

Cyclization of living polyalkenamers via intramolecular secondary metathesis. Dimerization of cycloheptene into cyclotetradeca-1,8-diene initiated by well-defined tungsten–carbene catalysts

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Abstract

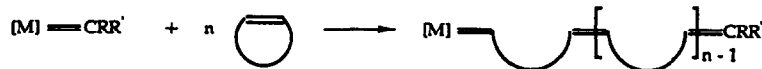
Tungsten–carbene complexes of the type $W(=CRR')(OR'')_2X_2 \cdot GaX_3$ [$CRR' = \overline{C(CH_2)_3CH_2}$, $\overline{C(CH_2)_4CH_2}$, $\overline{CHt-Bu}$ or $\overline{CHn-Bu}$; $OR'' = OCH_2t-Bu$, OCD_2t-Bu or $Oi-Pr$; $X = Br$ or Cl] (I) have been used as catalysts to initiate ring-opening metathesis polymerization (ROMP) of cyclopentene, cycloheptene and cyclooctene (M). These reactions were followed by 1H and ^{13}C NMR spectroscopy at variable temperature. Living polyalkenamers of the type $W(=CHP)(OR'')_2X_2 \cdot GaX_3$ [$CHP = CHC_mH_{2m}CH = (CHC_mH_{2m}CH)_{n-1} = CRR'$, $m = 3$ (cyclopentene), 5 (cycloheptene), 6 (cyclooctene); $n \geq 1$] (PC) were obtained in a first stage. These products undergo secondary metathesis reactions. In particular, intramolecular metathesis between the carbon–carbon double bonds and the tungsten–carbene chain-end function, within a given polymer chain, leads to regeneration of monomer or to cyclic oligomers. The thermodynamic equilibrium between these species is reached at varying rates depending on catalyst, monomer and temperature. For cyclopentene, only monomer was found at room temperature, while polypentenamers are the major species at low temperature. For cycloheptene, the corresponding polymerization equilibrium also exists, but is displaced more towards polyalkenamers. Moreover, the cyclic dimer, cyclotetradeca-1,8-diene (D), was obtained in high proportions under appropriate conditions, and its most stable *trans, trans* isomer was isolated from the reaction mixtures. For cyclooctene, conversion into polyoctenamers is rapid and complete at room temperature. In a third stage, catalysts I slowly convert olefins M, D and P into saturated polymers at room temperature. This reaction is also induced by $GaBr_3$ alone. Complexes of the type $W(=CRR')(OR'')_2X_2$ react similarly to their $GaBr_3$ adducts, although much more slowly.

Keywords: Cycloolefins; Polyalkenamers; Polymerization; Ring-opening metathesis polymerization; Secondary metathesis; Tungsten–carbene catalysts

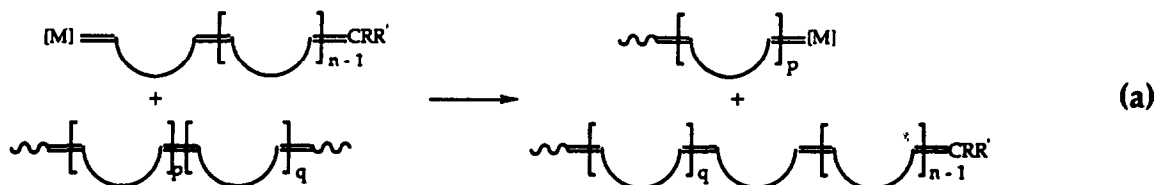
1. Introduction

Well defined metal–carbene complexes have been widely used as catalysts for the ring-opening metathesis polymerization (ROMP) of highly strained cycloolefins such as norbornenes, especially since the living systems thus built up enable

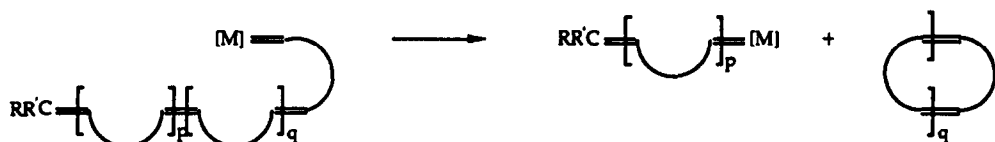
the synthesis of monodispersed polymers (Scheme 1) and block copolymers [1]. However, such results are obtainable only if the metal–carbene catalyst is inactive against the internal carbon–carbon double bonds of the polymer chains, or at least if the difference in reactivity between the double bond of the cyclic monomer and those



Scheme 1.



(a)



(b)

Scheme 2.

of the polymer chains is large enough to allow ROMP to be completed before the resulting polyalkenamers react in turn. As soon as more active metal-carbene catalysts or less ring-strained cycloolefins are involved, secondary metathesis occurs in the polymer chains (Scheme 2a) and higher polydispersities are obtained [1–5].

Further, these secondary metathesis reactions may occur intramolecularly, i.e. within each metal-carbene end-capped polyalkenamer chain, to yield cyclic oligomers of different size (Scheme 2b); a particular case is depolymerization to the starting cycloolefin. Such reactions are significant if the metal-carbene sites in the living polyalkenamers are not only reactive, but also sufficiently long-lived (just as for the formation of monodispersed polymers), and may lead to high yields of cyclic compounds if the thermodynamics are favourable [1,3–9].

We have studied the interactions between weakly strained cycloolefins (cyclopentene, cycloheptene, cyclooctene) and the well-defined and highly active tungsten-carbene catalysts of the type $W(=CRR')(OCH_2t-Bu)_2Br_2 \cdot GaBr_3$ [10]. These systems showed the right characteristics to allow competition between ROMP and intramolecular secondary metathesis reactions to be followed by NMR spectroscopy at variable

temperature. In the case of cycloheptene, the latter reactions can be exploited for the synthetical cycloaddimerization of this substrate into cyclotetradeca-1,8-diene.

2. Experimental

All manipulations of air-sensitive compounds were carried out in a N_2 -filled Vacuum Atmospheres dry box. The tungsten-carbene complexes and their adducts with $GaBr_3$ were synthesized as previously described [10]. Before use, all commercial cycloolefins were refluxed over a sodium-paraffin dispersion and distilled trap to trap under vacuum. $GaBr_3$ was sublimed under vacuum. CD_2Cl_2 was purchased from C.E.A. and used without further purification. 1H and ^{13}C NMR spectra were run at respectively 200.13 and 50.33 MHz on a Bruker SY 200 spectrometer, or at 100.62 MHz (^{13}C) on a Bruker AM 400 spectrometer. Low temperature measurements were controlled using a B-VT 1000 variable temperature set. Chemical shift calibration was based on CD_2Cl_2 peaks at 5.32 (1H) and 53.84 (^{13}C) ppm, or $CDCl_3$ peaks at 7.26 (1H) and 77.03 (^{13}C) ppm. The procedures for making up and handling the NMR samples have been described elsewhere

