Ring-opening metathesis polymerization of 5,6-bis(chloromethyl)–norbornene by tungsten(II) and molybdenum(II) complexes

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The reaction of endo,endo-5,6-bis(chloromethyl)bicyclo[2.2.1]hept-2-ene in the presence of seven-coordinate tungsten(II) and molybdenum(II) complexes of the type $[MCl(M'Cl_3)(CO)_3(NCMe)_2]$ ($M' = W$, Mo; $M = Sn$, Ge) leads to ring-opening metathesis polymerization and to the formation of high-molecular-weight soluble polymers with dispersity index in the range 1.4–2.0 and number average molecular weights in the range 300 000–790 000 g mol^{-1}. The geometric structure of these polymers was determined by means of ^{1}H- and ^{13}C-NMR spectroscopy. Molybdenum catalysts gave polymers with lower *cis* vinylene content (20–50%), whereas tungsten catalysts gave polymers with higher *cis* vinylene content (84–95%).

KEY WORDS: metathesis polymerization of norbornene; tungsten(II) catalyst; molybdenum(II) catalyst; polymer structure.

1. Introduction

A large number of 5,6-disubstituted norbornene and norbornadiene derivatives have been polymerized by ring-opening metathesis polymerization (ROMP) [1]. One set of substrates that has received relatively little attention, however, is the halogenated norbornenes; the ROMP of dichloro [2], dichloromethyl [3,4] and difluoromethyl [5] substituted are a few examples. For ROMP of these halogenated monomers, catalysts based on Ru, Os or Ir [2] and $TiCl_4$, $MoCl_5$, WCl_6 and $ReCl_5$ [3–5] were used. Our goal was to obtain more information about the possibility of initiating ROMP reaction of 5,6-substituted norbornene by tungsten(II) and molybdenum(II) compounds.

Over the past several years there has been considerable effort to explore the catalytic activity of seven-coordinate molybdenum(II) and tungsten(II) complexes [6–10]. In particular the $[MCl(M'Cl_3)(CO)_3(NCMe)_2]$ and $[(CO)_4M(\mu\text{-}Cl)_3M(M'Cl_3)(CO)_3]$ ($M = W$, Mo; $M' = Sn$, Ge) family of complexes has received much attention [7–10]. 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 ROMP of cyclic olefins such as norbornene and norbornadiene [10]. The tungsten(II) and molybdenum(II) compounds appeared to be efficient catalysts for the ROMP reaction.

In this communication, we report the preliminary observation that compounds of the type $[MCl(M'Cl_3)(CO)_3(NCMe)_2]$ ($M = W$, Mo; $M' = Sn$, Ge) can serve as a catalyst for ROMP of endo,endo-5,6-bis(chloromethyl)-bicyclo[2.2.1]hept-2-ene ($(CH_2Cl)_2$-NBE).

2. Experimental

2.1. General data

The synthesis and manipulation of all chemicals was carried out under nitrogen using standard Schlenk techniques or in a glove box (Braun). Dichloromethane was dried with CaH_2 and chlorobenzene (PhCl) with P_2O_5. NMR spectra were run using Varian Mercury-400 and Inova-500 spectrometers (^{1}H at 400 and 500 MHz and ^{13}C at 101 and 126 MHz). Molecular weights of the polymers (poly-$(CH_2Cl)_2$-NBE) were measured for solutions in $CHCl_3$ using a Waters 590 HPLC pump, a Waters R401 refractive index detector, and three PLgel columns with pore size of 10^2, 10^3 and 10^5 Å. The values recorded are the molecular weights of polystyrene that would exhibit the chromatograms observed.

2.2. Synthesis

The compounds $[MCl(M'Cl_3)(CO)_3(NCMe)_2]$ ($M = Mo$, W; $M' = Sn$, Ge) were prepared by reacting $[M(CO)_4(NCMe)_2]$ ($M = Mo$ or W) with $SnCl_4$ or $GeCl_4$ in a solution of CH_2Cl_2 using previously described procedures [8,11,12].

