(I) chloride show that the formation of the oxygen-complexed (chelated) species is reversible and they presumably exist in dynamic equilibrium with the uncomplexed propagating species. We have no quantitative information on the rates of interconversion and equilibrium constants for the species relating to the polymerisations discussed in this paper, but it seems that generally the formation of the oxygen-complexed species is slow compared to the rate of polymerisation in the cases where the polymerisation proceeds sufficiently rapidly to be practically useful.

4. Experimental

4.1. General

All reagents used were of standard reagent grade and purchased from Aldrich or Lancaster and used as supplied unless otherwise stated. The following solvents were dried and distilled prior to use: THF over sodium/benzophenone and $CDCl_3$ (Aldrich, 99.9% D, 0.03% (v/v) TMS) over P_2O_5. All other solvents were used without prior purification.

^{1}H NMR spectra were recorded on a Varian Mercury 400 or a Varian Inova 500 using deuterated solvent as lock. Chemical shifts are quoted in ppm, relative to tetramethylsilane (TMS). ^{13}C NMR spectra were recorded using broadband decoupling on a Varian Mercury 400 or Varian Inova 500 at 100 and 125 MHz, respectively. The highly symmetric nature of most of the monomers discussed means that the bulk of the signals appear as second-order multiplets with many couplings unresolved. Coupling patterns and, in particular, the *exo*- and/or *endo*- disposition of substituents were proven by two-dimensional NMR methods (COSY, HSQC, HMBC) as appropriate.

Electron impact (EI) mass spectra were recorded on a Micromass Autospec spectrometer operating at 70 eV with the ionisation mode as indicated.

Elemental analyses were obtained on an Exeter Analytical Inc. CE-440 elemental analyser.

4.2. General procedure for ^{1}H NMR scale ROMP reactions

All ROMP reactions were prepared in a Braun glove box under an inert atmosphere. Initiator **1** (10 mg) was dissolved in deuterated solvent (0.4 ml) and stirred for 5 min. The relevant monomer was dissolved in deuterated solvent (0.4 ml). The monomer solution was injected into the initiator solution and stirred for 5 min. The solution was transferred to an NMR tube fitted with a Young's tap, which allowed the vessel to be closed under a nitrogen atmosphere. The reactions were monitored by ^{1}H NMR spectroscopy every 15 min for the first 3 h and then at longer periods until no further reaction was observed. In all cases the integrated intensities of the alkylidene signals were compared to that of the TMS signal, which was assumed to remain constant throughout each experiment.

4.3. General procedure for the addition of PCy_3 and CuCl to a completed ROMP experiment in an NMR tube

All reactions were carried out in a Braun glovebox under an inert atmosphere. The ROMP solution is split into to two Young's tap NMR tubes. The required amount of PCy_3 and CuCl that corresponds to 10 molar equivalents of the initiator are weighed and each dissolved in separate 0.1 ml portions of $CDCl_3$. The PCy_3 solution is then transferred to the one of the ROMP reaction mixtures and the CuCl solution to the other.

4.4. Preparation of monomers

The preparations of monomers **2**, **6**, **9**, **10**, **11**, and **12** have been described previously in our work [5,6,13].

4.4.1. Preparation of 5-endo,6-endo-norbornenediacetate, (3)

0.56 ml acetic anhydride was added to a round-bottomed flask containing 0.46 g diol **(4)**, 0.94 ml pyridine, five crystals of dimethylaminopyridine and 10 ml dichloromethane. The reaction mixture was stirred at room temperature for 24 h before being poured onto cracked ice. The aqueous layer was extracted with dichloromethane (4 × 20 ml) and the combined organic layers washed with saturated $CuSO_4$ (40 ml), water (40 ml) and brine (40 ml), and dried over $MgSO_4$. The solvent was removed under vacuum and 0.21 g of purified **(3)** (31% yield) was obtained as a very pale yellow solid after recrystallisation from chloroform. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 6.21 (m, 2H H2,3), 5.22 (m 2H H5,6), 3.12 (m 2H H1,4), 1.98 (s 6H 2xCH_3), 1.57 (dt 1H H7 ^2J = 9.9 Hz ^3J = 2.1 Hz), 1.36 (dm 1H H7′) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 170.5 (C=O), 134.8 (C2,3), 73.2 (C5,6), 45.9 (C1,4), 42.8 (C7), 20.9 (CH_3) ppm.

*4.4.2. Preparation of 5-endo,6-endo-dihydroxynorbornene, (**4**)*

2.0 g of **(8)** was dissolved in 35 ml 10% (w/w) NaOH (aq.) and refluxed for 6 h before being stirred at room temperature for 16 h. The solution was saturated with NaCl, extracted with ethyl ether and dried over calcium carbonate. 1.23 g purified **(4)** (75% yield) was obtained after recrystallisation from chloroform. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 6.11 (m, 2H H2,3), 4.04 (m 2H H5,6), 3.52 (s 2H OH), 2.89 (m 2H H1,4), 1.39 (dt 1H H7 $^{2}J = 9.6$ Hz $^{3}J = 2.1$ Hz), 1.11 (dm 1H H7′) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 135.2 (C2,3), 71.3 (C5,6), 48.1 (C1,4), 42.0 (C7) ppm.

