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Nature of the Propagating Species in Ring-Opening Metathesis Polymerizations of Oxygen-Containing Monomers Using Well-Defined Ruthenium Initiators

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ABSTRACT: The propagating alkylidene species that arise during the ring-opening metathesis polymerization (ROMP) of a range of strained bicyclic monomers initiated by $RuCl_2(PCy_3)_2({=}CHPh)$ [**1**] and $RuCl_2(PCy_3)({=}CH\text{-}o\text{-}O\text{-}i\text{-}PrC_6H_4)$ [**2**] have been identified using ^1H NMR spectroscopy. For polymerizations initiated by **1** in which the monomers do not contain oxygen, a single set of two NMR signals are observed for the resting state of the propagating species. These correspond to bisphosphine−ruthenium complexes with the proximal backbone double bond either cis or trans. When the monomers contain oxygen, an additional set of two NMR signals are observed for the resting state of the propagating species. These correspond to monophosphine species which also have oxygen from the polymer backbone complexed to the ruthenium, again with the proximal backbone double bond either cis or trans. Resonances attributed to bisphosphine and monophosphine species have been conclusively assigned by the addition of CuCl or PCy_3. Assignments were further confirmed by the study of comparable ROMP reactions initiated by **2**. Bisphosphine propagating species are not normally observed during ROMP reactions initiated by **2**. If the monomer contains oxygen, then, in addition to the monophosphine species with complexation of the $-O-{}^iPr$ group to the ruthenium, additional monophosphine propagating species may be observable due to oxygen in the polymer backbone chelating to the Ru center. Bisphosphine propagating species and $RuCl_2(PCy_3)_2({=}CH\text{-}o\text{-}O\text{-}i\text{-}PrC_6H_4)$, **3**, are observable using ^1H NMR spectroscopy if PCy_3 is added to **2** prior to the ROMP of 5-*exo*,6-*endo*-dicarbomethoxynorbornene, **4**. The amount of added PCy_3 is found to affect the relative intensities of the propagating bisphosphine species and **3** as well as the rate of monomer consumption and the polydispersity of the resulting polymer.

Introduction

The field of olefin metathesis has received wide interest in recent years,[1] and remarkable progress has been made in the development and application of single-component, well-defined transition metal alkylidene complexes.[2−5] This is mainly due to advances in organometallic chemistry, which have been heavily influenced by the work of Schrock[6] and Grubbs.[7−9] ROMP reactions initiated by the new generation of catalysts generally result in polymers with a narrow polydispersity index (PDI ~ 1.05−1.2).

Grubbs et al.[8] reported ruthenium−alkylidene complexes of the type $RuCl_2(PCy_3)_2({=}CHPh)$ [**1**], which tolerate a wide range of functional groups such as acids, alcohols, aldehydes, esters, and amides. **1** is efficient for the initiation of ROMP reactions of strained cyclic olefins, and because of its tolerance of a wide range of functional groups, it permits the synthesis of polymers which incorporate high degrees of functionality. The alkylidene proton of **1** gives rise to a characteristic singlet at 19.98 ppm in ^1H NMR spectroscopy. The propagating species that form during ROMP reactions initiated by **1** generally appear between 17 and 20 ppm in the ^1H NMR spectrum. The exact chemical shift and multiplicity of a signal are dependent on the functionalities contained within the propagating polymer backbone. Recent publications have focused on determination of the identity of the propagating alkylidene species in particular ROMP reactions.[10−14] In this paper we study a range of ROMP reactions and use the addition of free phosphines and phosphine scavengers to probe the identity of the propagating alkylidene species. The results lead to improved characterization of the propagating alkylidene species formed and allow us to predict the chemical shift at which these species are likely to appear in ^1H NMR spectra of related systems.

These observations are further supported by the study of comparable ROMP reactions initiated by Hoveyda's catalyst, **2**, which has an oxygen atom complexed to the ruthenium prior to reaction with the monomer.

Experimental Section

Measurements. NMR spectra were recorded on a Varian Mercury 400 or a Varian Inova 500. Chemical shifts are quoted in ppm, relative to tetramethylsilane (TMS). ^{13}C NMR spectra were recorded using continuous broad-band proton decoupling and a 3 s recycle delay and are therefore not quantitative. Electron impact (EI) mass spectra were recorded on a Micromass Autospec spectrometer operating at 70 eV with the ionization mode as indicated. Elemental analyses were obtained on an Exeter Analytical Inc. CE-440 elemental analyzer. Gel permeation chromatography (GPC) data were obtained using a Viscotek TDA 302 equipped with 2 × 300 mm PLgel 5 μm mixed C columns. THF was used as the eluent, at a flow rate of 1.0 mL/min at 30 °C. The detectors were calibrated using polystyrene standards.

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

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$RuCl_2(PCy_3)_2({=}CHPh)$[8] [**1**], 5-*exo*,6-*endo*-dicarbomethoxynorbornene[15] [**4**], 7-*tert*-butoxynorbornadiene[16] [**5**], *exo*,*exo*-*N*-phenyl-5,6-dicarboxyimidonorbornene[17] [**6a**], *exo*,*exo*-*N*-phenylmethyl-5,6-dicarboxyimidonorbornene[17] [**6b**], *exo*-5-methoxymethylnorbornene[18] [**7**], *exo*,*exo*-5,6-bis(methoxymethyl)norbornene[19] [**8**], 7-methylnorbornadiene[20] [**9c**], and *endo*,*endo*-5,6-bis(chloromethyl)norbornene[21,22] [**12**] were synthesized according to literature procedures. Norbornene [**10**] was dried over sodium and distilled under vacuum prior to use. *exo*-5-Hexylnorbornene [**11**] was kindly provided by Promerus LLC.

NMR Scale Polymerizations. All ROMP reactions were prepared in a Braun glovebox under an inert atmosphere. The initiator (10 mg) was dissolved in $CDCl_3$ (0.4 mL) and stirred for 5 min. The relevant monomer was dissolved in $CDCl_3$ (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 ^1H NMR spectroscopy. To add portions of CuCl or PCy_3 (dissolved in 0.1 mL $CDCl_3$) to the systems, the NMR tube was taken back into the glovebox. Unless explicitly stated in the text or figure captions, the spectra presented were recorded as soon as possible after consumption of the monomer was complete.