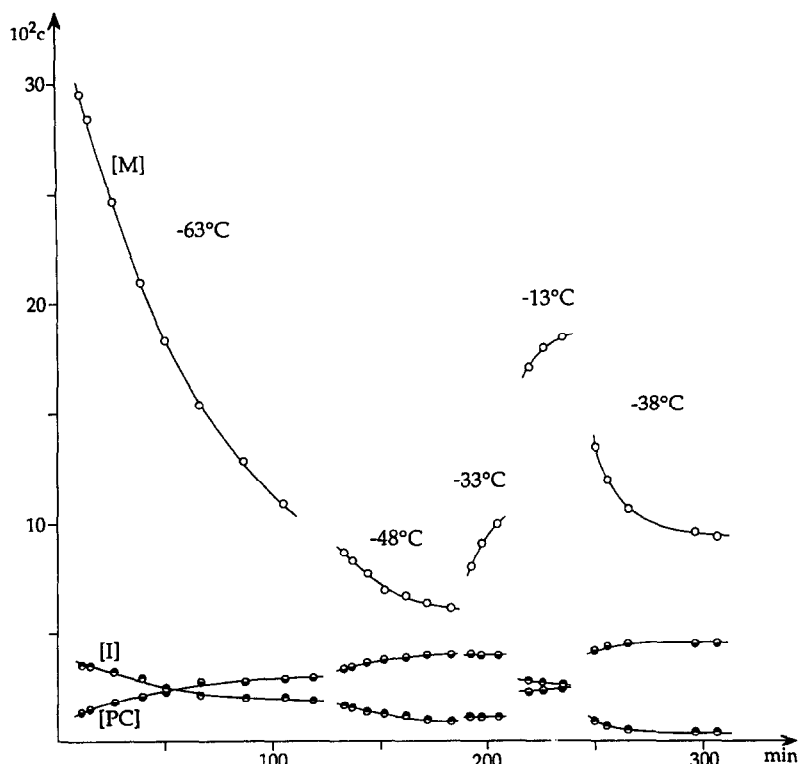


Fig. 1. Concentration–time plots for the reaction of (I) with 6.0 equiv. of cyclopentene (M) at different temperatures in CD_2Cl_2 . PC corresponds to the propagating carbene complexes.

[11]. Concentrations of species I, M and PC, as well as of the carbon–carbon double bonds in P and D, were obtained from the integrated intensities of chosen peaks in the spectrum, using the known initial concentration of initiator as reference. Main NMR data and assignments, and most important further experimental details, are given in the Results and discussion section.

3. Results and discussion

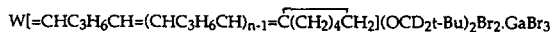
3.1. Cyclopentene

When cyclopentene (6 equiv., $c = 0.3 \text{ M}$) was added to a solution of



($c = 0.05 \text{ M}$) in CD_2Cl_2 at room temperature, no ROMP was detectable after several hours by NMR, despite the known high metathesis activity of this tungsten–carbene catalyst. Conversion into

poly(pentenamers) (P) only occurred on lowering the temperature. Variations in the concentration of monomer (M), initiator (I) and propagating carbene complexes



($n \geq 1$) (PC)¹, which can also be formulated as $\text{W}(\text{=CHP})(\text{OCD}_2\text{t-Bu})_7\text{Br}_2\cdot\text{GaBr}_3$, have been followed versus time at different temperatures (Fig. 1). At -63°C , one half of the initial monomer has ring-open polymerized after ca. 1 h, while the starting cyclohexylidene complex (I) was progressively converted into the propagating carbene complexes bearing a polymer chain substituent P in the carbene function (PC·M). At -48°C , the reaction was faster but tended towards an equilibrium after one more hour, where about 15% of initial M was still present. Raising the temperature at this stage (to -13°C) resulted in depolymerization of cyclopentene, which was

¹ This species with cyclopentene forms a π -olefin adduct PC·M similar to those described for cycloheptene and cyclooctene [12,13].

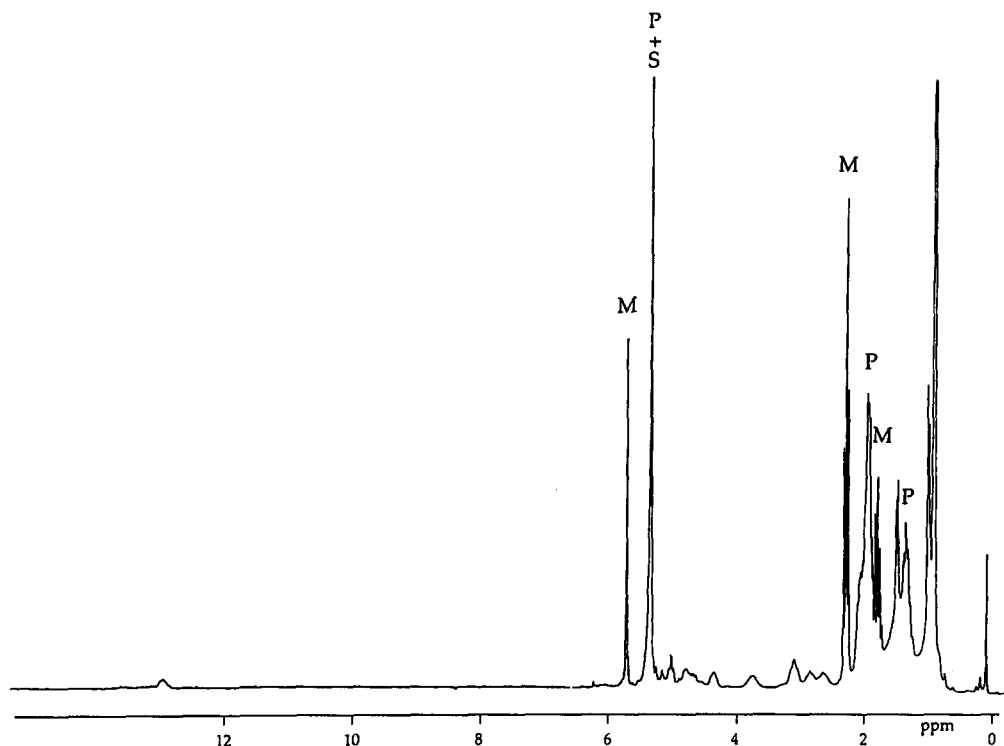
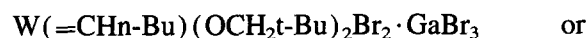


Fig. 2. 200 MHz ^1H NMR spectrum of the equilibrium mixture obtained at -38°C after addition of cyclopentene (M, 6 equiv.) to (I, $c=0.05$ M) in CD_2Cl_2 (S). P corresponds to polypentenamer chains.

regenerated from the living polypentenamers in up to 65% of its initial concentration, while $\text{PC}\cdot\text{M}$ partially converted back into I. Decreasing the temperature again to -38°C displaced the equilibrium back towards the formation of P and $\text{PC}\cdot\text{M}$, leaving ca. 30% of initial M and 10% of I. Bringing the system to room temperature then fully regenerated M and I (but cf. Section 3.4).

The ^1H NMR spectrum of the equilibrium mixture at -38°C is shown in Fig. 2. Beside monomer (M) and polymer chain (P) lines, all lower intensity signals arise from the organometallic part of $\text{PC}\cdot\text{M}$, especially those at 12.97 and 13.62 ppm corresponding to the carbene H_α signal of two distinct isomers.

