The Ru(=CHPh)$Cl_2(PCy_3)_2$-initiated ring-opening metathesis polymerization of 7-*tert*-butoxybicyclo[2.2.1]hepta-2,5-diene: regeneration of initiator and the implied formation of macrocycles

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The ring-opening metathesis polymerization (ROMP) of 7-*tert*-butoxybicyclo[2.2.1]hepta-2,5-diene initiated by Ru(=CHPh)$Cl_2(PCy_3)_2$ proceeds rapidly in organic solvents with almost complete consumption of initiator to form propagating ruthenium carbene species that are then converted slowly but not completely back to initiator, implying a secondary ring-closing metathesis reaction at the chain ends to form macrocycles.

The ROMP of the title monomer (7-TBONBD) initiated by $MoCl_5/Me_4Sn/Et_2O$ and $OsCl_3$ is known to give polymers containing both *anti* and *syn* units, depending on which double bond is opened in the propagation step (Scheme 1). The double bonds formed between the rings are mainly *trans* in the first case, and *cis* in the second.[1]

The ROMP of this monomer (M) has now been studied in various solvents at 20 °C, initiated by the well-defined ruthenium carbene complex[2] Ru(=CHPh)$Cl_2(PCy_3)_2$, (I), using ^{1}H, ^{13}C and ^{31}P NMR to follow the reaction. In $CDCl_3$, with $[I]_o$ = 0.0176 mol l^{-1}, $[M]_o$ = 1.016 mol l^{-1}, $[M]_o/[I]_o$ = 57.7, $t_{½}$ for the polymerization of M was about 3 min and most of the initiator was also rapidly consumed. The polymer consisted largely of *anti* units, with 34% *cis* double bonds between the rings. The consumption of M was slower in both CD_2Cl_2 ($t_{½}$ ~12 min) and C_6D_6 ($t_{½}$ ~17 min) under comparable conditions, but the *cis* content was similar. Experiments at $[M]_o/[I]_o$ = 5–10 allowed the determination of the ratio of propagation to initiation rate constants, k_p/k_i, from $[M]_o/[I]_o$ and the value of $[I]/[I]_o$ immediately after the completion of polymerization.[3] These gave k_p/k_i ~ 15, independent of solvent.

Fig. 1 is a stack plot of the carbene proton region taken at intervals over a period of 12 h for the reaction in $CDCl_3$, after the monomer had been consumed. This shows several remarkable and unexpected features, in particular (i) fine structure for the propagating species (P_n) which is not due to spin coupling, (ii) the regeneration of I at the expense of P_n, and (iii) the formation of another carbene species (X).

The positions of the three P_n lines (δ 19.38, 19.36, 19.33) were the same in a 400 MHz spectrum as in the 500 MHz spectrum. The fine structure is therefore not due to PH_α ^3J coupling nor to $H_\alpha H_\beta$ ^3J coupling. The absence of PH_α coupling is normal in ruthenium carbene complexes containing two PCy_3 ligands as in the initiator,[2] but the absence of $H_\alpha H_\beta$ coupling is very abnormal. Thus in complexes of the type [Ru]=CHR containing two PCy_3 ligands, $^3J_{\alpha\beta}$ ranges from 5.0 (R = Et) to 10.5 Hz (R = CH=CPh_2).[2,4–6] In the present case it would appear therefore that (i) rotation about the C_α–C_β bond in the propagating species is severely restricted by the interaction between the PCy_3 ligands and the enchained cyclopentene ring, (ii) the favoured conformation (**1**) has a HC–CH dihedral angle close to 90°; and (iii) the observed fine structure is due to sensitivity of the chemical shift to the *c/t* isomerism of the adjacent double bond and to the *m/r* isomerism of the adjacent dyad. The intensity pattern of the three P_n lines (31 : 39 : 30) can be interpreted in terms of similar *c/t* and *m/r* splittings (giving rise to three lines rather than four), a *cis* content of 34%, and somewhat different tacticities (*m/r* ratio) with respect to the adjacent *cis*- and *trans*-centred dyads.

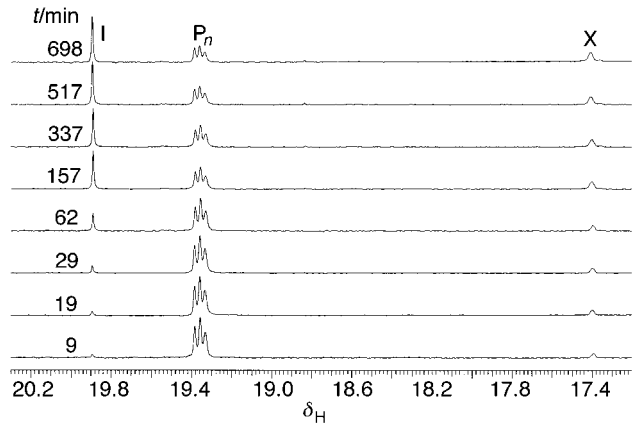
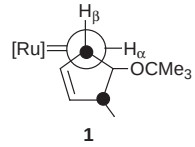


Fig. 1 Carbene proton region as a function of reaction time (t) in the 500 MHz ^{1}H NMR spectrum. Solvent $CDCl_3$: $[I]_o$ = 0.0176 mol l^{-1}, $[M]_o$ = 1.016 mol l^{-1}. P_n is the propagating species; X, see text. The intensities were referenced to the total integral of the δ 4.0–2.7 region (H-1,4 + H-7 signals). There was an overall loss of carbene proton signal of 24% during the first 700 min.