7-Neopentylnorbornadiene [9a]. Under a nitrogen atmosphere, dry ether (80 mL) was transferred into an oven-dried two-necked round-bottom flask containing magnesium turnings (3.07 g, 0.126 mol). The flask was cooled in an ice bath, and neopentyl iodide (23.85 g, 0.120 mol) was added dropwise with stirring over a 30 min period. The solution was refluxed for 30 min. Benzene (80 mL) was added to the solution in four portions (4 × 20 mL), and the ether was removed by distillation. The solution was cooled to room temperature, and **5** (10.60 g, 0.065 mol) was added. The reaction was refluxed under nitrogen for 4 days. The solution was cooled to room temperature, and water (30 mL) was added dropwise to destroy any remaining Grignard reagent. The resulting magnesium residue was solubilized by addition of 50% HCl (30 mL). The benzene layer was separated, washed with 10% Na_2CO_3 solution (3 × 100 mL) followed by H_2O (3 × 100 mL), and was then dried over sodium sulfate. After filtration, the benzene was removed under reduced pressure. The residue was purified by reduced pressure fractional distillation to afford 6.1 g (46−54 °C/18 mbar) of a mixture of unreacted **5** and the desired product **9a**. These were separated by column chromatography (12:1 pet ether/ethyl acetate), and 0.74 g of **9a** was obtained (yield 7.1%). ^1H NMR (500 MHz, $CDCl_3$): δ 6.81 (m, 2H), 6.58 (m, 2H), 3.33 (m, 2H), 2.57 (t, 1H, $J = 6.4$ Hz), 1.24 (d, 2H, $J = 6.4$ Hz), 0.83 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 140.2, 84.7, 55.4, 44.1, 30.6, 29.9 ppm. Elemental analysis: calcd (found) for $C_{12}H_{18}$: C, 88.82 (87.63); H, 11.18 (10.96). MS (EI): $m/z = 162.0$ $[M]^+$, 147.0 $[M{-}CH_3]^+$, 104.6 $[M{-}C(CH_3)_3]^+$, 90.9 $[M{-}CH_2C(CH_3)_3]^+$.

7-Ethylnorbornadiene [9b]. By the same procedure as **9a**, **9b** was prepared by the Grignard reaction between magnesium turnings (5.84 g, 0.240 mol), ethyl iodide (37.58 g, 0.242 mol), and **5** (18.60 g, 0.113 mol). After removal of benzene under reduced pressure, the residue was purified by reduced pressure fractional distillation to afford 2.05 g (24−28 °C/18 mbar) of a clear oil. The oil was passed through a silica column (1:1 dichloromethane/hexane) to obtain 0.85 g of **9b** (yield 6.3%). ^1H NMR (400 MHz, $CDCl_3$): δ 6.82 (t, 2H, $J = 2.0$ Hz)), 6.56 (t, 2H, $J = 0.8$ Hz), 3.33 (m, 2H), 2.43 (t, 1H, $J = 7.2$ Hz), 1.30 (m, 2H), 0.74 (t, 3H, $J = 7.2$ Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 139.9, 89.3, 53.3, 22.6, 12.3 ppm. Elemental analysis: calcd (found) for C_9H_{12}: C, 89.93 (88.91); H, 10.06 (10.06). MS (EI): $m/z = 120.0$ $[M]^+$, 105.0 $[M{-}CH_3]^+$, 91.0 $[M{-}CH_2CH_3]^+$.

Results and Discussion

Studying the Propagating Species That Arise When Initiator 1 Is Used. When **4** is subjected to ROMP initiated by **1**, two sets of propagating species (**IIa** and **IIIa**) appear in the alkylidene region (21−17 ppm) of the ^1H NMR spectrum alongside residual **1** (Figure 1a).

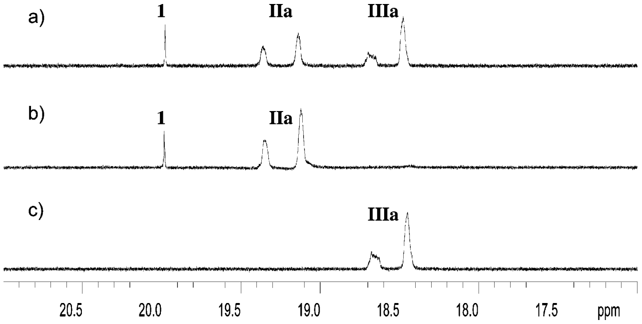
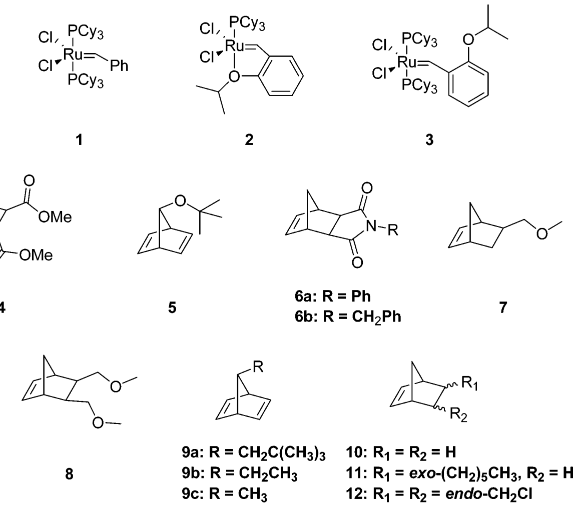


Figure 1. Alkylidene region of the ^1H NMR spectra when (a) **4** is subjected to ROMP initiated by **1**, (b) upon the addition of 5 equiv of PCy_3, and (c) upon the addition of 10 equiv of CuCl. $[M]_0/[I]_0 = 20$, $[I]_0 = 15$ mM.

Scheme 1



The two peaks assigned as **IIa** correspond to propagating alkylidene species, with the proximal backbone double bond either cis or trans, in which a pair of PCy_3 ligands are bound to the Ru center, whereas the two peaks of **IIIa** correspond to the equivalent species with only one PCy_3 ligand, the remaining coordination site being occupied by an oxygen atom emanating from the polymer backbone (Scheme 2).

The identity of **IIa** and **IIIa** is confirmed by the addition of an excess of either PCy_3 or CuCl to the ROMP system. When 5 equiv of PCy_3 is added, only traces of **IIIa** are observed and **IIa** becomes the dominant propagating species (Figure 1b). The addition of free phosphine enhances k_{1a} relative to k_{-1a} and hence the chelating oxygen atom in **IIIa** is displaced by PCy_3 (Scheme 2). CuCl is known to act as a "phosphine sponge" by undergoing reaction with free phosphines to form marginally soluble, ill-defined complexes.[23] When CuCl is added to ROMP reactions mediated by **1**, labile PCy_3 ligands are "trapped". This leaves a vacant coordination site on the Ru center, allowing oxygen in the polymer backbone to chelate. The addition of CuCl to the ROMP of **4** initiated by **1** effectively eliminates the k_{1a} process, and therefore only **IIIa** is observed in the ^1H NMR spectrum (Figure 1c).

The above observations prompted the study of propagating species that arise during the ROMP reactions of other strained bicyclic monomers initiated by **1**.