Similar results were obtained with other carbene complexes such as

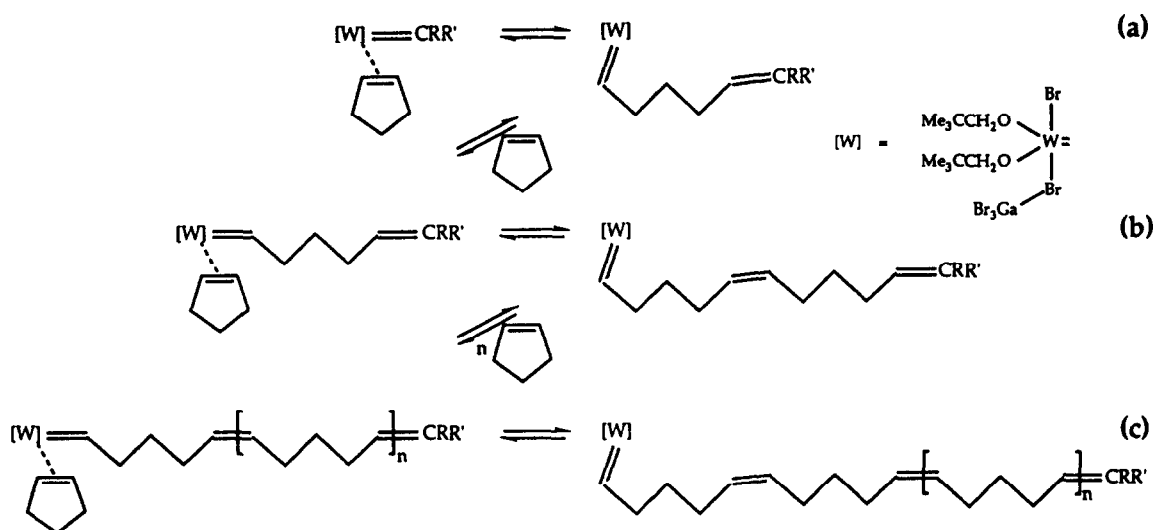


^{13}C NMR studies of the system involving



($[\text{I}]_0=0.25$ M, $[\text{M}]_0/[\text{I}]_0=2$) confirm these observations and show, in addition, that the polymer chains obtained at -78°C initially contain as much as 70% *cis* carbon-carbon double bonds ($\delta_{\text{CH}}=129.4$ ppm), and that the proportion of *trans* units ($\delta_{\text{CH}}=130.0$ ppm) then increases progressively to reach 50% after 2 h reaction at this temperature. The *cis* content decreases further at higher temperature to reach ca. 15% at -23°C , while M (and I) becomes preponderant again. The propagating carbene complex $\text{PC}\cdot\text{M}$ is characterized inter alia by a broad carbene C_α signal at 299.3 ppm at -78°C .

The reversibility of cyclopentene polymerization has been known for years [5,6], but has only been observed once in a living system involving a well-defined catalyst [1]. Our observations confirm the existence, for cyclopentene in the presence of a metal-carbene catalyst, of a temperature-dependent equilibrium between the



Scheme 3.

monomeric and polymeric forms. The polymeric form, which is favoured at low temperature, results from successive insertions of monomer into the metal–carbon double bond of the catalyst to yield metal–carbene end-capped polypentenamers which coordinate cyclopentene [12,13] and are unequivocally identified on the NMR spectra. The monomeric form results from the reverse depolymerization of these living polypentenamers (Scheme 3a–c). This involves intramolecular metathesis between the chain-end $M=C$ bond and the carbon–carbon double bond adjacent to it. It must be pointed out that, under the conditions of ^{13}C NMR experiments, the other carbon–carbon double bonds of the polymer chains also probably undergo secondary metathesis reactions, even at -78°C , according to the progressive *cis* content decrease found at this temperature [14]. These reactions may be inter- or intramolecular, leading to chain transfer or cyclic oligomers respectively (Scheme 2). The latter could, however, not be clearly distinguished by ^1H and ^{13}C NMR.

3.2. Cycloheptene

We have already reported [12] that cycloheptene (M) interacts at low temperature with



to yield a π -olefin adduct $I \cdot M$, and that the stability of this adduct is responsible for the extremely low polymerization rate observed below -20°C . Above this temperature, however, ROMP of cycloheptene takes place and the order of disappearance of monomer in CD_2Cl_2 was found by ^1H NMR ($[I]_0 = 0.05 \text{ M}$, $[M]_0/[I]_0 = 4.5$) to be slightly larger than 0 at -13°C . About one half of initial M had polymerized after 2 h under these conditions. Unexpectedly, in addition to polyheptenamers (P), characterized by signals at δ 5.35 (2H), 1.96 (4H) and 1.25 (6H), a small multiplet was found to grow in progressively at δ 5.15. After addition of a further 9 equiv. of cycloheptene, the reaction was maintained at 0°C for 5 h. This latter signal then became approximately as strong as that of the polymer at 5.35 ppm, while the monomer had considerably diminished, but was still present in non-negligible amounts (8% of $[M]_0$). These relative proportions did not change further with time, showing that the system had reached an equilibrium. I , whose conversion into a propagating carbene complex PC was not detected in this case, was still present in high amounts ($>95\%$ of $[I]_0$) at this stage. This confirms that initiation is very slow versus propagation, and indicates that the system was still active.

The system was then neutralized by successive additions of THF (3 equiv.) and benzaldehyde (1

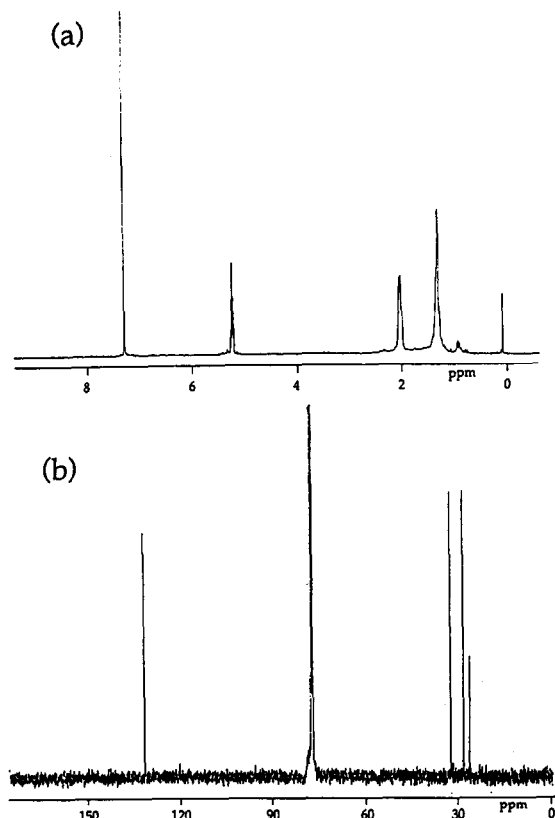


Fig. 3. ^1H (a) and ^{13}C (b) NMR spectra of *trans,trans*-cyclotetradeca-1,8-diene (D) in CDCl_3 at room temperature.

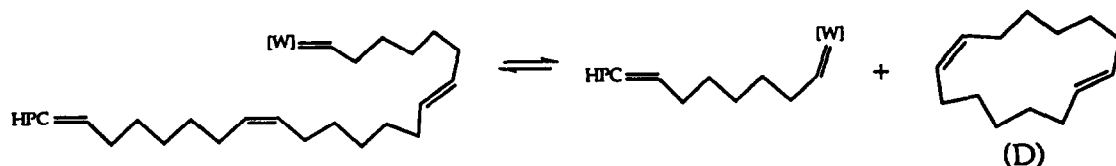
equiv.) and the volatiles were evaporated under vacuum (10^{-1} mmHg) at room temperature. Trap to trap distillation of the residue under strong heating, followed by pumping on the distillate at room temperature under primary vacuum, afforded a white solid residue corresponding to the product which gave rise to the ^1H NMR multiplet at 5.19 ppm (2H) (CDCl_3 , r.t.). This is the only olefinic signal on the spectrum of this compound. Two further lines were found at 2.01 (4H) and 1.28 ppm (6H) (Fig. 3), giving an overall pattern which is analogous to that of the polyheptenamers P. The corresponding ^{13}C NMR pattern (Fig. 3) is also analogous to that of polyheptenamers [15],

the chemical shifts being similarly slightly different ($\delta_{=\text{CH}} = 131.7, 32.1, 27.9$ and 26.0 ppm). The simplicity of this spectrum, corresponding to a highly stereoregular species, and the presence of the signal at 32.1 ppm [15] indicate that all carbon-carbon double bonds in this compound are *trans*. Further, a molecular weight of 192 was found by GC-MS for this compound, which we thus propose to be the cyclic dimer of cycloheptene, *trans,trans*-cyclotetradeca-1,8-diene (D), which would be formed in catalytic yield ($[\text{D}]_{\text{eq}}/[\text{I}]_0 = 3$) in this ROMP system. The *cis,trans* isomer (vide infra) of D is depicted in Scheme 4.