Endo,endo-5,6-bis(chloromethyl)bicyclo[2.2.1]hept-2-ene ($(CH_2Cl)_2$-NBE) was obtained from the Diels–Alder reaction of cyclopentadiene with 1,4-dichlorobut-2-ene according to the method described by Bow [13] and modified by Shahada and Feast [4].

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Table 1
Results of ROMP of $(CH_2Cl)_2$-NBE by tungsten(II) and molybdenum(II) complexes[a]

Complex	T (K)	Solvent	Time (h)	Yield (%)	M_n 10^{-5}	M_w 10^{-5}	M_w/M_n	*cis* vinylene (%)	
								^{1}H NMR[b]	^{13}C NMR[c]
$[MoCl(SnCl_3)(CO)_3(NCMe)_2]$	298	CH_2Cl_2	25	9	7.9	15.7	2.0	50	49
	313	CH_2Cl_2	5	4	–	–	–	41	42
	298	PhCl	96	1	–	–	–	–	–
	348	PhCl	5	5	6.9	9.8	1.4	20	19
$[WCl(GeCl_3)(CO)_3(NCMe)_2]$	298	CH_2Cl_2	96	<1	–	–	–	–	–
	348	PhCl	5	7	3.0	4.9	1.7	95	90
$[WCl(SnCl_3)(CO)_3(NCEt)_2]$	298	CH_2Cl_2	96	8	4.7	7.9	1.7	84	87
$[WCl(SnCl_3)(CO)_3(NCMe)_2]$	348	PhCl	5	5	4.7	7.3	1.5	94	91

[a] Catalyst to $(CH_2Cl)_2$-NBE molar ratio 1/100.
[b] Integral of signals at $\delta_H = 3.10$ (*cis*) and $\delta_H = 2.80$ (*trans*).
[c] Integral of resonances due to $C^{1,4}$.

2.3. Polymerization procedure

In a typical experiment the reaction mixture composed of solvent ($5\,cm^3$), $(CH_2Cl)_2$-NBE ($5\,mol\,dm^{-3}$) and a metal complex ($0.05\,mol\,dm^{-3}$) was stirred in a $50\,cm^3$ glass reactor under nitrogen in a glove box at ambient temperature. For reactions carried out at 348 K the reaction mixture was placed under nitrogen in a flask equipped with a condenser and heated using a silicone oil-heating bath. Chlorobenzene was the usual solvent for reactions carried out at 348 K. Room-temperature reactions were conducted in CH_2Cl_2.

The reaction was terminated by the addition of a large excess of methanol ($50\,cm^3$). The polymer was filtered off, dried and reprecipitated from $CHCl_3-CH_3OH$. Polymerization yield (%) was defined by comparing the weight of the polymer with the weight of the cyclic olefin used.

The polymer was analyzed by gel-permeation chromatography in $CHCl_3$ and NMR spectroscopy (^{1}H, $^{13}C\{^1H\}$, DEPT and COSY) in $CDCl_3$.

3. Results and discussion

3.1. Catalytic conversion of $(CH_2Cl)_2$-NBE

The compounds $[MCl(M'Cl_3)(CO)_3(NCMe)_2]$ (M = Mo, W; M′ = Sn, Ge) initiate the ROMP of $(CH_2Cl)_2$-NBE at room temperature, but the reaction is very slow (table 1). However, it has previously been shown that NBE polymerizes selectively to ROMP polymer, *i.e.* poly(1,3-cyclopentylene)vinylene [10]. The temperature of 348 K was chosen as convenient for investigations. At this temperature the conversion of $(CH_2Cl)_2$-NBE is in the range 4–7% after a 5 h reaction initiated by $[MCl(M'Cl_3)(CO)_3(NCMe)_2]$ complexes.

Poly-$(CH_2Cl)_2$-NBEs have high molecular weights, but their polydispersities (PD) are higher than 1 ($1.4 < PD < 2.0$), as is typical for initiators which transform to catalytically active alkylidene species during the induction period.