*4.4.3. Preparation of 5-endo,6-endo-dimethoxynorbornene, (**5**)*

0.32 g sodium hydride was weighed into a nitrogen flushed three-necked round bottomed flask, covered with 10 ml dry THF and cooled to 0 °C. 0.5 g diol **(4)** in 10 ml dry THF was added dropwise through a syringe and the mixture was stirred for 1 h. 1.02 g methyl iodide (0.45 ml) was added dropwise, with the temperature of the solution not rising above 10 °C. The mixture was stirred for 1 h before wet ether was added until no bubbling was noted. The solution was dried over $MgSO_4$, filtered and the solvent removed under vacuum. 0.48 g **(5)** (84% yield) was obtained as a yellow solid. ^{1}H NMR (500 MHz, THF-D_8): δ_H 6.21 (m, 2H H2,3), 3.88 (m 2H H5,6), 3.32 (s 6H 2xCH_3), 3.05 (m 2H H1,4), 1.31 (dt 1H H7 $^{2}J = 9.8$ Hz $^{3}J = 2.0$ Hz), 1.09 (dm 1H H7′) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 134.1 (C2,3), 81.4 (C5,6), 57.5 (CH_3), 45.7 (C1,4), 41.6 (C7) ppm.

The same method was used in an attempt to synthesize **(6)**, using neopentyl iodide in place of methyl iodide, but no product was obtained.

*4.4.4. Preparation of 5,6-endo-norbornenedicarboxylic anhydride, (**7**)*

The *endo* monomer was prepared by a literature method [12].

*4.4.5. 5,6-endo-norbornenecarbonate, (**8**)*

1.2 ml of dicyclopentadiene, 5 g of vinylene carbonate, and 0.04 g of hydroquinone were added to 1.2 ml of xylene in a round-bottomed flask. The mixture was refluxed at 160 °C for 18 h, then allowed to stand until it cooled to 45 °C. The pressure was reduced to 6 mbar and the residual vinylene carbonate was removed by distillation. The product was recovered by sublimation after the temperature was raised to 160 °C and the pressure reduced to 2 mbar. 2.1 g of purified **(8)** (78% yield) was obtained as a white solid after recrystallisation from chloroform. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 6.20 (m, 2H H2,3), 4.99 (m 2H H1,4), 3.26 (m 2H H5,6), 1.79 (dt 1H H7 $^{2}J = 10.4$ Hz $^{3}J = 1.7$ Hz), 1.30 (dm 1H H7′) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ_C 156 (C=O), 134.5 (C2,3), 79.3 (C5,6), 45.9 (C1,4), 42.8 (C7) ppm.

Acknowledgement

The authors would like to thank Catherine Heffernan for assistance with NMR facilities.

References

[1] K.J. Ivin, J.C. Mol, Olefin Metathesis and Metathesis Polymerization, Academic Press, San Diego, 1997.
[2] R.H. Grubbs (Ed.), Handbook of Metathesis, 3, Wiley-VCH, Weinheim, 2003.
[3] S. Riegler, C. Slugovc, G. Trimmel, F. Stelzer, Macromol. Symp. 217 (2004) 231.
[4] K.J. Ivin, A.M. Kenwright, E. Khosravi, J.G. Hamilton, Macromol. Chem. Phys. 202 (2001) 3624.
[5] D.M. Haigh, A.M. Kenwright, E. Khosravi, Tetrahedron 60 (2004) 7217.
[6] D.M. Haigh, A.M. Kenwright, E. Khosravi, Macromolecules 38 (2005) 7571.
[7] B.R. Maughon, R.H. Grubbs, Macromolecules 30 (1997) 3459.
[8] C. Slugovc, S. Demel, S. Riegler, J. Hobisch, F. Stelzer, Macromol. Rapid. Comm. 25 (2004) 475.
[9] S. Demel, W. Schoefberger, C. Slugovc, F. Stelzer, J. Mol. Catal. A: Chem. 200 (2003) 11.
[10] K.J. Ivin, A.M. Kenwright, E. Khosravi, Chem. Comm. (1999) 1209.
[11] T.-L. Choi, A.K. Chatterjee, R.H. Grubbs, Angew. Chem. Int. Ed. 40 (2001) 1277.
[12] K.F. Castner, N. Calderon, J. Mol. Catal. 16 (1982) 47.
[13] D.M. Haigh, PhD Thesis, Durham University (2005).