

Ring-opening metathesis polymerization of norbornene and norbornadiene by tungsten(II) and molybdenum(II) complexes

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Abstract

The reaction of norbornene (NBE) and norbornadiene (NBD) in the presence of seven-coordinate tungsten(II) and molybdenum(II) complexes of the $[(\text{CO})_4\text{M}(\mu\text{-Cl})_3\text{M}(\text{SnCl}_3)(\text{CO})_3]$ and $[\text{MCl}(\text{M}'\text{Cl}_3)(\text{CO})_3(\text{NCMe})_2]$ ($\text{M} = \text{W}, \text{Mo}$; $\text{M}' = \text{Sn}, \text{Ge}$) types leads to ring-opening metathesis polymerization (ROMP) and to the formation of high molecular weight polymers. The geometric structure of these polymers was determined by means of ^1H - and ^{13}C -NMR spectroscopy. The monitoring of the reaction between cyclic olefins and the metal complex by means of ^1H -NMR spectroscopy allowed us to observe the coordination of NBD to metal atoms in the initiation step of the polymerization process. Compounds of the $[\text{MCl}(\text{SnCl}_3)(\text{CO})_3(\eta^4\text{-NBD})]$ type prepared directly from $[(\text{CO})_4\text{M}(\mu\text{-Cl})_3\text{M}(\text{SnCl}_3)(\text{CO})_3]$ or $[\text{MCl}(\text{M}'\text{Cl}_3)(\text{CO})_3(\text{NCMe})_2]$ ($\text{M} = \text{W}, \text{Mo}$) in the presence of an excess of NBD initiate the ROMP reaction immediately. The detection of the first-formed products in the reaction between the metal complex and cyclic olefins provides valuable information concerning the nature of the initiating species. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Metathesis polymerization of cyclic olefins; Tungsten(II) catalyst; Molybdenum(II) catalyst; Seven-coordinate complexes

1. Introduction

Over the past several years there has been considerable effort in our group to explore the catalytic activity of seven-coordinate molybdenum(II) and tungsten(II) complexes [1–3]. In particular, the $[\text{MCl}(\text{M}'\text{Cl}_3)(\text{CO})_3(\text{NCMe})_2]$ and $[(\text{CO})_4\text{M}(\mu\text{-Cl})_3\text{M}(\text{M}'\text{Cl}_3)(\text{CO})_3]$ ($\text{M} = \text{W}, \text{Mo}$; $\text{M}' = \text{Sn}, \text{Ge}$) family of complexes has recently received much attention. These compounds are very efficient catalysts for the polymerization reaction of terminal alkynes, such as phenylacetylene or *tert*-butylacetylene [1–3].

Recently, we have been particularly intrigued by the reaction of seven-coordinate molybdenum(II) and tungsten(II) compounds with cyclic olefins and the opportunity to initiate ring-opening metathesis polymerization (ROMP) [4]. The first step in this reaction is undoubtedly the coordination of olefin to metal. However, only in the reaction with a chelating ligand, such as norbornadiene (NBD), was it possible to isolate and characterize the reaction product $[\text{MCl}(\text{SnCl}_3)(\text{CO})_3(\eta^4\text{-NBD})]$ ($\text{M} = \text{Mo}$ [4], W [5]).

Our goal was to obtain more information about the catalytically active species formed in the initiating step of ROMP by tungsten(II) and molybdenum(II) compounds being the adducts of the transition metal and the main group metal (Lewis acid) compounds. These complexes, like the compounds of the type $[\text{MX}_2(\text{CO})_3\text{L}_2]$ ($\text{M} = \text{Mo}, \text{W}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{L} =$

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PPh_3 , AsPh_3 , SbPh_3) studied earlier by Bencze and co-workers [6–8], do not need to be activated by the organometallic component. However, the catalytic activity of the complexes $[\text{MX}_2(\text{CO})_3(\text{NCMe})_2]$ ($\text{M} = \text{Mo}, \text{W}$; $\text{X} = \text{Br}, \text{I}$) investigated by Baker and co-workers [9], drastically increases after the addition of small amounts of Lewis acid, such as AlCl_3 or ZrCl_4 .

2. Experimental

2.1. General data

The synthesis and manipulation of all chemicals was carried out under nitrogen using standard Schlenk techniques. Solvents and reagents were pre-dried with CaH_2 and vacuum transferred into small storage flasks prior to use. NMR spectra were run using a Bruker AMX-300 and 500 MHz spectrometer. The analysis of the catalytic reaction products was performed on a Hewlett-Packard GC–MS system as well as by ^1H - and ^{13}C -NMR. Molecular weights of the polynorbornene (poly-NBE) and poly-NBD were measured using CHCl_3 solutions, a refractive index detector and a Plgel 10 m MIXED-B column. The values recorded are the weight of polystyrene that would exhibit the chromatograms observed.

2.2. Synthesis

The compounds $[\text{MCl}(\text{M}'\text{Cl}_3)(\text{CO})_3(\text{NCMe})_2]$ ($\text{M} = \text{Mo}, \text{W}$; $\text{M}' = \text{Sn}, \text{Ge}$) were prepared by reacting $[\text{M}(\text{CO})_4(\text{NCMe})_2]$ ($\text{M} = \text{Mo}, \text{W}$) with SnCl_4 or GeCl_4 in a solution of CH_2Cl_2 using the familiar procedures [2,10,11]. $[(\text{CO})_4\text{M}(\mu\text{-Cl})_3\text{M}(\text{SnCl}_3)(\text{CO})_3]$ ($\text{M} = \text{W}, \text{Mo}$) was obtained in the photochemical reaction of $\text{W}(\text{CO})_6$ and SnCl_4 as reported in the literature [12,13]. The $[\text{MCl}(\text{SnCl}_3)(\text{CO})_3(\eta^4\text{-NBD})]$ ($\text{M} = \text{Mo}$ [4], W [5]) complexes were synthesized according to the literature method.

2.3. Procedure for testing catalytic activity

In a typical experiment the reaction mixture composed of solvent (5 cm^3), heptane as the internal chromatographic standard (0.25 mol dm^{-3}), NBE or NBD (5 mol dm^{-3}) and a metal complex (0.05 mol dm^{-3}) was stirred at a suitable temperature under nitrogen in

a 50 cm^3 glass reactor provided with a septum through which liquid reactants were introduced and removed by means of a syringe. Chlorobenzene (PhCl) was the usual solvent; a few experiments were conducted in CH_2Cl_2 and toluene.

The conversion of cyclic olefins was confirmed by the GC method. The reaction was terminated by the addition of a large excess of methanol (20 cm^3). The polymer was purified by re-precipitation from CHCl_3 into methanol. Polymerization yield (%) was defined by comparing the weight of the polymer with the weight of the cyclic olefin used.