In a recent publication,[18] we reported that if **5** is subjected to ROMP by **1**, regeneration of the initiator

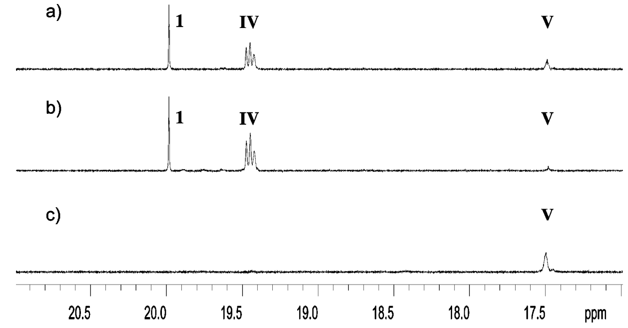
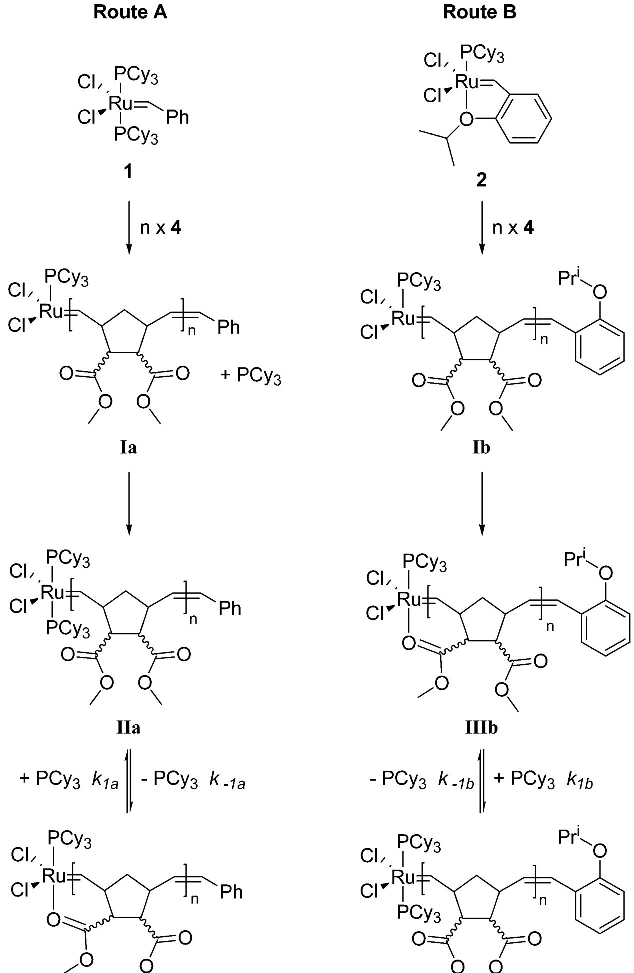


Figure 2. Alkylidene region (21−17 ppm) of the ^{1}H NMR spectra 3 h after (a) the ROMP of **5** is initiated by **1**, (b) upon the addition of 5 equiv of PCy_3, and (c) upon the addition of 10 equiv of CuCl. $[M]_0/[I]_0 = 50$, $[I]_0 = 15$ mM.

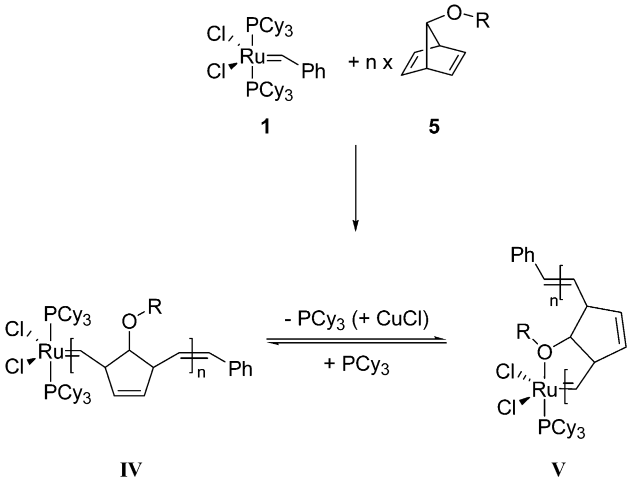
Scheme 2



is observed, and propagating alkylidene resonances appear at 19.36 ppm (**IV**, t) and 17.5 ppm (**V**, broad) in the ^{1}H NMR spectra (Figure 2a). It was proposed that **IV** is a bisphosphine species, whereas **V** is a monophosphine species in which an ethereal oxygen atom from the polymer backbone chelates to the Ru center (Scheme 3). The appearance of species **V** and the regeneration of the initiator, **1**, take place after consumption of the monomer is complete and on a time scale much longer than that for consumption of the monomer.[24]

The addition of PCy_3 or CuCl to the ROMP of **5** initiated by **1** after 3 h of reaction conclusively reveals the identity of **IV** and **V**. When 5 equiv of PCy_3 is added

Scheme 3



to the reaction, **V** noticeably diminishes in intensity and **IV** becomes more pronounced (Figure 2b). Conversely, when 10 equiv of CuCl is added to the reaction, **IV** disappears and **V** increases in intensity (Figure 2c). These observations indicate that **IV** is a bisphosphine propagating species and **V** is a propagating species in which oxygen in the polymer backbone chelates to the Ru center (Scheme 3).

The relatively low chemical shift value observed for the oxygen-complexed propagating species obtained when **1** is used to initiate ROMP of **5** is worthy of comment. The value of ~17.5 ppm is much lower than observed for any other oxygen containing monomer studied (see below) but is almost the same as observed for the alkylidene proton of **2** where it is due to complexation to an ethereal oxygen in a five-membered ring. This suggests that the signal **V** is due to complexation to the monomer closest to the ruthenium center via a five-membered ring (Scheme 3), rather than to an oxygen further down the polymer chain (cf. ROMP of **4**, **6**, **7**, and **8** reported below), and this may be significant in explaining the anomalous behavior previously reported in the ROMP of 7-alkoxynorbornadienes.[18]

The ROMP of monomers **6a**, **6b**, **7**, and **8** initiated by **1** were also studied in order to establish whether regeneration of the initiator occurs in any of these systems.[18] It does not. However, it is now recognized that two types of propagating species are apparent. This is confirmed by the addition of PCy_3 or CuCl to the ROMP reactions of **6a**, **6b**, **7**, and **8** initiated by **1** in the same manner as described above.

The alkylidene region of the ^{1}H NMR spectra when **6a**, **6b**, **7**, and **8** are subjected to ROMP initiated by **1** are shown in Figure 3, and their appearance when 5 equiv of PCy_3 or 10 equiv of CuCl is added to the systems is portrayed in Figures 4 and 5, respectively.

In the case of the ROMP of monomers **6a** and **6b**, the resonances at 19.52 and 19.48 ppm, respectively, are assigned to bisphosphine species of the type **VI** (Figure 3 and Scheme 4) on the basis that their intensity increases upon the addition of PCy_3 and that they disappear upon the addition of CuCl (Figures 4 and 5). The broad resonances at 18.70 and 18.65 ppm for **6a** and **6b**, respectively, display the opposite behavior when either PCy_3 or CuCl is added to the system, and hence they are assigned to a monophosphine propagating species of the type **VII**.