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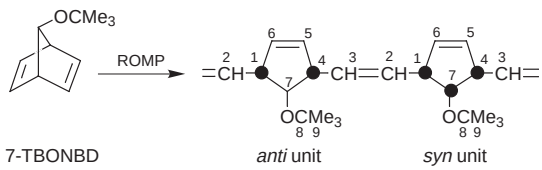
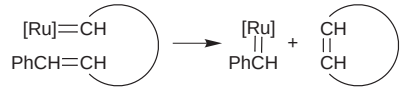
The regeneration of I (δ 19.89) at the expense of P_n can only occur by a ring-closing metathesis reaction in which the entire chain forms a macrocycle and the PhCH= end group re-attaches itself to the ruthenium centre (Scheme 2). When a second batch of monomer was added, [I] again fell to a very low level and slowly recovered, while $[P_n]$ immediately rose and then again declined. However X (δ 17.40) did not fall but continued to



Scheme 1



Scheme 2

grow. The relative intensities of the three P_n lines (Fig. 1) remained unchanged during the reversion of P_n to I, indicating that the probability of ring closure is independent of the stereochemistry close to the Ru=C bond.

When a small amount of ethyl vinyl ether was added to a portion of the reaction mixture in $CDCl_3$ some time after the first addition of monomer, the peaks due to species I, P_n and X all disappeared and new carbene proton peaks appeared at δ 18.91 (2%), in the position expected for [Ru]=CH_2,[5] and δ 14.54 (98%), attributed to [Ru]=CHOEt. The P_n chains had thus been terminated to give mainly vinyl end groups. GPC measurements on polymers that had been terminated just before and some time after the second addition of monomer showed the expected increase in molecular weight after the second addition, but in both cases the distributions were broad and unimodal for the main fraction. The DP was of the same order of magnitude as $[M]_o/[I]_o$ so that back-biting at other points in the chain to yield smaller cyclic oligomers cannot be a serious competitor, probably because of the difficulty of access of the Ru=C bond to double bonds situated between two substituted rings.

GPC traces of polymers that had been made in CD_2Cl_2 and terminated (i) immediately after consumption of monomer, and (ii) later after the initiator had been regenerated, showed differences in the low molecular weight region (300–700) consistent with the presence of different proportions of linear and cyclic oligomers, but further work is needed to characterise the species associated with the observed peaks.

Regeneration of initiator was also observed for the reaction in CD_2Cl_2 and C_6D_6 except that the whole process was somewhat slower than in $CDCl_3$ and the P_n signal consisted of two lines instead of three, in the ratio 28:72 in CD_2Cl_2 (δ 19.44, 19.40 relative to initiator δ 20.02) and 24:76 in C_6D_6 (δ 19.66, 19.60 relative to initiator δ 20.31). This is consistent with the presence of four underlying structures (*c/m*, *c/r*, *t/m*, *t/r*) of which three have the same chemical shift.

When the reaction was carried out in CD_2Cl_2 in the presence of added PCy_3 ($[PCy_3]/[I]_o$ = 1.88) it was greatly retarded (factor of ~50) but followed the same general course with eventual complete consumption of M, regeneration of I, and the formation of X. This strongly suggests a mechanism in which a PCy_3 ligand must first be released from the initiator before monomer can be coordinated to the Ru centre and react by metathesis. The magnitude of the effect was consistent with a constant for the dissociation of the PCy_3 ligand from the initiator of the order of 10^{-5} mol l^{-1}.

The reaction in CD_2Cl_2 was also followed by ^{31}P NMR. The initiator gave a singlet (δ 37.24), while P_n gave four signals (δ 36.80, 36.45, 36.36, 36.10) of approximately equal intensity. After the consumption of monomer, these rose and fell respectively as for the ^{1}H NMR signals. A small peak also emerged at δ 11.52 (PCy_3), and grew in parallel with the X peak in the ^{1}H NMR spectrum. By analogy with the recent work of Grubbs [7] one may speculate that X is a monophosphine complex formed by displacement of one of the PCy_3 ligands in P_n by chelation of an oxygen atom (in the polymer chain) to the Ru centre. A number of other small peaks appeared in the ^{31}P NMR spectrum between δ 55 and 25, comparable in intensity with that at δ 11.52, one of which may be due to the PCy_3 ligand in X. The slow rate of formation of X may arise from the necessity for the C_α–C_β bond in **1** to rotate against a substantial barrier to a position where the adjacent oxygen atom comes into juxtaposition with the ruthenium centre. Conversion of P_n to X does not go to completion and is probably a slow equilibrium process [eqn. (1)].

$$P_n \rightleftharpoons X + PCy_3 \quad (1)$$

It appears that the regeneration of initiator is peculiar to the ROMP of 7-TBONBD initiated by $Ru(=CHPh)Cl_2(PCy_3)_2$. To date we have been unable to observe this phenomenon using this initiator with other monomers, *e.g.* norbornene, or this monomer with other initiators, *e.g.* $Mo(=CHCMe_3)(=NAr)(OCMe_3)_2$.

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