The polymer was analyzed by ^1H - and ^{13}C -NMR spectroscopy in CDCl_3 and gel-permeation chromatography in CHCl_3 .

3. Results and discussion

3.1. Catalytic conversion of NBE

The compounds $[\text{MCl}(\text{M}'\text{Cl}_3)(\text{CO})_3(\text{NCMe})_2]$ ($\text{M} = \text{Mo}, \text{W}$; $\text{M}' = \text{Sn}, \text{Ge}$) initiate the ROMP of NBE at room temperature, but the reaction is very slow (Table 1 and Fig. 1). However, NBE polymerizes selectively to ROMP polymer, i.e. poly(1,3-cyclopentylenevinylene). The conversion of NBE in the presence of binuclear $[(\text{CO})_4\text{M}(\mu\text{-Cl})_3\text{M}(\text{SnCl}_3)(\text{CO})_3]$ ($\text{M} = \text{W}, \text{Mo}$) complexes is faster, but the reaction occurs with low selectivity (Table 1). The effect of temperature on the ROMP of NBE is shown in Fig. 1. From this relationship the temperature of 348 K was chosen as more convenient for future investigations. At this temperature the conversion of NBE reaches about 80% (with 100% selectivity to ROMP polymer) after a 5 h reaction initiated by $[\text{MCl}(\text{M}'\text{Cl}_3)(\text{CO})_3(\text{NCMe})_2]$. The disappearance of NBE during ROMP is first order and dependent on the catalyst/NBE molar ratio (Fig. 2).

Poly-NBDs have high molecular weights, but their polydispersities are higher than 1 ($1.8 < \text{PD} < 3.6$), as is typical for initiators, which transform to catalytically active alkylidene species during the induction period.

3.2. Catalytic conversion of NBD

As was observed earlier, NBD is often less readily polymerized than NBE [4,15]. Also, in the presence of

Table 1

Results of metathesis polymerization of NBE using seven-coordinate complexes as catalysts^a

Catalyst	T (K)	Solvent	Conversion (%)	Yield (%)	$\bar{M}_n (\times 10^{-5})$	$\bar{M}_w (\times 10^{-5})$	\bar{M}_w/\bar{M}_n	σ_c	r_c	r_t	$r_c r_t$
[WCl(SnCl ₃)(CO) ₃ (NCMe) ₂]	298	CH ₂ Cl ₂	– ^b	4	0.41	0.23	1.8	0.61	1.9	2.0	3.7
	298	PhCl	– ^b	2	1.90	4.30	2.3	0.67	5.0	1.9	9.5
	348	PhCl	76	76	3.30	9.20	2.8	0.52	1.3	1.4	1.8
[WCl(GeCl ₃)(CO) ₃ (NCMe) ₂]	298	PhCl	– ^b	5	4.80	13.40	2.8	0.65	2.3	1.4	3.3
	348	PhCl	60	60	– ^c	– ^c	– ^c	0.59	2.1	0.6	1.3
[MoCl(SnCl ₃)(CO) ₃ (NCMe) ₂]	298	CH ₂ Cl ₂	– ^b	4	1.97	6.23	3.2	0.45	0.7	3.9	2.9
	348	PhCl	17	17	5.90	14.80	2.5	0.33	0.5	2.5	1.2
[(CO) ₄ Mo(μ-Cl ₃)Mo(SnCl ₃)(CO) ₃]	298	CH ₂ Cl ₂	93	21	0.03	0.05	1.8	– ^c	– ^c	– ^c	– ^c
	298	PhMe	93	45	0.06	0.16	2.5	0.45	0.7	1.9	1.4
[(CO) ₄ W(μ-Cl ₃)(CO) ₃ W(SnCl ₃)(CO) ₃]	298	PhMe	43	22	– ^c	– ^c	– ^c	– ^c	– ^c	– ^c	– ^c
	298	CH ₂ Cl ₂	81	17	0.60	2.26	3.6	0.41	0.9	2.6	2.2

^a Catalyst/NBE ratio of 1/100; reaction time 5 h at 348 K and 24 h at 298 K.^b Conversion low to determine precisely.^c Not determined.

tungsten(II) and molybdenum(II) catalysts, the ROMP of NBD is slow and not very selective (Table 2). Poly-NBD separated from the reaction mixture was no longer soluble. However, during the ROMP of NBD in the NMR tube it is possible to observe the formation of poly-NBD and to determine its microstructure from ¹H- and ¹³C-NMR spectra (Figs. 3 and 4).

3.3. Geometric structure of polymers

¹H- and ¹³C-NMR spectroscopic data for polymers obtained in the presence of W and Mo catalysts are

consistent with data previously reported for polymers of NBE [15–17] and NBD [14,15] prepared via ROMP.

The geometric structure of poly-NBE was determined from ¹H and ¹³C-NMR spectra according to Ivin et al. [15–17]. The relative proportions of double bond pair sequences, represented as *trans*–*cis* (*tc*), *trans*–*trans* (*tt*), *cis*–*cis* (*cc*) and *cis*–*trans* (*ct*) units, were determined from the four methine carbon (C^{1,4}) signals of the ¹³C-NMR spectrum of poly-NBE at δ_C 43.40 (*tc*), 43.12 (*tt*), 38.62 (*cc*) and 38.39 (*ct*) (Fig. 5). The fraction of *cis* double bonds ($\sigma_c = 0.67$) estimated from this ¹³C-NMR spectrum is in good

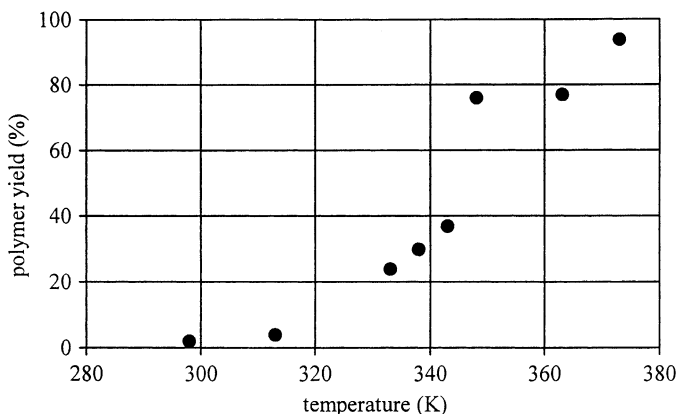


Fig. 1. Effect of temperature on the ROMP of NBE promoted by [WCl(SnCl₃)(CO)₃(NCMe)₂] in PhCl at a monomer/catalyst ratio of 100/1, for a reaction time of 5 h.