When PCy_3 or CuCl is added to the ROMP reactions of **7** and **8** initiated by **1**, the relative intensity and the

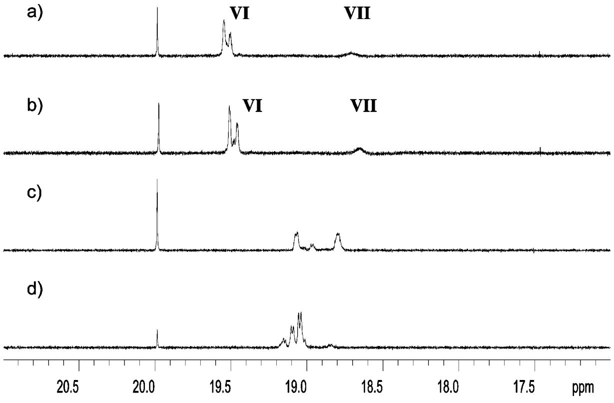


Figure 3. Alkylidene region (21−17 ppm) of the ^{1}H NMR spectra when monomers (a) **6a**, (b) **6b**, (c) **7**, and (d) **8** are subjected to ROMP initiated by **1** using a ratio of $[M]_0/[I]_0 = 50$ and $[I]_0 = 15$ mM.

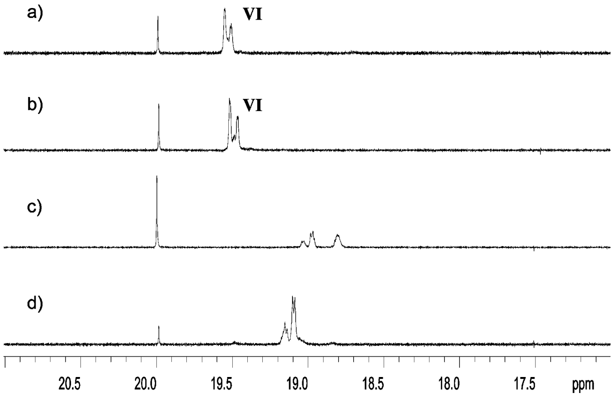


Figure 4. Alkylidene region (21−17 ppm) of the ^{1}H NMR spectra when monomers (a) **6a**, (b) **6b**, (c) **7**, and (d) **8** are subjected to ROMP initiated by **1** with 5 equiv of PCy_3 added to the reaction once the monomer has been consumed. $[M]_0/[I]_0 = 50$, $[I]_0 = 15$ mM.

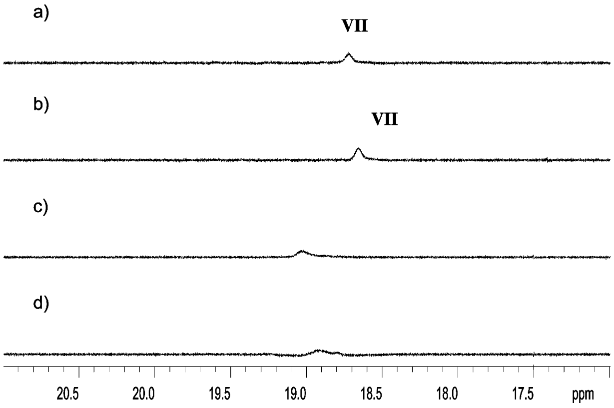


Figure 5. Alkylidene region (21−17 ppm) of the ^{1}H NMR spectra when monomers (a) **6a**, (b) **6b**, (c) **7**, and (d) **8** are subjected to ROMP initiated by **1** with 10 equiv of CuCl added to the reaction once the monomer has been consumed. $[M]_0/[I]_0 = 50$, $[I]_0 = 15$ mM.

appearance of the propagating species in ^{1}H NMR spectra are seen to change (Figures 3−5). This suggests the presence of propagating species of the bisphosphine type, **VI**, as well as those with oxygen chelation from the polymer backbone to the Ru center, **VII**, but their identity cannot be conclusively determined, possibly due to the effects of rapid ligand exchange.

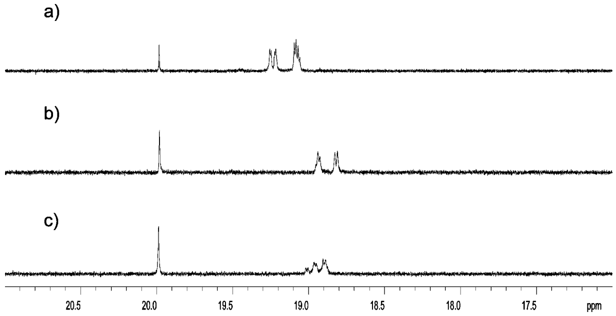


Figure 6. Alkylidene region (21−17 ppm) of the ^{1}H NMR spectra when monomers (a) **9a**, (b) **9b**, and (c) **9c** are subjected to ROMP initiated by **1** using a ratio of $[M]_0/[I]_0 = 50$, $[I]_0 = 15$ mM.

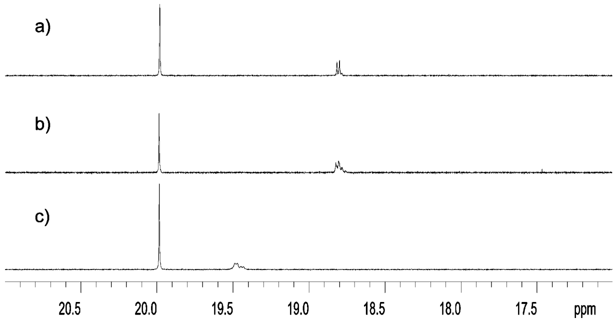
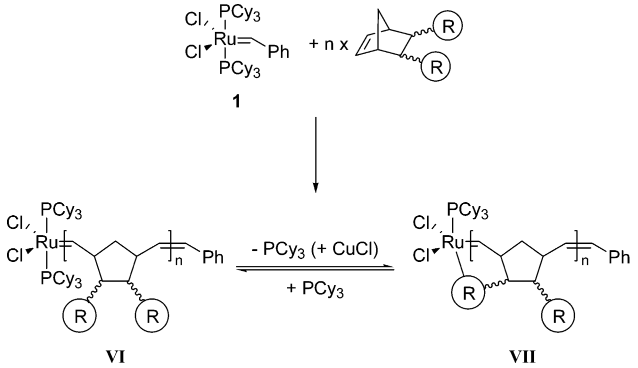


Figure 7. Alkylidene region (21−17 ppm) of the ^{1}H NMR spectra when monomers (a) **10**, (b) **11**, and (c) **12** are subjected to ROMP initiated by **1** using a ratio of $[M]_0/[I]_0 = 50$ and $[I]_0 = 15$ mM.