Further experiments on this system indicated qualitatively that the equilibrium position depends on various factors. Lower $[\text{M}]_0/[\text{I}]_0$ ratios will favour D over P, but also M over D. On the other hand, higher $[\text{M}]_0/[\text{I}]_0$ values will favour D over M, but also P over D. Temperature variations give rise to similar effects, the lowest molecular weight species being favoured at high temperature, where the equilibrium is reached more rapidly. Thus, only a few minutes are necessary to equilibrate the system at room temperature, at which PC,

$\text{W}[\text{=CHC}_5\text{H}_{10}\text{CH}=(\text{CHC}_5\text{H}_{10}\text{CH})_{n-1}=\overline{\text{C}}(\text{CH}_2)_3\text{CH}_2](\text{OCD}_2\text{t-Bu})_2\text{Br}_2\text{GaBr}_3$ ($n \geq 1$, $\delta^1\text{H}_\alpha = 12.62$ ppm), can be detected in the spectra (also cf. Section 3.4). The optimal conditions for obtaining high yields of D are thus intermediate and probably not far from those described above.

The equilibrium shifts are as expected reversible. When the system was brought to equilibrium at 0°C and then kept in dry ice over a six-week period, fast acquisition of the ^1H NMR spectrum at 0°C indicated that the equilibrium had shifted at low temperature towards the formation of P, at the expense of M. The system then moved back to the equilibrium state initially found at 0°C . Sim-

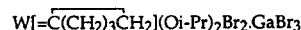
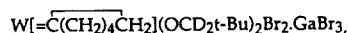


Scheme 4.

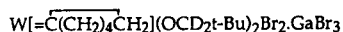
ilarly, addition to I of isolated D led, at 0°C, to the same equilibrium mixture of M, D and P.

Formation of D and P was also followed in situ by ^{13}C NMR in the presence of the same initiator ($[\text{I}]_0 = 0.24 \text{ M}$, $[\text{M}]_0/[\text{I}]_0 = 2$) at -13°C . The limiting *cis/trans* ratio of 1/3 was reached very rapidly for P, while D appeared to contain 95% of *trans* double bonds, much as the isolated product. A small additional signal at 130.8 ppm is however assigned to 5% of *cis* double bonds in D.

Other carbene complexes such as



lead to similar observations. For example, Fig. 4 illustrates the course of the reaction of cycloheptene with



at -3°C ($[\text{I}]_0 = 0.05 \text{ M}$, $[\text{M}]_0/[\text{I}]_0 = 5.5$). The equilibrium is not completely reached after 1 h 40 min, but cycloheptene concentration $[\text{M}]$ can be seen to tend towards a limit of about 0.03 M. At the beginning, cycloheptene is mainly converted into polymers ($[-\text{CH}=\text{CH}-]_{\text{P}}/[-\text{CH}=\text{CH}-]_{\text{D}} \approx 15$ after 5 min). The concentration of polymer carbon-carbon double bonds, $[-\text{CH}=\text{CH}-]_{\text{P}}$, then goes over a maximum, while the dimer concentration, $[-\text{CH}=\text{CH}-]_{\text{D}}$, increases continuously throughout the reaction to finally overcome $[-\text{CH}=\text{CH}-]_{\text{P}}$. This is consistent with fast conversion of M into P, followed by slower conversion of P into D. A significant difference with the previous system is that almost half of initial I is converted into PC already at this relatively low temperature, showing that initiation is easier in this case. The initial polymer chains are thus probably shorter than in the preceding case. A ^1H NMR spectrum corresponding to this system is shown on Fig. 5. M, P and D are clearly distinguished in the olefinic region, while the multiplet at δ 4.72 (4H, H_β) and the triplet at 12.62 (1H, H_α) are characteristic of the carbene functions in I and PC respectively.

In the presence of

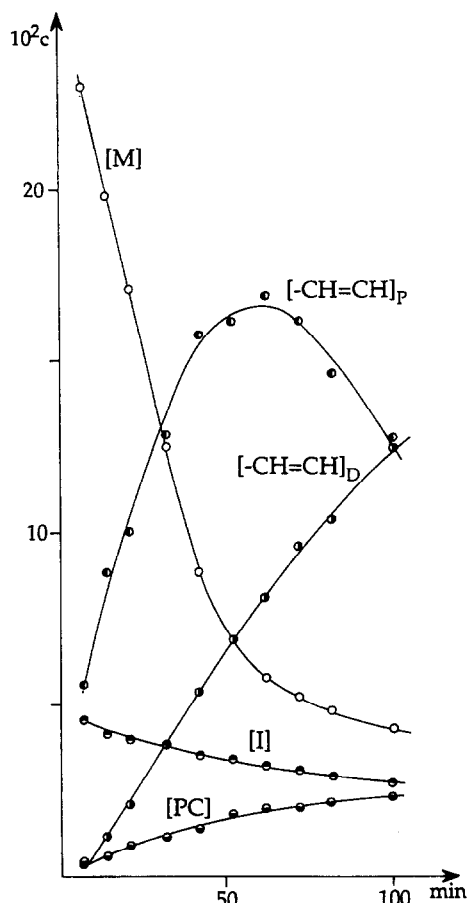


Fig. 4. Concentration–time plots for the reaction of (I) with 5.5 equiv. of cycloheptene (M) at -3°C in CD_2Cl_2 . PC corresponds to the propagating carbene complexes. $[-\text{CH}=\text{CH}-]_{\text{D}}$ and $[-\text{CH}=\text{CH}-]_{\text{P}}$ correspond to the concentration of carbon–carbon double bonds involved in the dimeric and polymeric forms, respectively.



($[\text{I}]_0 = 0.055 \text{ M}$, $[\text{M}]_0/[\text{I}]_0 = 5$), the π -olefin adduct $\text{I}\cdot\text{M}$ [12] is stable enough to be still detected by ^1H NMR at -3°C (ca. 20% of I). Also PC is found again, although in lower amounts (ca. 10% of I, $\delta^1\text{H}_\alpha = 12.39 \text{ ppm}$).



($[\text{I}]_0 = 0.035 \text{ M}$, $[\text{M}]_0/[\text{I}]_0 = 6$) and $\text{W}(\text{=CHt-Bu})(\text{OCH}_2\text{t-Bu})_2\text{Br}_2\cdot\text{GaBr}_3$ ($[\text{I}]_0 = 0.04 \text{ M}$, $[\text{M}]_0/[\text{I}]_0 = 4$) are slightly different catalysts since cycloheptene already ring-open polymerizes at -35°C in their presence. This is due to the lower stability of the cycloheptene adducts of