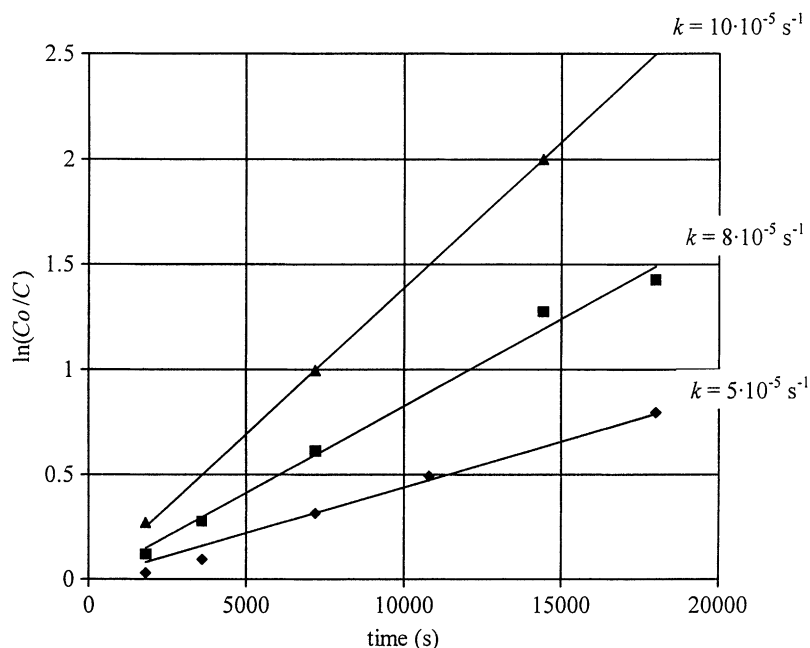


Fig. 2. First-order plot of NBE (C) disappearance during its ROMP by $[\text{WCl}(\text{SnCl}_3)(\text{CO})_3(\text{NCMe})_2]$ at 348 K in PhCl for various initial concentrations C_0 and monomer/catalyst molar ratios: (◆) 200/1; (■) 100/1; (▲) 50/1.

agreement with that obtained from the $^1\text{H-NMR}$ spectrum ($\sigma_c = 0.68$ from the integrals of the signals at $\delta_{\text{H}} = 2.77$ ($\text{HC}^{1,4}$ *cis*-poly-NBE) and at $\delta_{\text{H}} = 2.41$ ($\text{HC}^{1,4}$ *trans*-poly-NBE) (Fig. 6).

The qualitative observation was made that molybdenum catalysts generally gave polymers with a lower fraction of double bonds with a *cis* structure than tungsten catalysts. The *cis* content of polymers (σ_c) prepared using molybdenum complexes as the initiator varied from about 0.30 to 0.45, while with tungsten catalysts it varied from about 0.41 to 0.67 and was

temperature dependent (Table 1 and Fig. 7), higher *cis* polymers being formed at lower temperature. Increasing the temperature from 293 to 393 K reduced σ_c from 0.65 to 0.52 and the blockness $r_c r_t$ [15,17] (reactivity ratios $r_c = cc/ct$ and $r_t = tt/tc$ were calculated from the heights of relevant signals in $^{13}\text{C-NMR}$ spectra) from 3.7 to 2.4 (Table 1).

In the observed $^1\text{H-}$ and $^{13}\text{C-NMR}$ spectra, the microstructure of the poly-NBD formed in the above reactions (Figs. 3, 4, 8 and 9) can be analyzed [14,15]. From the integral ratio of signal due to olefinic protons

Table 2

Results of metathesis polymerization of NBD using tungsten(II) and molybdenum(II) compounds^a

Catalyst	T (K)	Solvent	Time (h)	Conversion (%)	Yield (%)	\bar{M} ($\times 10^{-4}$)
$[\text{WCl}(\text{SnCl}_3)(\text{CO})_3(\text{NCMe})_2]$	298	CH_2Cl_2	72	18	9	1.1
	313	PhCl	5	19	19	– ^b
	348	PhCl	5	30	17	– ^b
$[\text{MoCl}(\text{SnCl}_3)(\text{CO})_3(\text{NCMe})_2]$	298	CH_2Cl_2	168	30	10	1.1
$[(\text{CO})_4\text{Mo}(\mu\text{-Cl})_3\text{Mo}(\text{SnCl}_3)(\text{CO})_3]$	298	CH_2Cl_2	168	30	9	57.0
$[(\text{CO})_4\text{W}(\mu\text{-Cl})_3\text{W}(\text{SnCl}_3)(\text{CO})_3]$	298	CH_2Cl_2	72	33	22	9.8

^a Catalyst/NBD ratio of 1/100.

^b Not determined.

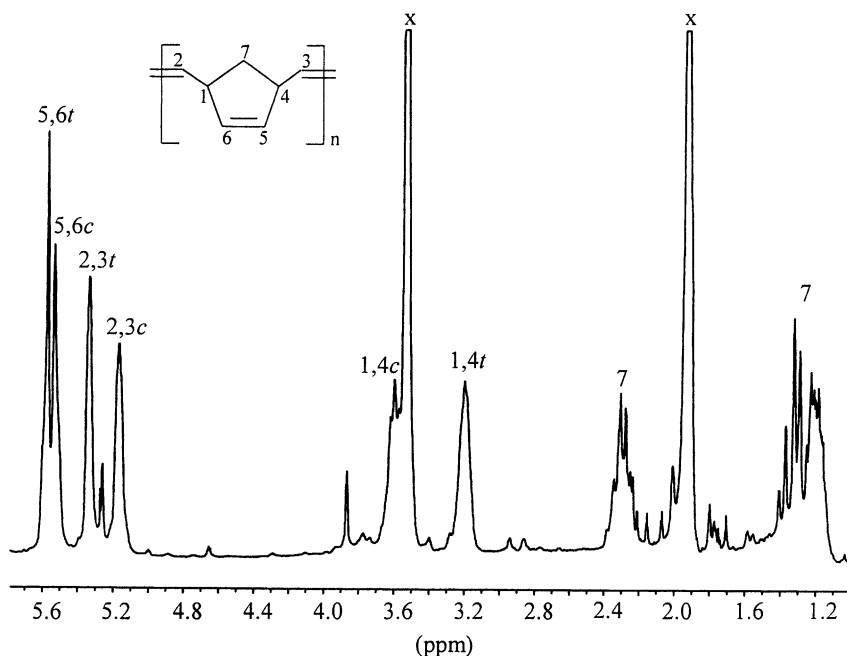


Fig. 3. $^1\text{H-NMR}$ spectrum (300 MHz, $\text{CDCl}_3/\text{CD}_2\text{Cl}_2$) of poly-NBD formed during the reaction of $[\text{WCl}(\text{SnCl}_3)(\text{CO})_3(\eta^4\text{-NBD})]$ and NBD in the NMR tube at 293 K. The signal marked (x) is derived from NBD.

