

The initiation of ring-opening metathesis polymerisation of norbornadiene by seven-coordinate molybdenum(II) compounds. X-ray crystal structure of $[\text{Mo}(\mu\text{-Cl})(\text{SnCl}_3)(\text{CO})_3(\eta^4\text{-NBD})]^\star$

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Abstract

The new heterobimetallic complex $[\text{Mo}(\mu\text{-Cl})(\text{SnCl}_3)(\text{CO})_3(\eta^4\text{-NBD})]$ (**1**) has been prepared by reaction of $[(\text{CO})_4\text{Mo}(\mu\text{-Cl})_3\text{Mo}(\text{SnCl}_3)(\text{CO})_3]$ with norbornadiene (NBD) at room temperature. The structure of complex **1** was established by X-ray crystallography. The IR, ^1H - and ^{13}C -NMR spectra of **1** are also described and can be correlated with the crystallographically observed geometry. In the presence of an excess of NBD compound **1** initiates the ring-opening metathesis polymerisation (ROMP). The initiation mechanism of ROMP by seven-coordinate molybdenum(II) compounds have been discussed. The microstructure of polynorbornadiene formed was determined by ^1H - and ^{13}C -NMR spectroscopy. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Molybdenum; Tin; Crystal structures; Metathesis; Polymerisation; Norbornadiene

1. Introduction

Over the past two decades, the study of seven-coordinate molybdenum(II) and tungsten(II) complexes has greatly expanded [2–4]. These complexes are generally highly reactive, and many have been applied as catalysts [5–14]. 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 recently has received much attention [12,13,15–20]. These complexes readily react with alkynes in mild conditions to give CO or nitrile substitution products. In the presence of an excess of terminal alkyne such compounds are catalysts for the polymerisation reaction.

Olefin binding to the metal centre has often been suggested and transition metal–alkene complexes have been proposed as key intermediates in several catalytic

reactions; however, only a few examples of molybdenum(II) and tungsten(II) cyclic diene complexes have been reported [15,21–26].

The first tungsten(II) cyclic diene, e.g. norbornadiene (NBD), compound was prepared by Davidson and Vasapollo [21] via reaction of the tungsten(II) complex $[\text{WBr}_2(\text{CO})_4]_2$ with NBD. Next, by means of an X-ray crystallographic study, the compound was shown to be $[\text{WBr}_2(\text{CO})_2(\text{NBD})]$ [22]. Recently it was observed that the heterobimetallic complex $[\text{WCl}(\text{SnCl}_3)(\text{CO})_3(\text{NCMe})_2]$ reacts with NBD at room temperature, liberating two acetonitrile ligands to form the seven-coordinate complex $[\text{WCl}(\text{SnCl}_3)(\text{CO})_3(\eta^4\text{-NBD})]$ [15]. We now wish to report a new synthesis for the complex $[\text{Mo}(\mu\text{-Cl})(\text{SnCl}_3)(\text{CO})_3(\eta^4\text{-NBD})]$ (**1**) from the reaction of $[(\text{CO})_4\text{Mo}(\mu\text{-Cl})_3\text{Mo}(\text{SnCl}_3)(\text{CO})_3]$ with NBD. The unknown coordination geometry of the cyclic diene compound **1** together with the fact that compounds of this class can be used as models of catalytic centres make it an interesting problem for X-ray structural analysis.

Additionally, we were especially intrigued by the opportunity to initiate the ring-opening metathesis polymerisation (ROMP) of the cyclic olefins by the

* For a preliminary account of this research see Ref. [1].

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seven-coordinate molybdenum(II) and tungsten(II) compounds.

2. Experimental

2.1. General data

All reactions were carried out under nitrogen by standard Schlenk line techniques. The solvents and reagents applied were dried, distilled and deoxygenated. Solution IR spectra were obtained using KBr or NaCl plates while solid samples were recorded using KBr pellets in an FT-IR model-400 Nicolet instrument. Far-IR spectra were recorded (600–100 cm^{-1}) with a Brüker IFSv instrument in a Nujol mull on a polyethylene film. ^1H - and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra were recorded in a AMX 300 Brüker spectrometer. An UV–vis absorption spectra were recorded in a Hewlett Packard 8452A spectrophotometer.