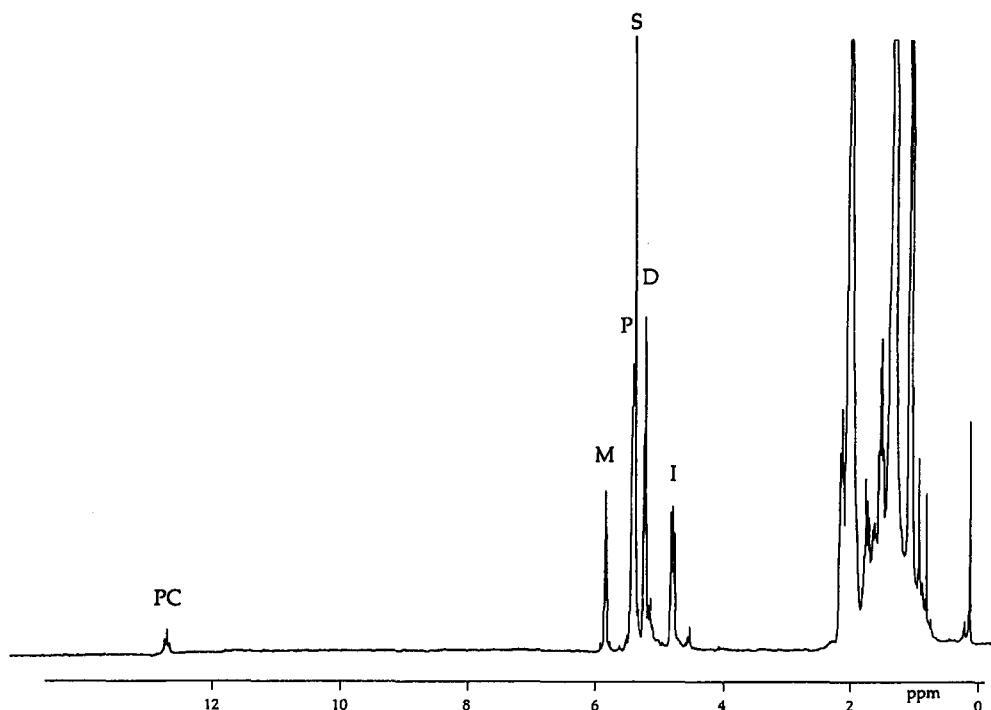


Fig. 5. 200 MHz ^1H NMR spectrum of the system obtained at -3°C after 1 h 20 min reaction between cycloheptene (M, 5.5 equiv.) and (I, $c = 0.05$ M) in CD_2Cl_2 (S).

these complexes [12]. Initiation is, however, still slower than propagation, almost no I being consumed in these reactions. Interestingly, the ^1H NMR spectra indicate that D is already present at -35°C for the latter, but only above -20°C for the first one. This arises probably from the different set of ancillary ligands in these two complexes.

The system involving $\text{W}(=\text{CHt-Bu})(\text{OCH}_2\text{t-Bu})_2\text{Br}_2 \cdot \text{GaBr}_3$ was also investigated by ^{13}C NMR ($[\text{I}]_0 = 0.22$ M, $[\text{M}]_0/[\text{I}]_0 = 2$). At -30°C , the variation with time of [I], [PC], [M], $[-\text{CH}=\text{CH-}]_D$ and $[-\text{CH}=\text{CH-}]_P$ followed a profile similar to that of Fig. 4. The conversion of I into PC, in particular, is more pronounced under these conditions than under the ^1H NMR ones. PC, $\text{W}[\text{=CHC}_5\text{H}_{10}\text{CH}(\text{CHC}_5\text{H}_{10}\text{CH})_{n-1}=\text{CHt-Bu}](\text{OCH}_2\text{t-Bu})_2\text{Br}_2 \cdot \text{GaBr}_3$ ($n \geq 1$) in this case, is characterized in particular by the carbene C_α , signal at 314.0 ppm, as well as by the chain end olefinic signals $-\text{CH}=\text{CHt-Bu}$ at 141.6 (*cis*) and 141.3 (*trans*) ppm, and $-\text{CH}=\text{CHt-Bu}$ at 124.7 (*trans*) and 124.3 (*cis*) ppm. A significant difference with

respect to Fig. 4, however, is the formation of higher amounts of P and the subsistence of lower amounts of M, which is consistent with the lower temperature in this experiment. After 1 h 40 min., when the equilibrium state was not yet completely reached, the $[\text{M}]/[-\text{CH}=\text{CH-}]_D/[-\text{CH}=\text{CH-}]_P$ ratios were approximately equal to 1/15/30 (Fig. 6).

The signal at 130.8 ppm assigned to *cis* carbon-carbon double bonds in D was much stronger in this case. The *cis/trans* ratio in D varied from 1/1 at the beginning of the reaction to 1/2 after 1 h 40 min. (Fig. 6). In the meantime, the *cis/trans* ratio in P changed from 1/2 to 1/3, and the chain-end double bonds isomerized reversibly from *cis/trans* = 1/5 to *cis/trans* = 2/5. The olefinic signals corresponding to *cis,trans*-D were not distinguished from those of *cis,cis*-D and *trans,trans*-D, and the high field lines corresponding to *cis,cis*-D and *cis,trans*-D could not be confidently identified in the reaction mixture. On raising the temperature, D rapidly and fully isomerized into the *trans,trans* species. This explains why all

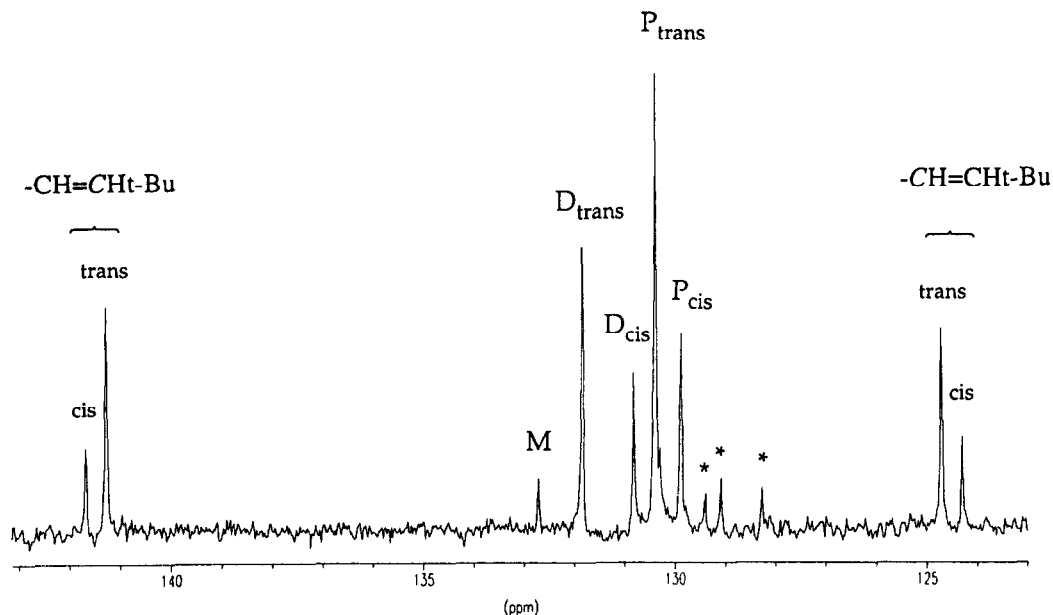


Fig. 6. 100 MHz ^{13}C NMR spectrum (olefinic region) of the mixture obtained at -30°C after 1 h 40 min reaction between cycloheptene (M, 2 equiv.) and $\text{W}(=\text{CHt-Bu})(\text{OCH}_2\text{t-Bu})_2\text{Br}_2 \cdot \text{GaBr}_3$ (I, $c = 0.22$ M) in CD_2Cl_2 (S). * corresponds to impurities.

attempts to neutralize the system before all *cis* double bonds in D have disappeared failed.