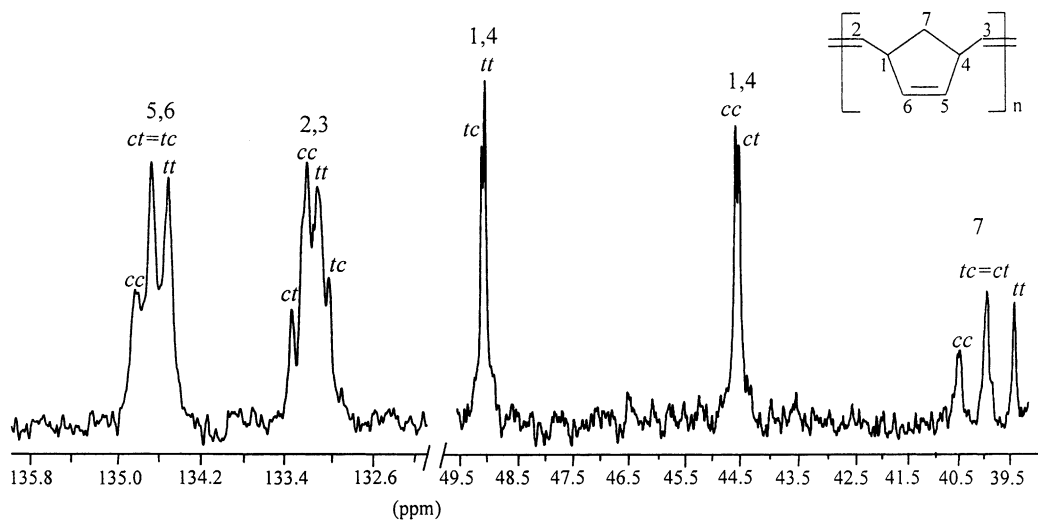


Fig. 4. $^{13}\text{C-NMR}$ spectrum (125 MHz, $\text{CDCl}_3/\text{CD}_2\text{Cl}_2$) of poly-NBD formed during the reaction of $[\text{WCl}(\text{SnCl}_3)(\text{CO})_3(\eta^4\text{-NBD})]$ and NBD in the NMR tube at 293 K.

at δ_{H} 5.37 (trans double bond) and δ_{H} 5.20 (*cis* double bond), the value of the *cis* double bond content was calculated to be ca. 60% during the course of the reaction (Fig. 8). A *cis* double bond content of ca. 50%

was obtained from the $^{13}\text{C-NMR}$ spectrum (Fig. 4). For this purpose the well-resolved signals of the methine carbons ($\text{C}^{1,4}$) at δ_{C} 49.20 (*trans* double bond) and at δ_{C} 44.49 (*cis* double bond) were integrated.

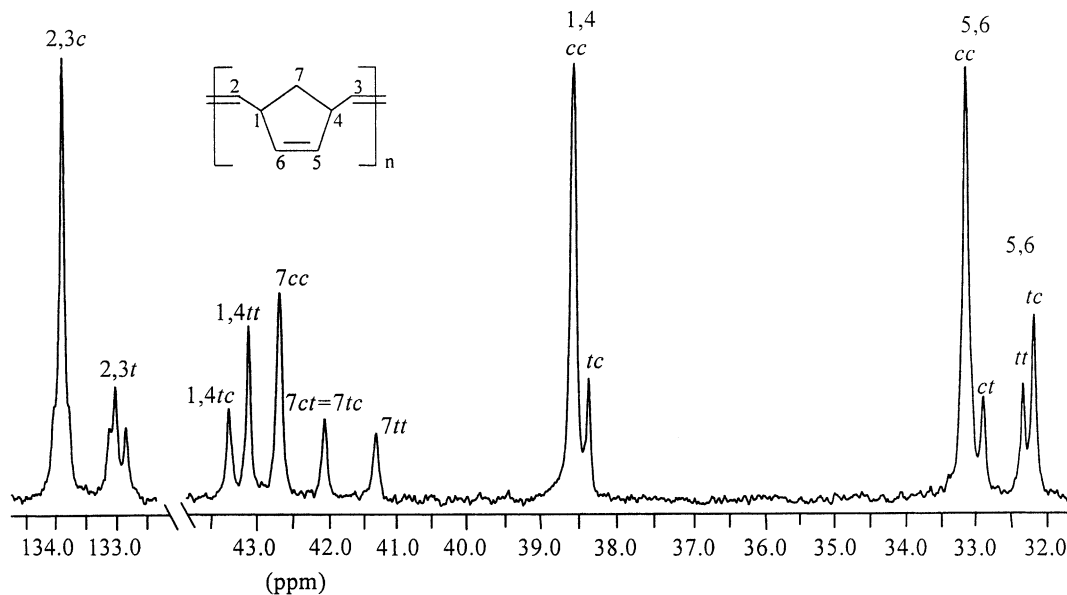


Fig. 5. Representative ^{13}C - ^1H -NMR spectrum (75 MHz, CDCl_3) of poly-NBE produced after 2 h in PhCl at 348 K with $[\text{WCl}(\text{SnCl}_3)(\text{CO})_3(\text{NCMe})_2]$ as catalyst.

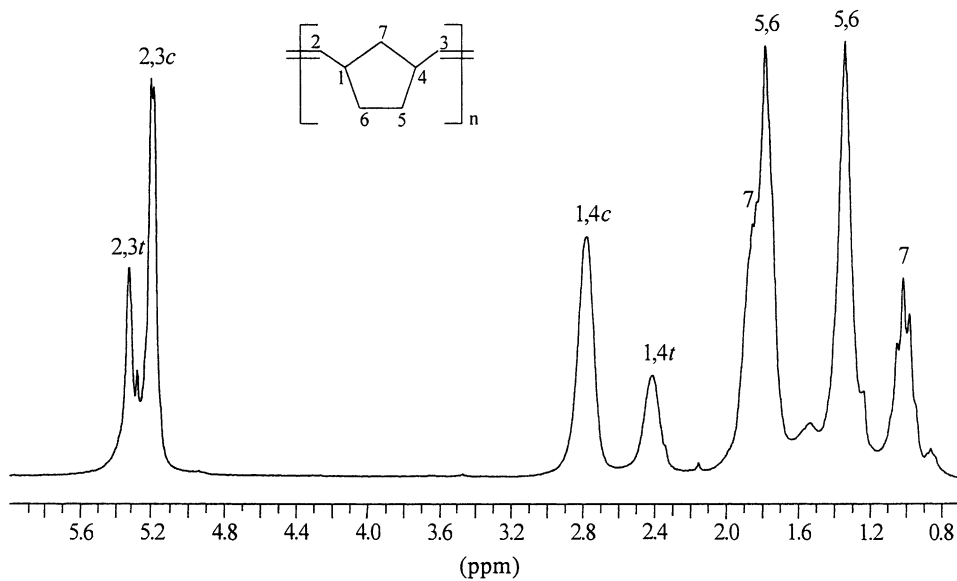


Fig. 6. Representative ^1H -NMR spectrum (300 MHz, CDCl_3) of poly-NBE obtained in the presence of $[\text{WCl}(\text{SnCl}_3)(\text{CO})_3(\text{NCMe})_2]$ in PhCl at 348 K after 2 h.