3.2. Geometric structure of polymers

Typical ^{1}H-NMR spectra of the polymers obtained using molybdenum(II) and tungsten(II) catalysts are shown in figures 1 and 2, respectively. These spectra have shown a generally similar pattern of proton signals but differ in intensity. According to Ivin *et al.* [14–16] and as confirmed by $^1H-^1H$ and $^1H-^{13}C$ correlation spectra, these signals can be assigned (scheme 1) as follows: 5.48 ($HC^{2,3}$), 3.66, 3.63, 3.59, 3.57 ($H_2C^{8,9}$), 3.10, 2.80 ($HC^{1,4}$), 2.56, 2.20 ($HC^{5,6}$), 2.06, 1.56 (H_2C^7). The relative proportion of *cis* and *trans* vinylene units in the polymers can be obtained by integration of resonances due to protons on the bridgehead methine carbons ($HC^{1,4}$) at $\delta_H = 3.10$ (*cis*) and $\delta_H = 2.80$ (*trans*) (table 1). The fraction of *cis* double bonds estimated from the ^{1}H-NMR spectra is in good agreement with that obtained by analysis of ^{13}C-NMR spectra. Typical $^{13}C\{^1H\}$-NMR spectra of the polymers obtained using molybdenum(II) and tungsten(II) catalysts are shown in figures 3 and 4, respectively. The assignment of signals was possible by the application of DEPT and heteronuclear correlation experiments, and is as follows: 132.31, 132.03, 131.94, 131.56, 131.11 ($C^{2,3}$), 49.07, 48.87, 48.80 ($C^{5,6}$), 44.06, 43.83, 39.11, 38.87, 38.69 ($C^{1,4}$), 42.69, 42.55 ($C^{8,9}$), 40.14, 39.80, 39.58, 39.38, 36.81 (C^7). The relative proportion of *cis* and *trans* vinylene units in the polymers can be obtained by integration of resonances due to bridgehead carbons ($C^{1,4}$) at δ_C about 44 ppm (*trans*) and 39 ppm (*cis*) (table 1).

^{1}H and $^{13}C\{^1H\}$-NMR spectroscopic data for poly-$(CH_2Cl)_2$-NBEs obtained in the presence of W and Mo catalysts are consistent with data previously reported for polymers of NBE [10,14–16], where four methine

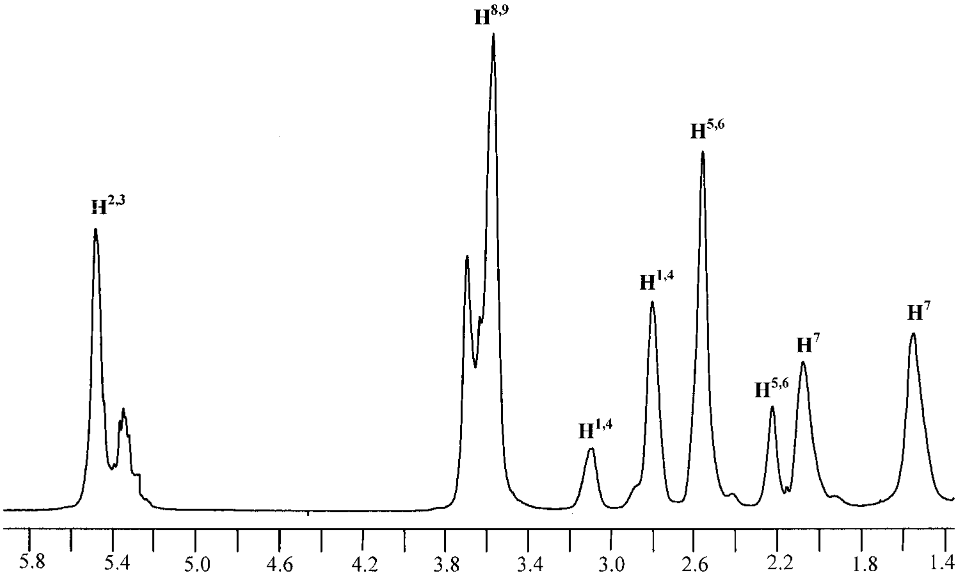


Figure 1. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of poly-$(CH_2Cl)_2$-NBE formed during the ROMP reaction of $(CH_2Cl)_2$-NBE initiating by $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$ at 348 K. Signals are denoted as in scheme 1.