Scheme 4

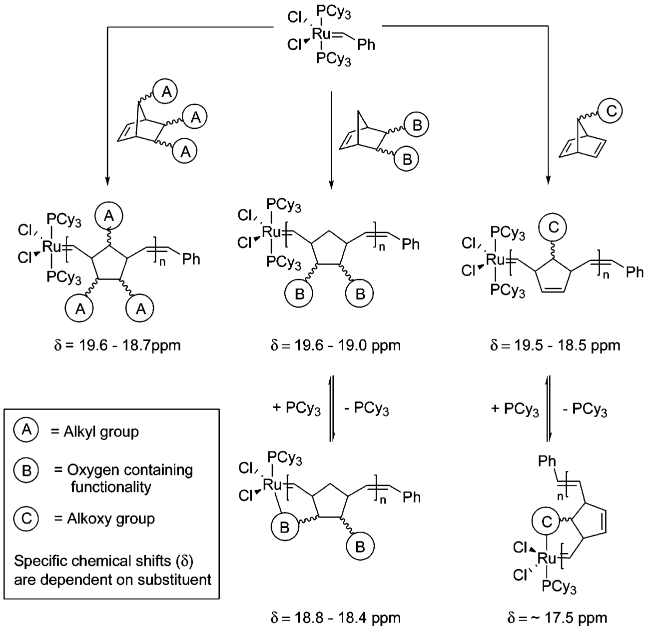


In light of the above observations, it is anticipated that when non-oxygen-containing strained bicyclic monomers are subjected to ROMP initiated by **1**, only one set of propagating alkylidene signals, corresponding to bisphosphine species of the type **VI**, will be observed in the ^{1}H NMR spectra.

This phenomenon has been investigated by performing the ROMP of non-oxygen-containing monomers (**9a**−**c** and **10**−**12**) initiated by **1**. The alkylidene regions of the ^{1}H NMR spectra are shown in Figures 6 and 7, respectively, and as predicted, each system exhibits only one set of propagating species. The appearance of the resonances remain unchanged upon the addition of PCy_3 and disappear when CuCl is added, confirming that they are propagating species of the type **VI** and not **VII**. It will be apparent in later discussions that it is of significant interest that the propagating species of **9a**−**c** are relatively unstable in solution, and no alkylidene resonances are present after 75 h of reaction.

The nature of propagating species that arise in the alkylidene region of ^{1}H NMR spectra during ROMP reactions of strained bicyclic olefin initiated by **1** have been identified. These are summarized in Scheme 5.

Scheme 5



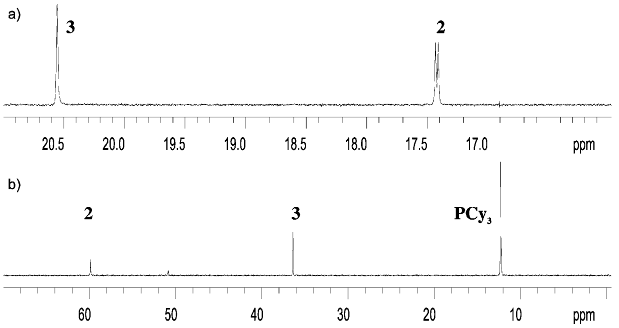
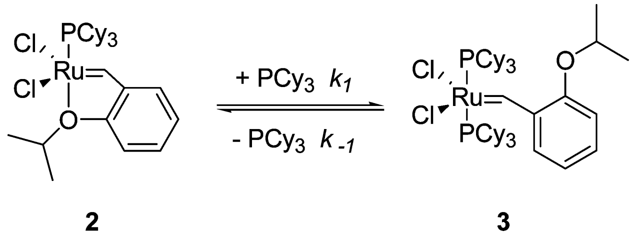


Figure 8. (a) Alkylidene region (21−16 ppm) of the ^{1}H NMR spectra and (b) the ^{31}P NMR spectra, when 5 equiv of PCy_3 is added to **2**. $[I]_0 = 20$ mM.

Scheme 6



In all cases, alongside residual **1**, a bisphosphine propagating species is apparent at 19.6−18.5 ppm (the exact chemical shift depends on the specific position and nature of the pendant groups). If the monomer is a hydrocarbon, then this is the only propagating species present.

If the monomer contains oxygen functionalized pendant groups, then additional resonances are observed. These are attributed to monophosphine species in which oxygen in the propagating backbone chelates to the Ru center. This type of species appears at 18.8−18.4 or ∼17.5 ppm, depending on the specific position and nature of the pendant groups.

We previously proposed that chelation of oxygen from the propagating polymer backbone to the Ru center promotes regeneration of the initiator. The results above clearly show that oxygen chelation in ROMP systems does not necessarily result in regeneration of the initiator. But, if the monomer specifically contains oxygen attached to the 7-position, then regeneration of the initiator may be observed.[18]

Studying the Propagating Species That Arise When Initiator 2 Is Used. The observation that oxygen in the propagating polymer backbone is able to chelate to the Ru center during ROMP reactions initiated by **1** prompted the study of the ligand exchange and ROMP behavior of $RuCl_2(PCy_3)(=CH\text{-o-}O\text{-}i\text{-}PrC_6H_4)$ (**2**).[25] This complex is similar in structure to **1**, except that one of the PCy_3 ligands is replaced by an oxygen atom which emanates from the isopropoxy functionality of the benzylidene moiety. It is of interest that the alkylidene proton of **2** exhibits a characteristic doublet at 17.42 ppm in the ^{1}H NMR spectra ($CDCl_3$). This is the same region of the spectrum as the monophosphine propagating species (**V**) which appear when 7-alkoxynorbornadiene monomers are subjected to ROMP initiated by **1**.[18] The proton resonance of **2** appears as a doublet ($J = 4.8$ Hz) due to coupling with the phosphorus nucleus of the PCy_3 ligand. This coupling is not seen in the case of **1** ($P{-}Ru{-}C_\alpha{-}H_\alpha$ dihedral angle = 90°), and it arises due to the formation of the chelated five-membered ring coinciding with a 90° rotation about the carbon−metal double bond, thus moving the alkylidene proton into the same plane as the phosphorus nucleus.[25] In the ^{1}H {^{31}P} NMR spectrum of **2**, the alkylidene proton resonance appears as a singlet, confirming the presence of phosphorus−proton coupling.

Initiator **2** is extremely stable in comparison to **1**, and it can be isolated using standard chromatographic techniques in air.[25] The difference in the stability of **1** and **2** is apparent when they are dissolved in dry degassed $CDCl_3$. The intensity of the alkylidene signal of **1** is found to diminish by 20% after only 24 h in solution, and the remaining 80% steadily decomposes over a 35 day period. The pathway to decomposition of **1** is believed to occur by dissociation of a phosphine ligand followed by the coupling of two monophosphine species to form unstable bimetallic centers.[26] The decrease in the rate of decomposition of the remaining initiator is attributed to the stabilizing effect of free PCy_3 which is generated as a byproduct from decomposed complex. Over the same 35 day period, the intensity of the alkylidene resonance of **2** is found to diminish by less than 5%. The enhanced stability of **2** relative to **1** is attributed to the presence of the internal Ru−O chelation. This is consistent with the observation that monophosphine oxygen chelated propagating species of the type **V** are more stable than the bisphosphine propagating species that arise when 7-alkylnorbornadiene monomers are subjected to ROMP initiated by **1**.[18]

Previously, we stated that oxygen which chelates to the Ru center during ROMP reactions initiated by **1** can be displaced by the addition of PCy_3 to the system. To assess whether the chelating oxygen atom in **2** could be displaced in the same manner, 1 and 5 equiv of PCy_3 were added to separate portions of **2** dissolved in $CDCl_3$. In both systems, the ^{1}H NMR spectrum exhibits resonances at 17.42 and 20.55 ppm, corresponding to **2** and $RuCl_2(PCy_3)_2(=CH\text{-o-}O\text{-}i\text{-}PrC_6H_4)$, **3**, respectively (Figure 8a).