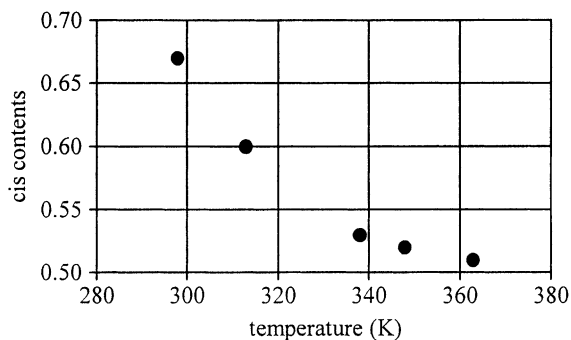


Fig. 7. Effect of temperature on the *cis* content of poly-NBEs formed in reactions initiated by $[\text{WCl}(\text{SnCl}_3)(\text{CO})_3(\text{NCMe})_2]$ in PhCl .

3.4. Initiation of ROMP by tungsten(II) and molybdenum(II) compounds

The ability of bimetallic seven-coordinate compounds to initiate the polymerization of cyclic olefins signifies their ability to generate metal alkylidene. In the process of studying reactions between seven-coordinate complexes and NBD, we discovered what we believed might be the initiating step in a polymerization process consisting of the coordination of monomer.

The reaction between $[\text{WCl}(\text{SnCl}_3)(\text{CO})_3(\text{NCMe})_2]$ and an excess of NBD was followed by means of $^1\text{H-NMR}$ spectroscopy, which confirmed the formation of $[\text{WCl}(\text{SnCl}_3)(\text{CO})_3(\eta^4\text{-NBD})]$ due to the

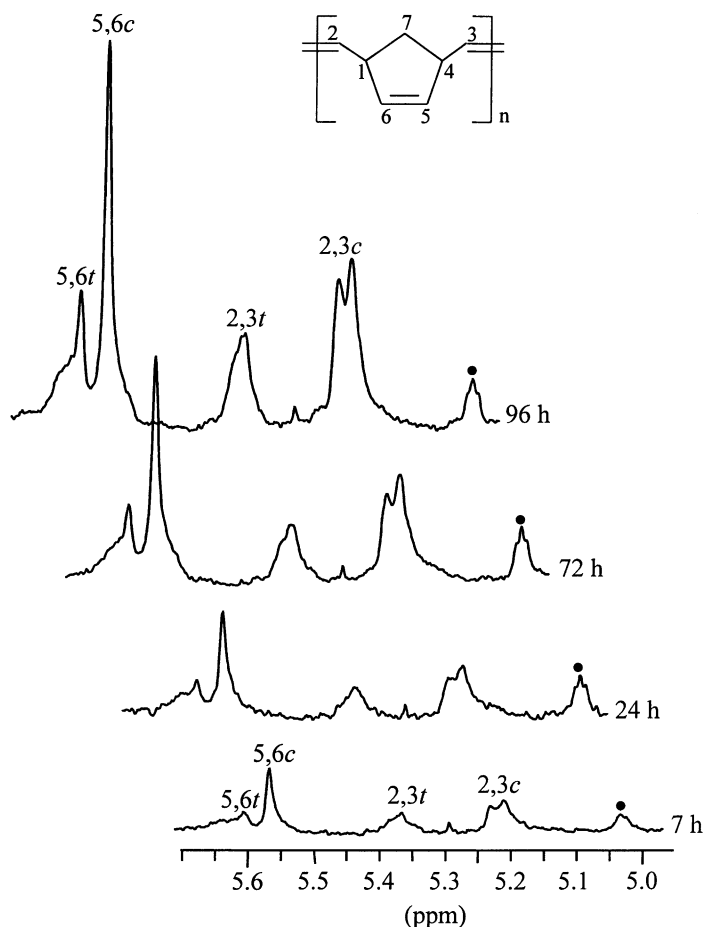


Fig. 8. Time evolution of the $^1\text{H-NMR}$ spectra (300 MHz, CDCl_3) during the reaction of $[\text{WCl}(\text{SnCl}_3)(\text{CO})_3(\text{NCMe})_2]$ with NBD. The signal at $\delta_{\text{H}} 5.04$ marked with (●) is due to $[\text{WCl}(\text{SnCl}_3)(\text{CO})_3(\eta^4\text{-NBD})]$.