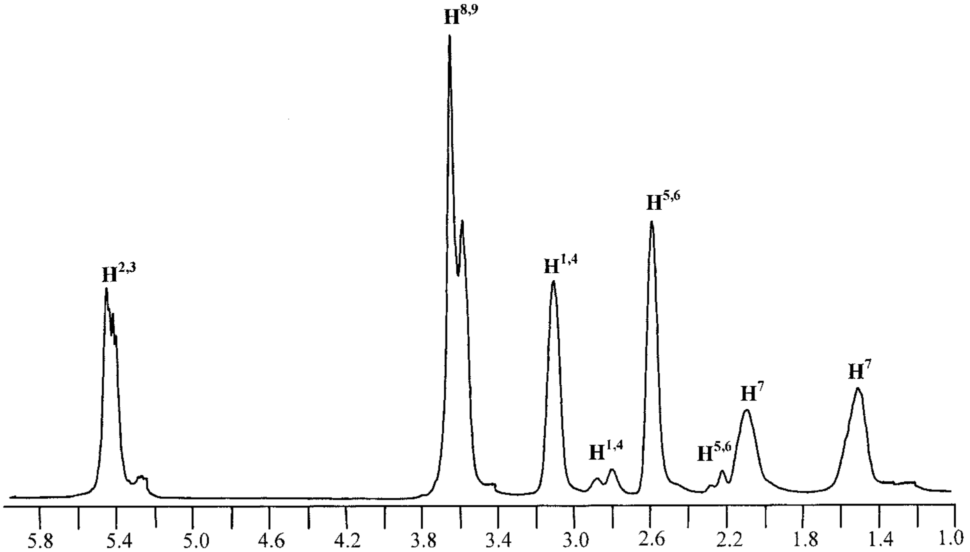
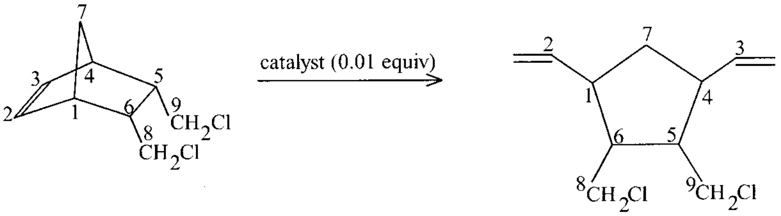


Figure 2. Representative ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of poly-$(CH_2Cl)_2$-NBE obtained in the presence of $[WCl(SnCl_3)(CO)_3(NCEt)_2]$ in PhCl at 293 K after 5 h. Signals are denoted as in scheme 1.



Scheme 1. General reaction showing the carbon atoms—numbering scheme.