2.2. Synthesis of $[\text{Mo}(\mu\text{-Cl})(\text{SnCl}_3)(\text{CO})_3(\eta^4\text{-NBD})]$ (**1**)

$[(\text{CO})_4\text{Mo}(\mu\text{-Cl})_3\text{Mo}(\text{SnCl}_3)(\text{CO})_3]$ (0.31 g, 0.43 mmol) prepared by the method described previously [20], was dissolved in toluene (20 cm^3) with continuous stirring under an inert atmosphere and solution of

NBD (0.20 g, 2.17 mmol) in toluene was added via a cannula. During the stirring (24 h), the solution became like a gel and yellow precipitates of **1** were formed. Compound **1** was separated from toluene solution containing mainly polynorbornadiene (poly-NBD), washed with toluene and pump-dried. The yellow crystals of **1** were formed during the slow crystallisation from CH_2Cl_2 –toluene–heptane solution at ca. 273 K. IR (KBr disk, cm^{-1}): $\nu(\text{CO})$ 2088(vw), 2017(vs); IR (Nujol, cm^{-1}): $\nu(\text{SnCl})$ 347, 328, 320, 279. ^1H -NMR (CD_2Cl_2 , 293 K, δ ppm): 5.27 (t, $J_{\text{HH}} = 2.4$ Hz, 2 =CH), 4.02 (t, $J_{\text{HH}} = 2.4$ Hz, 2 =CH), 3.90 (broad s, 2 CH), 1.78 and 1.77 (1 CH_2); ^{13}C -NMR (CD_2Cl_2 , 293 K, δ ppm): 211.17 (1 CO), 205.09 (2 CO), 88.88 (d, $J_{\text{CH}} = 179$ Hz, 2 =CH), 64.08 (d, $J_{\text{CH}} = 135$ Hz, 1 CH_2), 46.32 (d, $J_{\text{CH}} = 137$ Hz, 2 CH), 46.10 (d, $J_{\text{CH}} = 179$ Hz, 2 =CH); Abs. max.: λ (nm) (ϵ , $1 \text{ mol}^{-1} \text{ cm}^{-1}$) (CH_2Cl_2): 246 (19 736), 300 (12 838), 322 (10 906).

2.3. Crystal and refinement data for compound **1**

Crystal data and relevant refinement details are presented in Table 1. The yellow crystals of **1** were grown from a CH_2Cl_2 –toluene–heptane (5:1:2) solution. The crystals were stable enough when handled in an inert atmosphere or coated with a light hydrocarbon oil to protect them from the atmosphere.

Crystal data for **1** were collected on a Kuma KM4CCD κ -axis diffractometer with graphite-monochromated Mo– K_α radiation, μ (Mo– K_α) = 31.41 cm^{-1} . The data were corrected for Lorentz and polarisation effects. No absorption correction was applied. Data reduction and analysis were carried out with Kuma Diffraction (Wroclaw) programs. The structure was solved by direct methods (program SHELXS-97) [27] and refined by the full-matrix least-squares method on all F^2 data using the SHELXL-97 [28] programs to R values for **1** of $R_1 = 0.0253$, $wR_2 = 0.0514$. Non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included from the $\Delta\rho$ maps and refined with isotropic displacement parameters.

2.4. Reactions in NMR tubes

2.4.1. Reaction of $[(\text{CO})_4\text{Mo}(\mu\text{-Cl})_3\text{Mo}(\text{SnCl}_3)(\text{CO})_3]$ with NBD in CDCl_3

To the NMR tube containing the solution of $[(\text{CO})_4\text{Mo}(\mu\text{-Cl})_3\text{Mo}(\text{SnCl}_3)(\text{CO})_3]$ (0.1 g, 0.14 mmol) in CDCl_3 (0.5 cm^3) two equivalents of NBD (0.03 g, 0.28 mmol) in 0.2 cm^3 of CDCl_3 were added by means of a syringe and a sample was periodically analysed by ^1H -NMR spectroscopy at room temperature (r.t.) during few days.