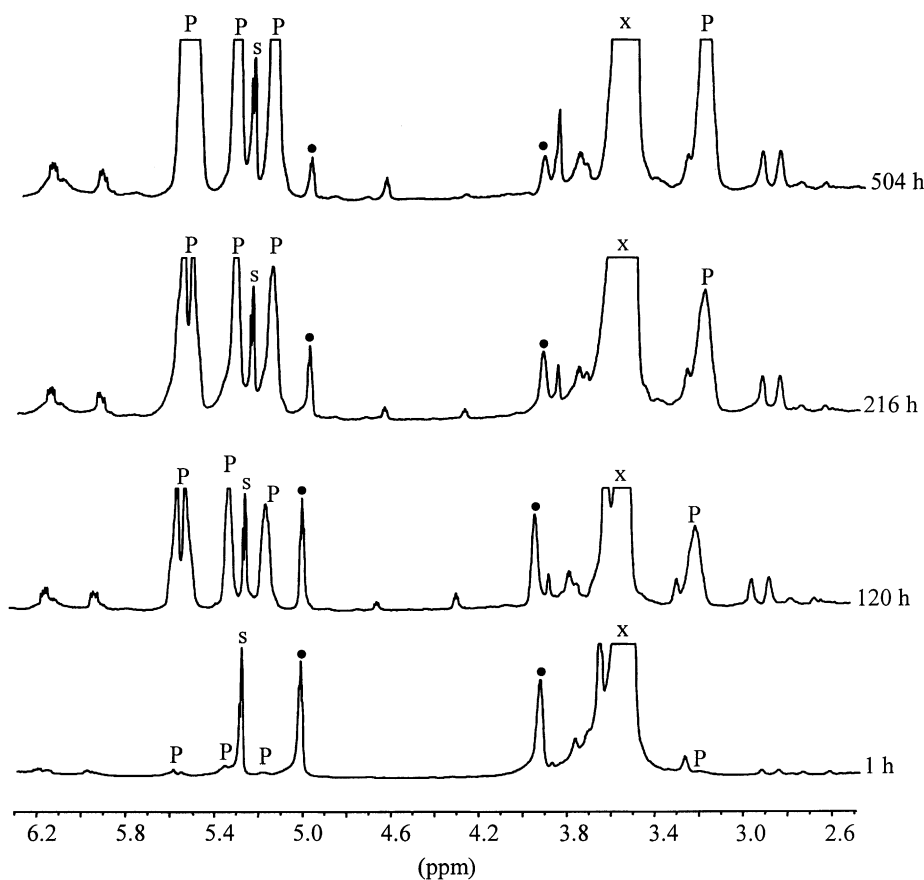


Fig. 9. Time evolution of the ^1H -NMR spectra (300 MHz, $\text{CDCl}_3/\text{CD}_2\text{Cl}_2$) during the reaction of $[\text{WCl}(\text{SnCl}_3)(\text{CO})_3(\eta^4\text{-NBD})]$ with NBD. Signals denoted by (•) are due to $[\text{WCl}(\text{SnCl}_3)(\text{CO})_3(\eta^4\text{-NBD})]$ and those denoted by 's' are due to the solvent. The signal marked (x) is derived from NBD and that denoted by 'P' from poly-NBD.

characteristic olefinic proton signal of coordinated NBD at δ_{H} 5.04 ppm [5] (Fig. 8). During the reaction, the olefinic proton signal of the coordinated NBD increases in intensity, but simultaneously olefinic proton signals above 5 ppm, characteristic for poly-NBD appearance and growth. After a prolonged reaction time the signal due to the NBD ligand decays but the intensity of signals due to poly-NBD increases.

In a reaction between the previously isolated $[\text{WCl}(\text{SnCl}_3)(\text{CO})_3(\eta^4\text{-NBD})]$ [5] complex and an excess of NBD monitored by ^1H -NMR spectra, the ROMP of NBD starts immediately after the reagents are mixed (Fig. 9). However, only a small part of the NBD complex rearranges to species initiating the polymerization reaction. Signals due to the protons

of the NBD ligand (denoted by black points in the spectrum) still remain in the spectrum, even after prolonged reaction time.

Based on the large amount of catalyst remaining, it is clear that the rate of propagation is much faster than the rate of initiation and very little of the catalyst precursor reacts. For that reason the resulting polymer possesses both a high molecular weight and a broad molecular weight distribution. Only systems in which the rate of polymer chain initiation is faster than chain propagation afford polymers with narrow polydispersities [18].

Polymerization reactions which proceed in the absence of termination step and chain transfer reactions are considered living [18]. ROMP of NBD initiated

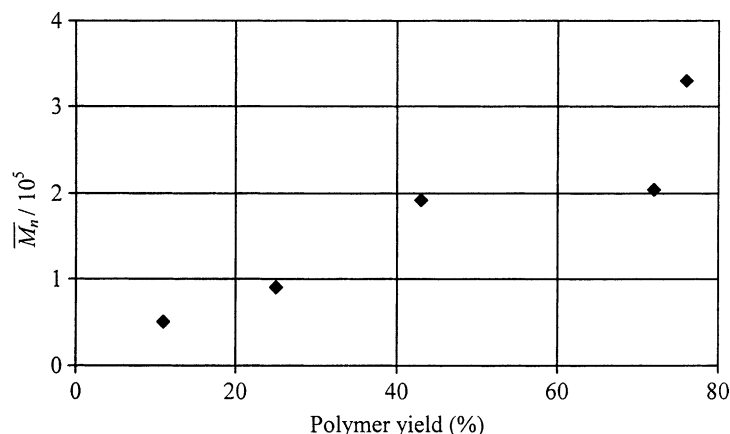


Fig. 10. Plot of number average molecular weight (\bar{M}_n) vs. polymerization yield during 5 h reaction of NBE initiated by $[\text{WCl}(\text{SnCl}_3)(\text{CO})_3(\text{NCMe})_2]$ at 348 K in PhCl.

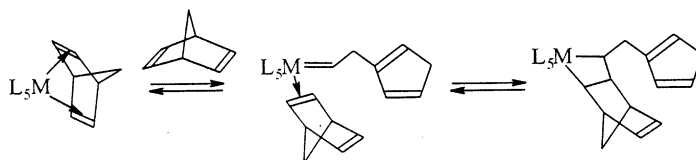
by tungsten(II) compound revealed a linear relationship between poly-NBE molecular weight and polymer yield what can demonstrate the presence of long-lived species or the living nature of the polymerization (Fig. 10). In all catalytic system applied, the reaction proceeds after further addition of monomer what can also suggest the living polymerization.

If the polymerization reaction is carried out in the NMR tube, it is also possible to detect end groups by ^1H - and ^{13}C -NMR spectroscopy when the polymers are of a sufficiently low molecular weight and to observe defect structures or other products resulting from secondary or concurrent reactions.

In Fig. 9, we can see that the decay of signals due to NBD coordinated to tungsten is accompanied by an increase in the signals due to poly-NBD. The simultaneously increasing signals at δ_{H} 6.22, 6.12, 5.95, 2.96, and 2.86 could be assigned to protons of a cyclopentadienyl moiety formed after the rearrangement of the NBD ligand (Scheme 1).

The very slowly increasing signal at δ_{H} 3.87 is most probably due to the olefinic proton of poly-NBD

coordinated to tungsten. This can mean that the last formed double bond (after metallacyclobutane splitting) does not leave the coordination sphere of the metal. In the ^1H - ^{13}C -NMR correlation spectrum (heteronuclear single-quantum correlation; HSQC), this signal correlates with the olefinic carbon signal at δ_{C} 65.24. Several other carbon signals that could be assigned to this species due to comparable intensity were detected at a higher field region of the spectrum (δ_{C} 36.95 (CH), 31.33, 29.97 (CH₂), 17.59, 13.53 and 10.95) (Fig. 11). It must be noted that the olefinic proton and the olefinic carbon signals of the cyclopentene ligand coordinated to tungsten in the *trans*- $[\text{W}(\text{CO})_4(\eta^2\text{-cyclopentene})_2]$ complex were observed in a similar region (δ_{H} 3.53, δ_{C} 62.20) [19]. On the other hand, we could not rule out the possibility that these new signals were due to a tungstacyclobutane moiety. Metallacyclobutane formation was observed in many reactions of alkylidene complexes with alkenes [20–25]; however, the positions of proton and carbon signals of this species differ very much from one system to another.



Scheme 1.