3 is formed by displacement of the chelating isopropoxy oxygen atom of **2** by PCy_3 which gives rise to an isopropoxy-substituted benzylidene analogue of **1** (Scheme 6).

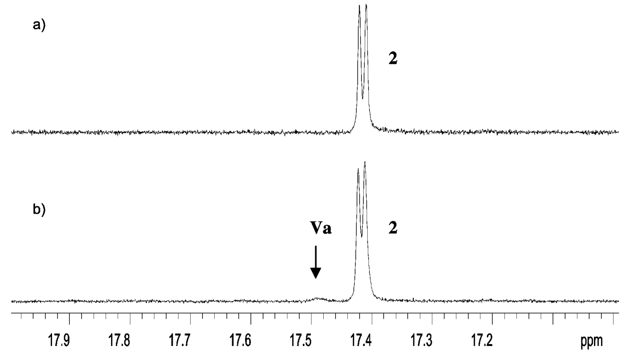


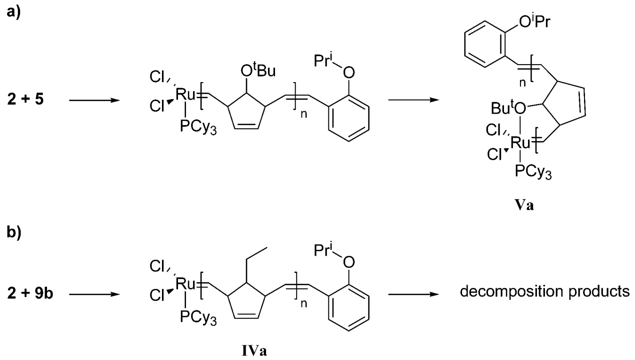
Figure 9. Alkylidene region (18−17 ppm) of the ^{1}H NMR spectra when monomers (a) **9b** and (b) **5** are subjected to ROMP initiated by **2** using a ratio of $[M]_0/[I]_0 = 50$ and $[I]_0 = 20$ mM.

With 1 and 5 equiv of PCy_3 added to **2**, the ratio of the signals at 17.42 and 20.55 ppm (**2** and **3**) were 85:15 and 50:50, respectively. The ^{31}P NMR spectrum of the two solutions exhibit three major signals at 59.82, 36.40, and 12.18 ppm which correspond to **2**, **3**, and free PCy_3, respectively (Figure 8b). The small resonance at 50.92 ppm is an impurity from the added PCy_3.

To evaluate the ROMP capabilities of **2**, it was used to initiate the polymerizations of **5** and **9b**. It is reported that during ROMP reactions initiated by **2** propagating alkylidene proton signals are not observed by ^{1}H NMR spectroscopy.[25] This is attributed to the highly active monophosphine propagating species being short-lived on the NMR time scale. When **9b** is subjected to ROMP initiated by **2**, no propagating alkylidene species are observed and the alkylidene region of the ^{1}H NMR spectrum simply shows a resonance for residual **2** (Figure 9a). The polymerization proceeds very quickly and **9b** is completely consumed by the time the first ^{1}H NMR spectrum is obtained (<20 min).

The ROMP reaction of **5** initiated by **2** proceeds much more slowly than that of **9b**, and the monomer is consumed over a 2 h period. The alkylidene region of the ^{1}H NMR spectrum exhibits a major peak for residual **2** and a small broad signal can be seen at 17.49 ppm (Figure 9b). The intensity of this resonance is about 1/40 of that of residual **2** and is tentatively attributed to a propagating alkylidene species in which an oxygen atom from the propagating **poly-5** backbone chelates to the Ru center (Scheme 7, **Va**). The species is also visible in ^{31}P NMR spectra at 56.27 ppm (Figure 10b). This alkylidene species is analogous to **V** (Scheme 3), which appears at 54.35 ppm in ^{31}P NMR spectra when **1** is used to initiate the ROMP of **5** (Figure 10c). A bisphosphine propagating species (19.36 ppm, t) is not seen due to the absence of free PCy_3. In an attempt to induce the appearance of bisphosphine propagating signals in this system, 5 equiv of PCy_3 was added once the monomer had been consumed. Although a bisphosphine species may have formed, it was undetectable by ^{1}H or ^{31}P NMR spectroscopy due to less than 5% of the alkylidene species in the system being attributed to propagating species.

Scheme 7



No propagating resonances are observed during the ROMP of **9b** initiated by **2** in either ^{1}H or ^{31}P NMR spectra due to the absence of both oxygen in the polymer

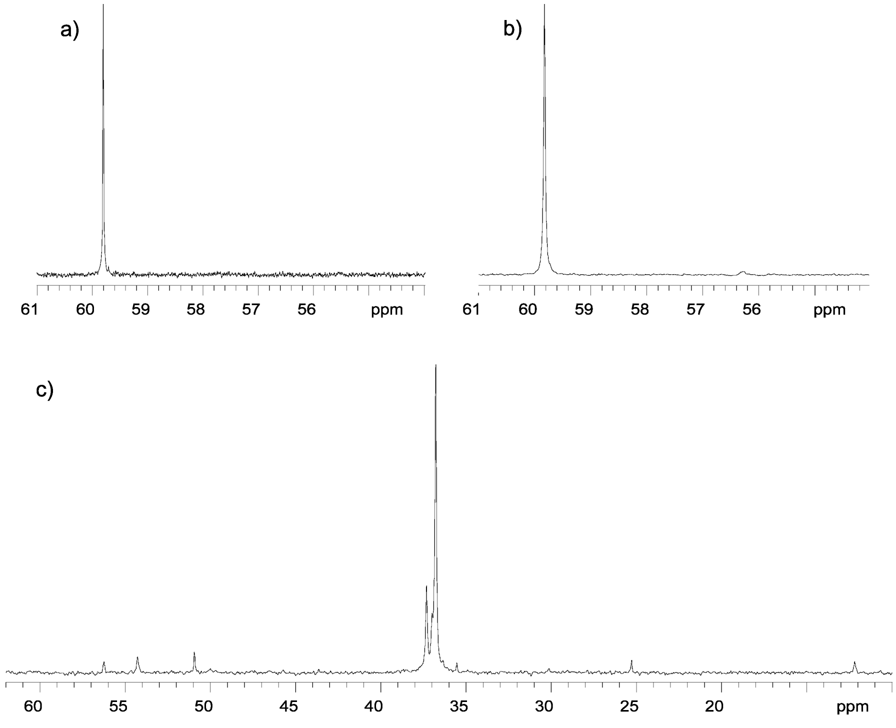


Figure 10. ^{31}P NMR spectra when monomers (a) **9b** and (b) **5** are subjected to ROMP initiated by **2** and (c) when **5** is subjected to ROMP initiated by **1.** $[M]_0/[I]_0 = 50$.