The *n*-pentylidene complex $\text{W}(=\text{CHn-Bu})(\text{OCH}_2\text{t-Bu})_2\text{Br}_2 \cdot \text{GaBr}_3$ is closely analogous to the active center of the PC species derived from it, and from the other initiators, showing for instance identical chemical shifts for the carbene $^1\text{H}_\alpha$ and $^{13}\text{C}_\alpha$ nuclei. The PC complex formed by insertion of cycloheptene into the $\text{W}=\text{C}$ bond of this initiator, $\text{W}[\text{=CHC}_5\text{H}_{10}\text{CH}(\text{CHC}_5\text{H}_{10}\text{CH})_{n-1}=\text{CHn-Bu}](\text{OCH}_2\text{t-Bu})_2\text{Br}_2 \cdot \text{GaBr}_3$ ($n \geq 1$), is therefore hard to distinguish in the NMR spectra. On the other hand, this analogy offers the opportunity to study the propagation steps on their own, no initiation step being expected in this case. Effectively, in the presence of the *n*-pentylidene initiator, cycloheptene ring-open polymerizes already at -63°C under ^{13}C NMR conditions ($[\text{I}]_0 = 0.27$ M, $[\text{M}]_0/[\text{I}]_0 = 2$) and at -50°C under ^1H NMR conditions ($[\text{I}]_0 = 0.05$ M, $[\text{M}]_0/[\text{I}]_0 = 3.5$), which is consistent with the fact that propagation was found to be faster than initiation in the previous systems. The reason for this lies in the lower stability of the intermediates involved in this case [12]. It has been previously reported that addition of cyclo-

heptene to the *n*-pentylidene complex leads at low temperature to a metallacyclobutane, and not to a π -olefin adduct $\text{I} \cdot \text{M}$ [12]. The same conclusion has to be applied to all PC species involved in our cycloheptene containing systems.

However, these metallacyclobutanes are stable enough to lead to an order of disappearance of M close to 0, as was found again for this system at -43°C before the reaction approaches equilibrium. At this temperature, half of M had ring-open polymerized after 2 h ($[\text{I}]_0 = 0.05$ M, $[\text{M}]_0/[\text{I}]_0 = 3.5$). The metallacyclobutane intermediates, initially detected in substantial amounts (ca. 35% of $[\text{I}]_0$), progressively diminished as well, at the expense of I and PC. At -3°C , the relative proportions of carbon-carbon double bonds of M, D and P became near to those of Figs. 4 and 5. Cyclodimer D was not yet detected at -63°C , but began to appear on the ^{13}C NMR spectra at -53°C , and continued to grow in at -43°C , where it was established to contain 60% of *cis* carbon-carbon double bonds.

Our studies show that, in the presence of stable and highly active tungsten-carbene catalysts, cycloheptene can display a polymerization/depolymerization behaviour similar to that of cyclo-

pentene. The similarity concerns in particular the observation of an equilibrium between monomeric and polymeric forms, the reversibility and the temperature dependence of this equilibrium, as well as the characterization of the carbene complexes mediating the equilibration reactions, which can alternatively be considered as living polyheptenamers. Also classical secondary metathesis involving all carbon–carbon double bonds of the polymer chains, including the chain end ones, is found again, even at low temperature. This stands out again from the variation of the configuration of these double bonds with time.

Several significant differences were however established. The polymeric forms of cycloheptene are, for instance, considerably favoured at a given temperature over those of cyclopentene. Secondly, the living polyheptenamers, formed in the first stage by successive insertions of cycloheptene into the metal–carbon double bond of the initiator, interact with cycloheptene to yield a metallacyclobutane intermediate which is less stable than the metal–carbene–olefin intermediate formed in the case of cyclopentene. Some of the initiators, however, give rise to the latter type of intermediate, in which case the stability of these initiation intermediates impedes cycloheptene from polymerizing at low temperature.

Further, these living polyheptenamers depolymerize not only into the monomer, but also into the cyclic dimer. This results from intramolecular metathesis, within the metal–carbene end-capped polyheptenamers, between the chain-end M=C bond and the second carbon–carbon double bond adjacent to it (Scheme 4). This particular secondary metathesis reaction seems to be thermodynamically favoured over the corresponding reactions involving the other double bonds of the polymer chains. Larger cyclic oligomers, which would certainly not be distinguished from the polymer chains by NMR, may however be obtained as well. Moreover, Fig. 4 shows that insertion of M into PC is faster than depolymerization of PC into D. This latter reaction was however found to occur already at -53°C in one of the systems. The dimer itself will undergo ROMP and insert into the M=C

bond of the initiator or of the propagating carbene complexes, to produce further living polyheptenamer chains, or to increase the length of the existing ones. This polymerization/depolymerization process of D already occurs at -30°C , according to the fact that the percentage of *cis* double bonds in D was found to change with time at this temperature. The initial value of 60% of *cis* double bonds at -43°C shows that this configuration is kinetically favoured in D. The thermodynamically stable isomer is however the *trans,trans* one, which is straightforwardly obtained free of *cis,cis* and *cis,trans* isomers at room temperature. The overall equations which account for the behaviour of M and D in these systems are described in Scheme 5. Analogous dimerization of silicon containing cycloolefins has been reported recently [3].

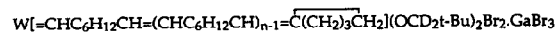
In addition to these mechanistic considerations, it must be emphasized that cyclodimerization of cycloheptene into *trans,trans*-cyclotetradeca-1,8-diene can be carried out catalytically and constitutes an attractive synthetical procedure for this product.

3.3. Cyclooctene

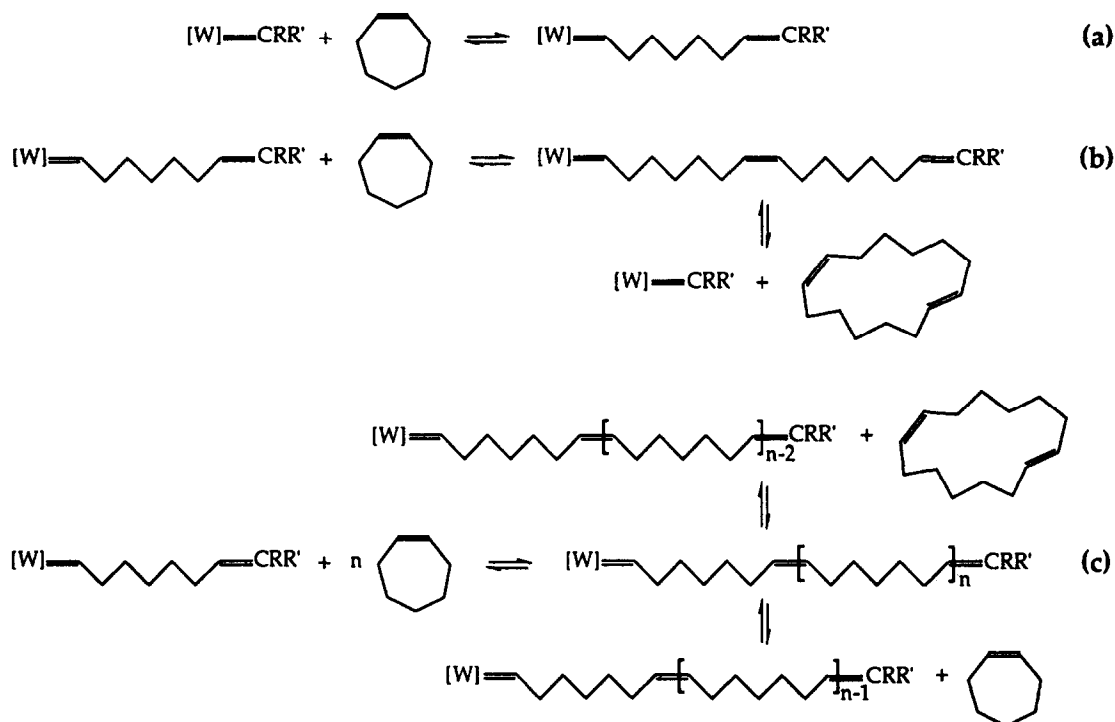
In the presence of



($[\text{I}]_0 = 0.05 \text{ M}$), cyclooctene ($[\text{M}]_0 = 0.20 \text{ M}$) ring-open polymerizes rapidly and completely in CD_2Cl_2 at -23°C . The first order consumption of M is achieved after 50 min, no more M being then detected on the ^1H NMR spectra. Except for I·M [12], which progressively disappears along with M to regenerate free I, and traces of PC,