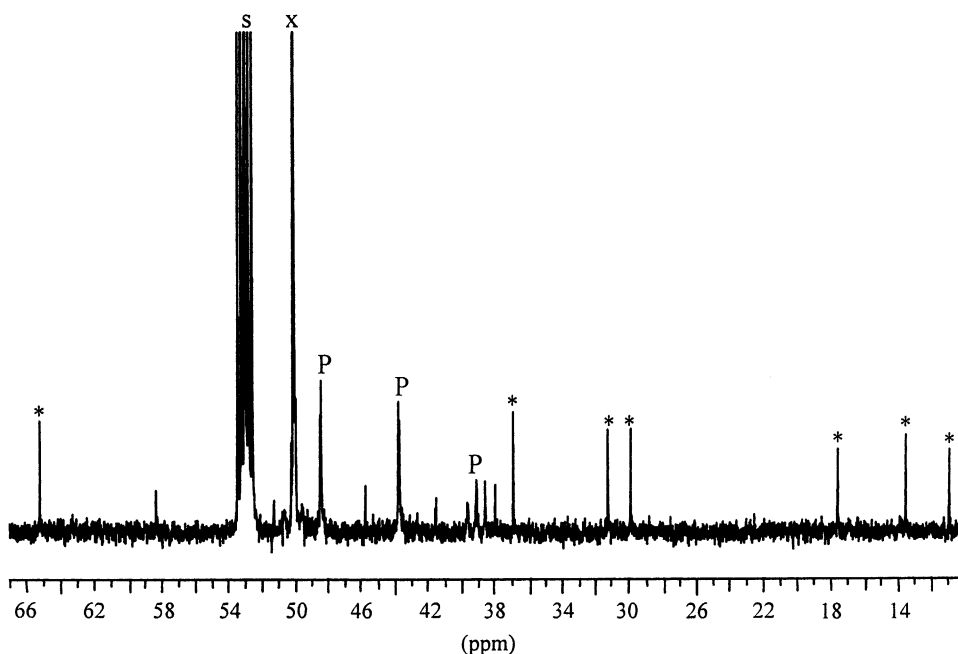


Fig. 11. Part of ^{13}C - ^1H -NMR spectrum (125 MHz, $\text{CDCl}_3/\text{CD}_2\text{Cl}_2$) showing the products formed during the reaction of $[\text{WCl}(\text{SnCl}_3)(\text{CO})_3(\eta^4\text{-NBD})]$ and NBD (\times) in the NMR tube at 293 K. Signals marked with an asterisk (*) are due to poly-NBD coordinated to the tungsten atom and the one marked with 's' is due to the solvent.

The ROMP of NBE catalyzed by seven-coordinate compounds is faster, so the NMR spectra observed during the reaction of NBE are not so clear as with NBD. In the ^1H -NMR spectra of the reaction mixture containing the $[(\text{CO})_4\text{Mo}(\mu\text{-Cl})_3\text{Mo}(\text{SnCl}_3)(\text{CO})_3]$ compound and NBE, beside proton signals due to poly-NBE, several other signals appear in the olefinic proton region (Fig. 12). The signal at δ_{H} 5.44 can be assigned to protons of very weakly coordinated NBE. This signal appears at the beginning of the reaction and disappears simultaneously with poly-NBE formation. The broad signal at δ_{H} 5.60, which appears at the beginning of the reaction, grows a little and remains almost constant after a prolonged reaction time, could be assigned to the olefinic protons of the cyclopentenyl fragment formed as a result of the rearrangement of coordinated NBE to an alkylidene ligand (Scheme 2). It must be noted that the new portions of NBE added during the NMR tube reaction polymerize to the end (Fig. 12).

The ROMP of NBE is also initiated by the $[\text{WCl}(\text{SnCl}_3)(\text{CO})_3(\eta^4\text{-NBD})]$ complex. In a reaction

of the latter complex with NBE, the decay of signals due to NBD coordinated to tungsten is accompanied by an increase in intensity signals due to poly-NBE (Fig. 13). The simultaneously increasing signals at δ_{H} 3.85 can be assigned to the olefinic proton of poly-NBE coordinated to the tungsten atom or a tungstacyclobutane moiety. Other proton signals that could be assigned to the same species due to comparable intensity were detected at δ_{H} 2.37, 2.29, 1.73, 1.25, 1.20, 1.19, 1.15 and 1.10 (Fig. 13). In the ^1H - ^{13}C -NMR correlation spectrum (HSQC) a signal at δ_{H} 3.85 correlates with an olefinic carbon signal at δ_{C} 62.35 (Fig. 14). Other carbon signals assigned to this species were detected at δ_{C} (CH), 43.47 (CH₂), 36.45 (CH), 34.91, 27.97 and 26.58 (CH₂) (Fig. 14).

In no case, however, was an alkylidene propagating species observed by NMR during the polymerization process. This may result from a very low concentration of the alkylidene ligand generated or from very fast reaction of this species with monomer.

The following mechanism for the initiation of the ROMP of NBD and NBE appears consistent with the

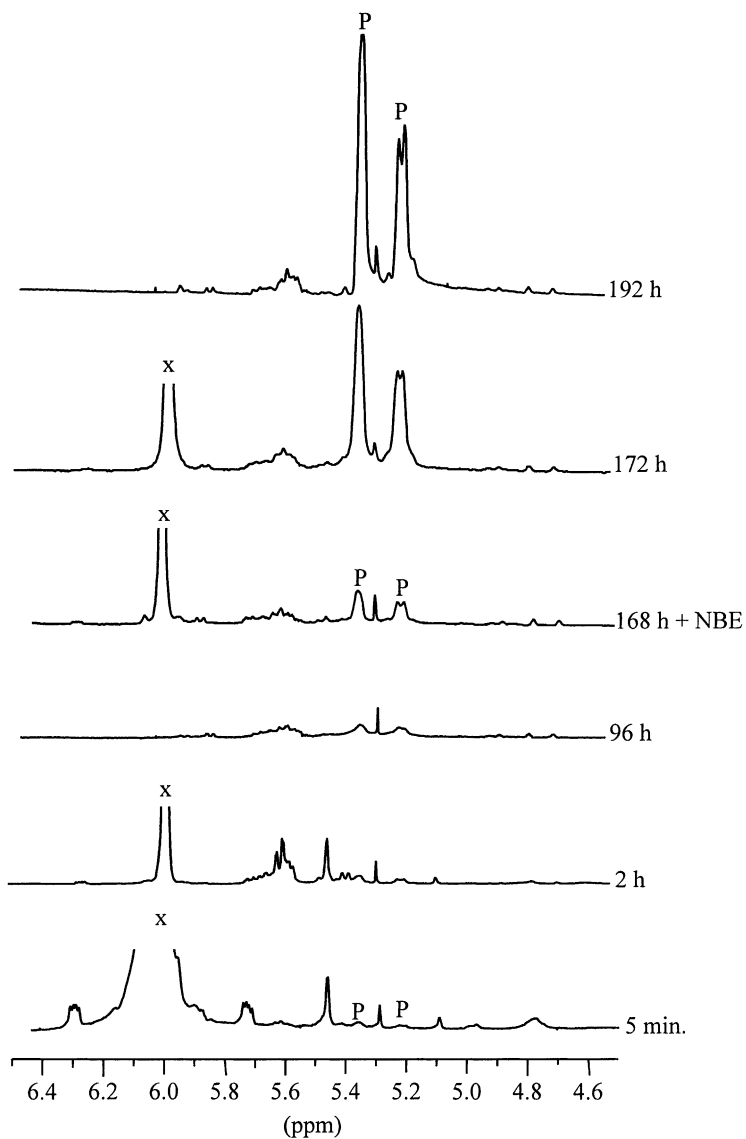
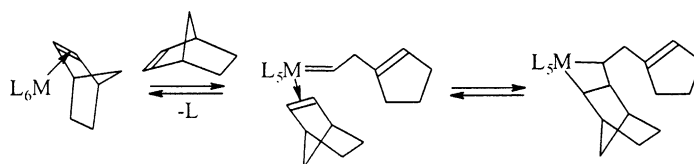