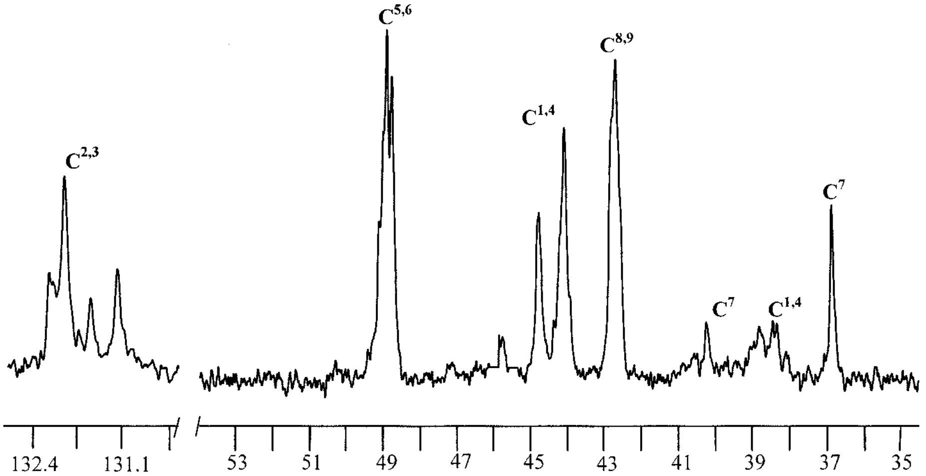


Figure 3. Representative $^{13}C\{^{1}H\}$-NMR spectrum (126 MHz, $CDCl_3$) of poly-$(CH_2Cl)_2$-NBE produced after 5 h in PhCl at 348 K with $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$ as catalyst. Signals are denoted as in scheme 1.

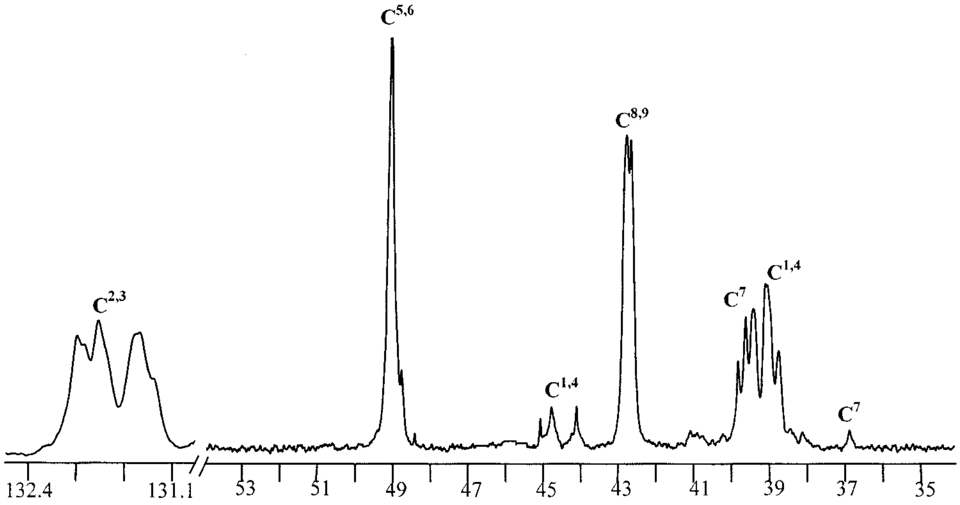


Figure 4. $^{13}C\{^{1}H\}$-NMR spectrum (126 MHz, $CDCl_3$) of poly-$(CH_2Cl)_2$-NBE formed during the reaction of $[WCl(SnCl_3)(CO)_3(NCEt)]$ and $(CH_2Cl)_2$-NBE at 293 K. Signals are denoted as in scheme 1.

carbon ($C^{1,4}$) signals of poly-NBE were observed at δ_C 43.40 (*trans–cis*), 43.12 (*trans–trans*), 38.62 (*cis–cis*), and 38.39 (*cis–trans*) and a signal for the proton on methine carbon ($C^{1,4}$) was observed at $\delta_H = 2.77$ (*cis*-poly-NBE) and at $\delta_H = 2.41$ (*trans*-poly-NBE) [10]. In both cases in the current work the $^{13}C\{^{1}H\}$-NMR spectra were complex, indicating that these polymers are essentially atactic.

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 prepared using molybdenum complexes as the initiator varied from about 20 to 50%, while with tungsten catalysts it varied from about 84 to 95% (table 1).

It should be noted that the initiating carbene species in the ROMP reaction must be formed by the rearrangement of an activated species through coordination of the mononer to the metal center.

In summary, the investigations presented here have shown for the first time that tungsten(II) and molybdenum(II) compounds are active unicomponent catalysts in the ring-opening metathesis polymerization of the halogenated norbornenes.

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