($n \geq 1$, $\delta^1\text{H}_\alpha = 12.63 \text{ ppm}$) in this case, no new product other than polyoctenamers P [6,15,16] can be found on the spectra. The extremely low conversion of I into PC, and the fact that final $[-\text{CH}=\text{CH}-]_P$ is only ca. 40% of initial $[\text{M}]_0$, suggest that very long polymer chains of low solubility are obtained. This is consistent with for-



Scheme 5.

mation of a substantial white precipitate in the NMR sample. No significant changes occur on raising the temperature to -3°C and eventually to room temperature, at which however [PC] rapidly reaches 10% of [I] and $[-\text{CH}=\text{CH}-]_{\text{P}}$ increases as a result of the higher solubility of P. However, neither M, nor any other species, appears even after 1 h (but cf. Section 3.4). Given the possibility that dimer D, cyclohexadeca-1,9-diene, may in this case show an ^1H NMR spectrum similar to that of P and would therefore not be distinguished from the polyoctenamer chains, the reaction mixture was then neutralized and worked up as the corresponding cycloheptene ones: no volatile fraction containing carbon-carbon double bonds could be separated this way, confirming that D is probably not present in high amounts in this ROMP system. ^{13}C NMR studies ($[\text{I}]_0 = 0.25 \text{ M}$, $[\text{M}]_0/[\text{I}]_0 = 2$) confirm these observations. Under these conditions, 60% of M had polymerized after 12 min at -33°C , and polymerization was almost instantaneously completed on raising the temperature at this stage to -18°C . No olefinic signal other than the two lines at 130.3 and 129.8

ppm, respectively assigned to *trans* and *cis* double bonds of the polyoctenamer chains [15], are detected. The *cis* content decreased from 75% to 65% over the first period, and then rapidly to 25% at -18°C , showing moreover that secondary metathesis of the polymer chain double bonds does take place, at least intermolecularly.

Using $\text{W}(=\text{CHt-Bu})(\text{OCH}_2\text{-Bu})_2\text{Br}_2 \cdot \text{GaBr}_3$ as catalyst ($[\text{I}]_0 = 0.05 \text{ M}$), the polymerization rate of cyclooctene (3 equiv.) at -30°C was close to that observed for cycloheptene. Similarly also, no π -olefin adduct $\text{I} \cdot \text{M}$ is detected in this case, even at lower temperature. After 45 min, 20% of I was converted into PC, $\text{W}[\text{=CHC}_6\text{H}_{12}\text{CH=}(\text{CHC}_6\text{H}_{12}\text{CH})_{n-1}\text{=CHt-Bu}](\text{OCH}_2\text{-Bu})_2\text{Br}_2 \cdot \text{GaBr}_3$ ($n \geq 1$, $\delta^1\text{H}_{\alpha} = 12.63 \text{ ppm}$), indicating that initiation is faster than in the presence of the above cyclopentylidene catalyst, and that shorter more soluble polyoctenamer chains are probably obtained. Consistent with this, no polymer precipitates from solution in this case.

These observations show that, contrarily to their polypentenamer and polyheptenamer analogues, living polyoctenamers do not undergo

depolymerization into monomer at (or below) room temperature. In the presence of tungsten–carbene catalysts also used for cyclopentene and cycloheptene, ROMP of cyclooctene is total and irreversible at room temperature. Furthermore, no equilibrium between polyoctenamers and a cyclic dimer could be established, despite secondary metathesis of the carbon–carbon double bonds of the polymer chains is already effective at low temperature. The stability and reactivity of the metal–carbene end-capped polyoctenamers being comparable to those of the corresponding polyheptenamers, we do not believe that this secondary metathesis is only intermolecular, and not intramolecular. We thus suggest that cyclic oligomers are also obtained for cyclooctene, but are not distinguished by ^1H and ^{13}C NMR. In addition, the cyclic dimer of cyclooctene is probably not thermodynamically favoured like that of cycloheptene. Thus, it may exist only in statistical amounts which would not be detectable in our experiments. Earlier results are in agreement with these observations [5–7,9].

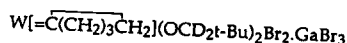
We also noticed that ROMP of cyclooctene at -25°C is faster than that of cycloheptene in the presence of



but not in the presence of $W(=\text{CHt-Bu})(\text{OCH}_2\text{t-Bu})_2\text{Br}_2\cdot\text{GaBr}_3$. This probably arises from the lower stability, at this temperature, of the π -olefin adduct of



and cyclooctene, as may be expected from the more negative ΔS° value of the cyclooctene complexation reaction [12]. Inhibition of the polymerization reaction by $\text{I}\cdot\text{M}$ is thus lessened. In the presence of $W(=\text{CHt-Bu})(\text{OCH}_2\text{t-Bu})_2\text{Br}_2\cdot\text{GaBr}_3$, this adduct is not observed and the polymerization rate is probably governed by the rate of reaction of M with I , rather than the rate of conversion of $\text{I}\cdot\text{M}$ into PC ($n=1$). Additionally, the first order rate of polymerization of cyclooctene in the presence of



suggests that the metallacyclobutane intermediate derived from the addition of monomer to PC is also less stable than in the case of cycloheptene.

3.4. Formation of saturated polymers

The ROMP systems described in this paper are only moderately stable at room temperature, at which not only tungsten–carbene catalysts I and PC , but also all monomers M , cyclic oligomers such as D , and polyalkenamers P progressively disappear over the period of a few days from the reaction mixture. The ^1H NMR spectra show that the three cycloolefins and their ROMP derivatives in fact undergo a second polymerization process converting them into saturated polymers possessing no more carbon–carbon double bonds. These polymers can be precipitated by addition of methanol, filtered and dried under vacuum. The ^1H NMR spectrum of the product separated from system $W(=\text{CHt-Bu})(\text{OCH}_2\text{t-Bu})_2\text{Br}_2\cdot\text{GaBr}_3/\text{cycloheptene}$ ($[\text{I}]_0=0.04\text{ M}$, $[\text{M}]_0/[\text{I}]_0=4$) after 2 days reaction at room temperature is shown on Fig. 7.

The corresponding polymers obtained from cyclopentene- or cyclooctene-containing systems show a slightly different NMR profile which may arise essentially from the fact that, initially, only monomer is present in the case of cyclopentene (cf. 1), and only polyalkenamers in the case of cyclooctene (cf. 3), while both coexist in the case of cycloheptene (together with D). In particular, the low field signal on Fig. 7 becomes preponderant for cyclopentene, and the higher field signals for cyclooctenamers. These signals can thus be approximately assigned to polymeric derivatives of cycloheptene monomer and of polyheptenamers respectively. We noticed further that polymerization of cyclopentene is much slower than that of the cycloheptene and cyclooctene derivatives. For the two latter reactions, rate of conversion in the presence of