Fig. 12. Time evolution of the $^1\text{H-NMR}$ spectra (300 MHz, CDCl_3) during the reaction of $[(\text{CO})_4\text{Mo}(\mu\text{-Cl})_3\text{Mo}(\text{SnCl}_3)(\text{CO})_3]$ with NBE. After the decay of NBE (signal marked with 'x') new portions of the reagent were added.



Scheme 2.

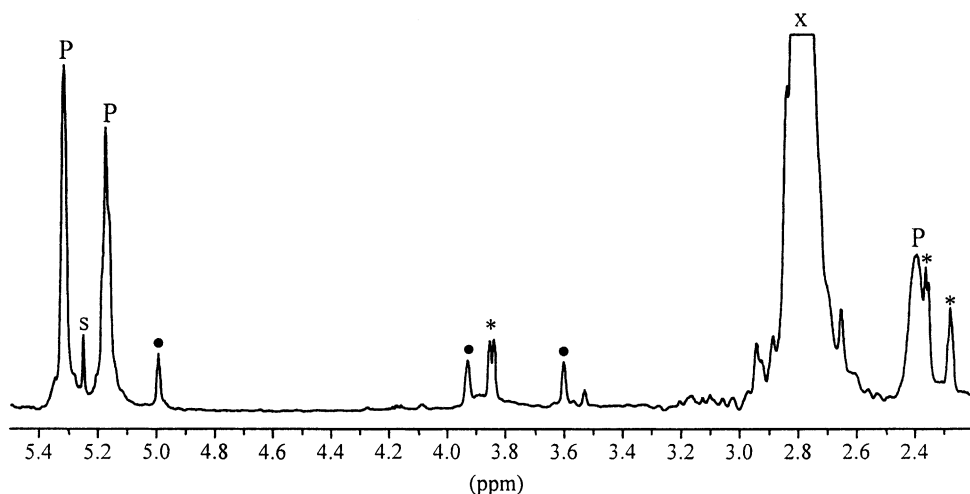


Fig. 13. Part of $^1\text{H-NMR}$ spectrum (500 MHz, $\text{CDCl}_3/\text{CD}_2\text{Cl}_2$) obtained during the reaction of $[\text{WCl}(\text{SnCl}_3)(\text{CO})_3(\eta^4\text{-NBD})]$ with NBE (\times). Signals denoted by (\bullet) are due to $[\text{WCl}(\text{SnCl}_3)(\text{CO})_3(\eta^4\text{-NBD})]$ and those marked with ($*$) are attributable to poly-NBE coordinated to tungsten. The signal denoted by 's' is due to the solvent.

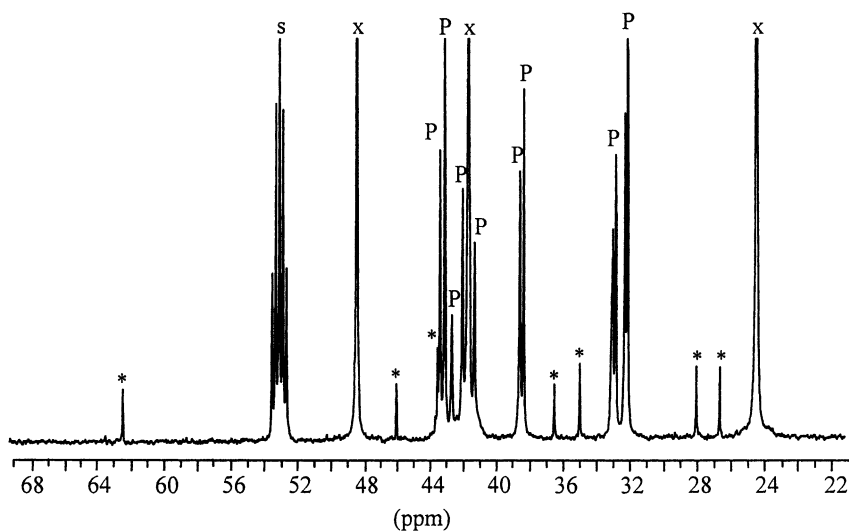


Fig. 14. Part of $^1\text{H-}^{13}\text{C-NMR}$ spectrum (125 MHz, $\text{CDCl}_3/\text{CD}_2\text{Cl}_2$) showing the products formed during the reaction of $[\text{WCl}(\text{SnCl}_3)(\text{CO})_3(\eta^4\text{-NBD})]$ and NBE (\times) in the NMR tube at 293 K. Signals marked as follows: (\times) NBE; (P) poly-NBE; ($*$) poly-NBE coordinated to tungsten; (s) solvent.

data available so far. Initially, monomer is activated through coordination to the metal atom. The ring opening, 1,2-hydrogen shift and alkylidene ligand formation occur in the presence of an excess of cyclic olefin (Scheme 1). Such a transformation may result from

the different type of coordination of two olefinic bonds to the metal center, as was shown by X-ray investigations of Mo and W complexes containing an NBD ligand [4,5]. In the presence of an excess of NBD, one of the weaker coordinating alkene bonds can be

substituted by the other olefin molecule leading to the formation of an alkylidene ligand and subsequently a metallacyclobutane unit.

4. Concluding remarks

The investigations presented here have shown that seven-coordinate bimetallic compounds are active uni-component catalysts in the ROMP of cyclic olefins.

The intermediates cyclic olefin complexes involved in the ROMP of NBE and NBD were identified by NMR when the seven-coordinate compounds were used as catalysts. The successive formation of these species was followed directly in the NMR tube.

In a reaction between tungsten(II) or molybdenum(II) complexes containing an NBD ligand and an excess of NBD monitored by $^1\text{H-NMR}$ new proton signals were detected which were assigned to the products of the rearrangement of coordinated NBD to an alkylidene ligand.

Future studies will be aimed towards the application of versatile seven-coordinate complexes as the polymerization catalysts for other monomers. The present results suggest these compounds have considerable potential.

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