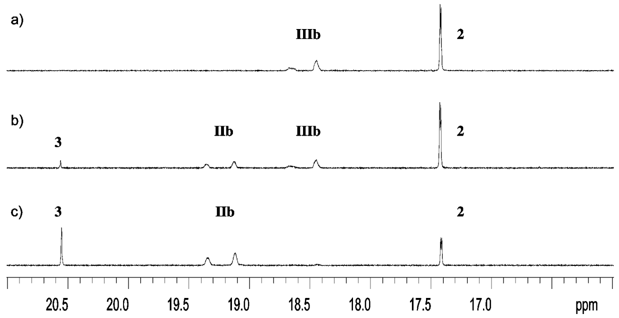


Figure 11. Alkylidene region (21−16 ppm) of the ^{1}H NMR spectra when **4** is subjected to ROMP initiated by **2** using a ratio of $[M]_0/[I]_0 = 20$, $[I]_0 = 20$ mM. (a) 0, (b) 0.75, and (c) 5 equiv of PCy_3 added to initiator 10 min before initiation of polymerization.

Table 1. Results of the ROMP Reactions of 4 Initiated by 2 in Which PCy_3 Was Added to the Initiator Prior to the Start of the Polymerization[a]

$[PCy_3]_0/[I]_0$	monomer consumption/h	M_n[b,c]	PDI[c]
0	5.5	6860	1.23
0.1	6	7658	1.20
0.25	6	6887	1.27
0.5	7	6365	1.19
0.75	8.5	6208	1.20
1.00	9	6083	1.15
2.00	15	3998	1.24
5.00	24	3294	1.25

[a] The reactions were initiated 10 min after the addition of PCy_3 to **2**. $[M]_0/[I]_0 = 20$, $[I]_0 = 20$ mM. [b] Predicted $M_n = 4200$. [c] The values are derived from GPC and quoted relative to polystyrene standards.

backbone and free PCy_3 to chelate to the Ru center (Figures 9a and 10a). Presumably, the monophosphine propagating species (**IVa**) decomposes in a fashion similar to **1** (Scheme 7).[26]

In contrast to **5**, when **4** is subjected to ROMP initiated by **1**, the intensity of the bisphosphine propagating signals (**IIa**) and the monophosphine oxygen chelated propagating signals (**IIIa**) are found to be similar in intensity in ^{1}H NMR spectra (Figure 1a). For this reason the ROMP of **4** initiated by **2** has been studied, and it is found that the monophosphine oxygen chelated propagating species (**IIIb**) give rise to pronounced resonances which are detectable by ^{1}H NMR spectroscopy (Figure 11a). This is due to a higher k_i/k_p ratio than for the ROMP of **5** initiated by **2**, which results in 35% of the initiator being consumed. The profile of the resonances due to **IIIb** match those of **IIIa**, and this is because they are almost identical in structure (Scheme 2). Structure **IIb** is not formed when **2** is used to initiate the ROMP of **4** because there is no free PCy_3 in the system to chelate to the Ru center, and hence it is not seen in ^{1}H NMR spectroscopy.

To induce the formation of **IIb** during the ROMP of **4** initiated by **2**, a series of reactions were performed. In each system, a known amount of PCy_3 (0−5 equiv) was added to a solution of **2** 10 min prior to initiation of the polymerization. The reactions were followed by ^{1}H NMR spectroscopy until **4** was completely consumed. The rate of consumption of **4** is found to decrease as the amount of PCy_3 added to the system is increased (Table 1). It is well established that addition of free phosphine to ruthenium-based ROMP systems reduces the magnitudes of both k_i and k_p, so it is not unexpected that the rate of monomer consumption is retarded.[12]

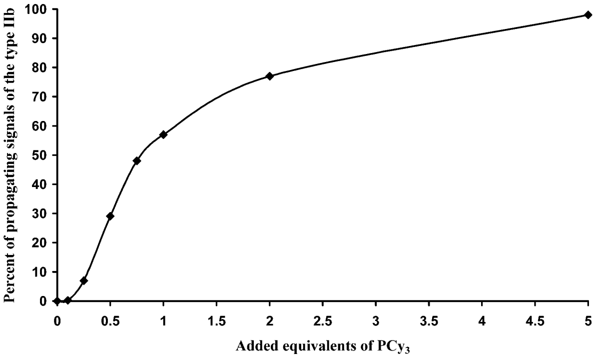
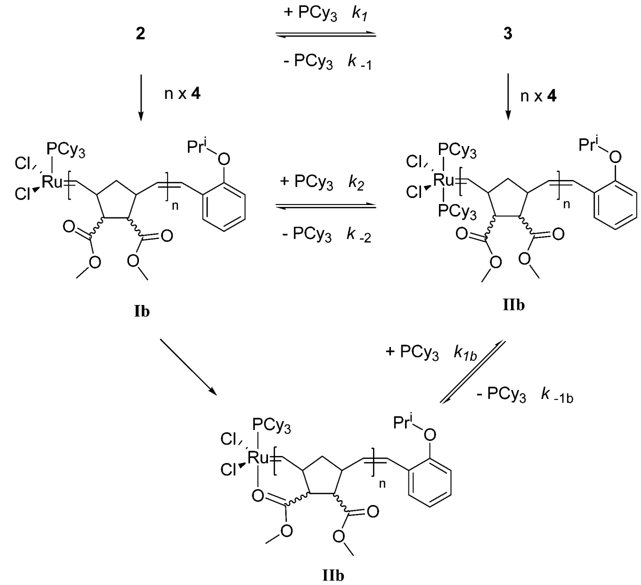


Figure 12. Plot showing the percent of **IIb** type alkylidene signals present relative to **IIIb** type alkylidene signals when **5b** is subjected to ROMP initiated by **2** in the presence of various amounts of added PCy_3.

Scheme 8



When PCy_3 is added to **2** and the mixture is used to initiate the ROMP of **4**, the Ru−benzylidene species **3** is observed alongside additional alkylidene resonances at 19.36 and 19.22 ppm in the ^{1}H NMR spectrum (Figure 11). These are attributed to the bisphosphine propagating species **IIb** (Scheme 2) that are analogous to those of **IIa** which arise when **1** is used to initiate the ROMP of **4**. The profiles of the resonances of **IIa** and **IIb** are identical.

As the amount of PCy_3 added to the system is increased, the ratio of **IIb** to **IIIb** increases accordingly (Figure 12). In the case of 5 added equiv of PCy_3, only traces of **IIIb** are present (Figure 11c). This is explained by the large excess of phosphine in the system converting 50% of **2** to **3** and also preventing oxygen from the propagating polymer backbone chelating to the Ru center. Therefore, in Scheme 8, k_1, k_{1b}, and k_2 become dominant over k_{-1}, k_{-1b}, and k_{-2}, and hence, **IIb** is the major species present.