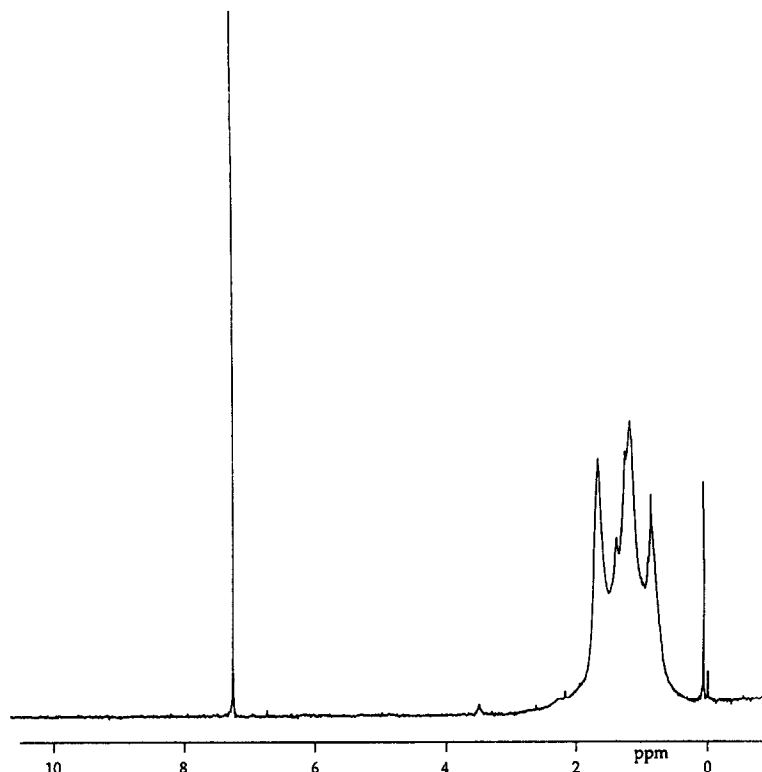


Fig. 7. 200 MHz ^1H NMR spectrum in CDCl_3 of the saturated polymer obtained in CD_2Cl_2 after 2 days reaction between $\text{W}(=\text{CHt-Bu})(\text{OCH}_2\text{t-Bu})_2\text{Br}_2 \cdot \text{GaBr}_3$ ($c = 0.04$ M) and 4 equiv. of cycloheptene at room temperature.

($[\text{I}]_0 = 0.05$ M, $[\text{M}]_0/[\text{I}]_0 = 4$) reached ca. 80% after 5 h and 100% after 1 day. Also cyclohexene, a ROMP-inactive substrate, polymerizes to an analogous saturated product under similar conditions, at a rate (60% conversion after 2 days, full conversion after six days) which is close to that observed for cyclopentene.

Hence, the present tungsten–carbene complexes not only initiate ROMP and metathesis reactions, but also, although much more slowly, addition polymerization of cyclic as well as of linear olefins. This no doubt arises from the presence of Lewis acid GaBr_3 in these catalysts. Although bound to the tungsten complexes [10], this Lewis acid may interact on its own with olefins to yield the final saturated products, probably by a cationic mechanism.

Indeed, we found that these addition polymerization reactions also occur in the presence of GaBr_3 alone (0.05 M in CD_2Cl_2), and are moreover much faster. Hence, 4 equiv. of cycloheptene

are polymerized at room temperature in less than 1 h. The ^1H NMR spectrum of the resulting polymer is similar to that of Fig. 7, the signal at 1.67 ppm being however stronger, in agreement with its assignment to polymers derived from non ring-open polymerized cycloheptene. Interestingly, a spectrum recorded after a short reaction time, while cycloheptene monomer was still present, showed that there is a relatively strong interaction between the carbon–carbon double bonds of this molecule and GaBr_3 , according to the chemical shift displacement of $\delta(-\text{CH}=\text{C})$ from 5.79 ppm in free cycloheptene to 6.53 ppm. Cyclopentene also polymerizes in the presence of GaBr_3 alone, although significantly more slowly: 2 days were necessary in this case to entirely polymerize 3.5 equiv. of monomer. Consistently, cyclopentene seems to interact less strongly with GaBr_3 , since the $\delta(-\text{CH}=\text{C})$ is only shifted from 5.75 to 5.97 ppm on addition of the 3.5 equivalents to GaBr_3 . As expected, the ^1H NMR spectrum of the poly-

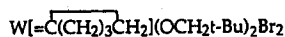
mer obtained in this manner is very close to that obtained using the tungsten–carbene catalysts, as well as to that obtained from cycloheptene in the presence of GaBr₃ alone.

These observations confirm that coordination of GaBr₃ to the tungsten–carbene complexes not only renders these complexes very active for olefin metathesis and ROMP reactions [10], but also prevents to some extent GaBr₃ from reacting itself with these olefins. This deactivation is however not sufficient to prevent cationic polymerization reactions from occurring at room temperature.

3.5. GaBr₃-free tungsten–carbene catalysts

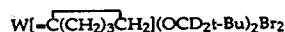
In the absence of coordinated Lewis acid, tungsten–carbene complexes of the type W(=CRR')(OCH₂t-Bu)₂Br₂ are much less active catalysts, but still initiate ROMP of strained olefins [17] and even metathesis of linear olefins [10] at room temperature. As expected, their reaction with the weakly strained cycloolefins of the present study is thus similar to, but slower than, that of the GaBr₃ containing complexes.

In the presence of



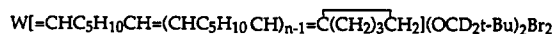
([I]₀ = 0.05 M in CD₂Cl₂), cyclopentene (5 equiv.) does not react at all after 1 day at room temperature, probably because the living polypentenamers are thermodynamically disfavoured again. Polypentenamers were, however, also not found at low temperature in this case. At the temperatures at which they would be expected thermodynamically, their formation by insertion of monomer into the metal–carbon double bond of I is probably too slow to be detectable after a few hours reaction.

Catalyst



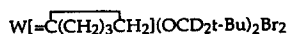
([I]₀ = 0.06 M in CD₂Cl₂) converts cycloheptene (3.5 equiv.) into an equilibrium mixture of M, D and P similar to that obtained in the presence of GaBr₃. This equilibrium is however only reached after ca. 4 days at room temperature, during which

time 40% of I is progressively converted into propagating carbene complexes PC,

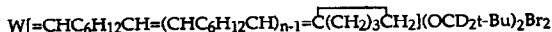


(*n* ≥ 1), characterized in particular by their carbene ¹H_α triplet at 11.63 ppm. Intramolecular secondary metathesis within the living polyheptenamer chains, thus, also occurs in the absence of GaBr₃, at a rate which, given the stability of the metal–carbene chain-end function in these species, is sufficient for the thermodynamic equilibrium between cycloheptene monomer, dimer and polymers to be reached at room temperature.

Finally, cyclooctene (3.5 equiv.) was shown to ring-open polymerize at room temperature in the presence of



([I]₀ = 0.06 M in CD₂Cl₂) within 20 h, after which time no more monomer could be detected on the ¹H NMR spectra, and 25% of I had been converted into PC,



(*n* ≥ 1) in this case, characterized again by the carbene ¹H_α triplet at 11.63 ppm. [PC] then continued to increase with respect to [I], probably as a result of continuing secondary metathesis reactions between the cyclopentylidene function in I and the carbon–carbon double bonds in the polyoctenamer chains. These results also are analogous to those obtained in the presence of GaBr₃, except again for the very different reaction rates.

4. Conclusion

These studies show that early mechanistic assumptions on secondary metathesis reactions in cycloolefin ROMP systems can be directly verified by NMR spectroscopy if stable, long-lived metal–carbene complexes are used as initiators and are formed as propagating intermediates in such systems. If this stability is combined with some metathesis activity against carbon–carbon double bonds of the initial polyalkenamer chains,

thermodynamic equilibrium between reactants and products can be reached more or less rapidly, depending on the temperature and the activity of the catalyst. The nature of the organic products depends on that of the cycloolefin substrate. In particular, cycloheptene leads to a significant proportion of the cyclic dimer derivative, an observation which has seemingly, and surprisingly, not been reported previously.

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