Ethyl vinyl ether was used to terminate the propagating **poly-4** chains in these systems once the monomer had been completely consumed, and the polymers were recovered (Table 1). It was found that as the amount of PCy_3 added to the system is increased from 0 to 5 equiv, the M_n of the resultant polymer decreases whereas the polydispersity remains relatively constant. The fall in M_n of the polymers is attributed to the increased concentration of PCy_3, leading to an increase in the ratio of **3** to **2**. In the case of 5 added equiv of PCy_3, the ratio of **3** to **2** is found to be 50:50. We demonstrated earlier that when **2** is used to initiate the ROMP of **4**, only 35% of the initiator is consumed, whereas with complexes of the type **3** generally >95% of the initiator is consumed. This means that as the ratio of **3** to **2** in the system rises, there will be an enhanced extent of initiation and therefore an increase in active propagating sites. Hence, the polymers formed exhibit a lower molecular weight. The observed fact that the PDI remains constant suggests that initiators **2** and **3** both perform ROMP in a controlled fashion.

General Discussion. We have observed signals due to additional propagating species in the proton NMR spectra of ROMP reactions of oxygen-containing monomers derived from norbornene and norbornadiene initiated by **1**. The nature of these species has been elucidated by addition of either excess PCy_3 or CuCl (a phosphine scavenger). The nature of the additional species observed in the reactions of 7-alkoxynorbornadiene monomers is qualitatively different from those observed using monomers where the oxygen is attached to pendant groups in the 5- and/or 6-positions of norbornene.

In the former case the peak due to the oxygen-complexed Ru−alkylidene species appears at a relatively low frequency in the proton NMR spectrum (~17.5 ppm) and grows in intensity after all the monomer present has reacted. In the latter case the corresponding signals are typically higher in frequency (between 18.5 and 19.0 ppm) and are present to a significant extent before all the monomer has been consumed. The additional signals are much more readily apparent in the latter case if the monomer contains carbonyl groups rather than, for example, ethers.

Our interpretation of these observations is that the additional signals are due to species in which one of the PCy_3 ligands has been replaced by complexation to the ruthenium of oxygen from the monomers. In the former case this complexation is from the oxygen on the monomer unit immediately adjacent to the ruthenium via a five-membered ring to give a species which is structurally similar to that found in **2**, while in the latter case the complexation can be from any oxygen along the polymer backbone.

In the case of the 7-alkoxy substituents, the fact that the additional signal at 17.5 ppm is largely absent until all the monomer has been consumed is significant. Molecular modeling shows that complexation of the type discussed can only arise if the double bond which was syn to the alkoxy substituent in the monomer is opened. It has previously been shown by ^{13}C NMR that polymerization of **5** initiated by **1** proceeds predominantly by opening the double bond which is anti to the alkoxy substituent ($\sigma_s < 0.07$ between 6 and 10 h after mixing).[24] When **5** was polymerized using the Schrock complexes **A** and **B**, $Mo(=CHCMe_2Ph)(=NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)(OR)_2$ [**A**, OR = $OCMe(CF_3)_2$; **B**, OR = $OCMe_3$], significantly more syn enchainment was observed ($\sigma_s = 0.47$ for **A** and $\sigma_s = 0.34$ for **B**). In these cases it was again concluded that syn enchainment involved complexation of oxygen to the metal center via a five-membered ring, and evidence to support this was obtained from nuclear Overhauser experiments (NOE).[24] This is further supported by the fact that when **9c** is polymerized using the same catalysts, the enchainment is essentially exclusively anti ($\sigma_s < 0.05$ in all cases).[27] ^{13}C NMR of the polymer formed when **5** is subjected to ROMP by **2** reveals that the polymerization proceeds predominately by anti enchainment. Therefore, it is possible that the low-intensity broad signal at 17.5 ppm is in fact a dormant alkylidene species which arises due to syn enchainment and that the active propagating species is not observable on the NMR time scale.

In the current work it was not possible to observe conclusive NOE evidence that the signal at 17.5 ppm in the proton spectrum arose from syn enchainment. However, it is known that the geometry associated with oxygen complexation via a five-membered ring leads to a significant coupling between the alkylidene proton and the phosphine ligand, which is not otherwise observed. Thus, the alkylidene signal due to **2** is a doublet ($^3J_{P-H} = 4.8$ Hz) while no coupling is observed on the alkylidene signal of **1**. While no coupling is immediately apparent on the additional signal at 17.5 ppm, it was noted that the line width is greater than the expected coupling which would mask the coupling. Since the relative sizes of the line width and coupling also preclude observation of the coupling in a 2D correlation experiment, the matter was investigated using selective ^{31}P decoupling, and it was shown that selective decoupling of the ^{31}P signal at 54.35 ppm resulted in a narrowing of the proton signal at 17.5 ppm from 12 to 9 Hz, thereby confirming the presence of the coupling.

The observation that the signal at 17.5 ppm grows in intensity after all the monomer has been consumed indicates that it arises because once the initiator has polymerized all the monomer via anti enchainment it goes on to react with the double bonds which were syn in the monomer and are now in the rings in the polymer chain. This gives rise to the formation of large rings in the polymer chain if the reaction is intramolecular or to chain branching if the reaction is intermolecular.

Conclusions

ROMP reactions of strained bicyclic monomers initiated by **1** have been performed, and the identity of the propagating alkylidene species that arise has been unambiguously identified using ^1H NMR spectroscopy. In all of the systems studied, bisphosphine propagating species are observed between 19.6 and 18.5 ppm, and their identity is confirmed by their disappearance upon the addition of CuCl (a phosphine sponge) to the system. In the case of hydrocarbon monomers, this is the only type of propagating species observed. When bicyclic monomers containing oxygen are subjected to ROMP initiated by **1**, additional propagating signals are apparent between 18.8 and 18.4 ppm or at ~17.5 ppm, depending on the specific position and nature of the oxygen-containing groups. These are attributed to monophosphine species in which oxygen in the propagating polymer backbone chelates to the Ru center. These species remain in solution upon the addition of CuCl, indicating that the Ru center does not possess labile phosphine ligands, but they disappear in the presence of excess free PCy_3, due to displacement of the chelating oxygen atom.

Initiator **2** is found to be extremely stable relative to **1**, and its ligand exchange and ROMP behavior has been studied. Polymerizations initiated by **2** are found to proceed more slowly than those initiated by **1**, and the extent of initiation is found to be lower. Bisphosphine propagating species are not normally observed due to the absence of a stoichiometric amount of PCy_3. When monomers containing oxygen are subjected to ROMP initiated by **2**, monophosphine propagating species are observable. No propagating resonances are observed during the ROMP of hydrocarbon monomers initiated by **2** due to the absence of both oxygen in the polymer backbone and free PCy_3 to chelate to the Ru center.

In the presence of free PCy_3, the chelating oxygen atom of **2** can be displaced to give rise to an isopropoxy-substituted benzylidene analogue of **1**. When PCy_3 is added to **2** prior to the polymerization of monomer **4**, the Ru−benzylidene species **3** is observed alongside additional bisphosphine−alkylidene species. As the concentration of added PCy_3 is increased, the intensity of **3** and the bisphosphine species increases at the expense of the **2** and the monophosphine propagating species, respectively. The rate of consumption of **4** is found to decrease with an increase in concentration of PCy_3, and the M_n of the resulting polymer is also affected.

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