Table 1

Crystal data and structure refinement parameters for $[\text{Mo}(\mu\text{-Cl})(\text{SnCl}_3)(\text{CO})_3(\eta^4\text{-NBD})]$ (**1**)

Empirical formula	$\text{C}_{10}\text{H}_8\text{Cl}_4\text{MoO}_3\text{Sn}$
Formula weight	532.59
Temperature (K)	100
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	6.852(2)
b (Å)	13.814(3)
c (Å)	16.393(3)
β (°)	98.87(3)
V (Å ³)	1533.1(5)
Z	4
Crystal size (mm)	$0.07 \times 0.07 \times 0.20$
D_{calc} (g cm^{-3})	2.307
λ (Mo– K_α) (Å)	0.71073
μ (Mo– K_α) (cm^{-1})	31.41
$F(000)$	1008
Method of collection	ω - 2θ scan
2θ Range	$6.81 < 2\theta < 57.4$
Index ranges	$-4 \leq h \leq 9$, $-18 \leq k \leq 18$, $-22 \leq l \leq 22$
Number of unique data	3707
Number of data with $[I \leq 2\sigma(I)]$	2938/204
Residuals R_1 , wR_2	0.0253, 0.0514
Goodness-of-fit	1.011
Final ($\Delta\rho$) (e Å^{-3})	1.075 and -0.679

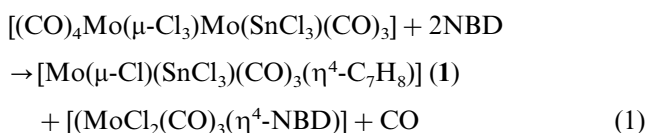
2.4.2. Reaction of compound **1** with NBD in CD_2Cl_2

To the NMR tube containing the solution of compound **1** (0.1 g, 0.19 mmol) in CD_2Cl_2 (0.5 cm^3) five equivalents of NBD (0.09 g, 0.9 mmol) in 0.2 cm^3 of CD_2Cl_2 was added by means of a syringe and a sample was periodically analysed by 1H -NMR spectroscopy at r.t. Complete transformation of NBD occurred within few days.

3. Results and discussion

3.1. Synthesis and spectroscopic characterisation of **1**

In the reaction with NBD halide bridge splitting in the binuclear compound of tungsten(II) by diene molecule occurs very easily and mononuclear compounds are formed [21,22]. Similar reaction takes place when the binuclear molybdenum(II) compound containing Mo–Sn bond interacts with NBD (Eq. (1)).



However, from the mixture of mononuclear compounds only **1** was separated and obtained in crystalline form. The seven-coordinate dichloride compounds are very unstable and can dimerise with a loss of one CO ligand to give the chloride-bridged polynuclear compounds [25,26]. The parallel formation of $[MoCl_2(CO)_3(\eta^4-NBD)]$ with **1**, was indicated by the presence of two pairs of $\nu(CO)$ bands in the IR spectrum of the reaction mixture: Bands at $2088(\text{vw})$ and $2017(\text{vs})\text{ cm}^{-1}$ are characteristic for **1** and those at 2083 and 2012 cm^{-1} are probably due to the dichloro species.

A noticeable feature of **1** are the exceptionally high $\nu(CO)$ frequencies $2088(\text{vw})$ and $2017(\text{vs})\text{ cm}^{-1}$, which is among the highest known for seven-coordinate $[MX_2(CO)_3L_2]$ type compounds. This frequency is significantly higher than that of analogous $[WBr_2(CO)_2(\eta^4-NBD)]$ at 2063 and 1992 cm^{-1} [22] and $[WI_2(CO)_2(\eta^4-NBD)]$ at 2058 and 1992 cm^{-1} [26]. This indicates that smaller electron density is being back donated into empty π^* -orbitals of the CO ligands in **1** and implies that $SnCl_3^-$ is capable of acting as a more effective π -acceptor than I or Br ligand and as a result there is smaller Mo \rightarrow CO back donation. The lower frequency region of the IR spectrum is dominated by $\nu(Sn-Cl)$ bands at $347, 328, 320, 279\text{ cm}^{-1}$.

The 1H -NMR spectrum of **1** shows five well-separated groups of signals. The absorption at $\delta 5.27$ is due to protons attached on the same double bond, while the peaks at $\delta 4.02$ are protons attached to the other double bond. The resonance of olefin protons is at a

higher field than that of the free NBD by 1.54 and 2.79 ppm, respectively.

The ^{13}C -NMR spectrum of **1** shows two carbonyl resonances at $\delta 211.17$ and 205.09 ppm, in an intensity ratio of 1:2. The resonance at $\delta 205.09$ ppm can be assigned to the carbonyls that are mutually *trans*. This resonance is slightly highfield shifted compared to the signal of the CO group that is approximately *trans* to the olefinic unit of NBD. Carbon signals of the coordinated NBD were correctly assigned by observing the $^{13}C-^1H$ coupling constants. One of the olefinic carbon resonances ($\delta 46.10$) shifts more upfield than other carbon signals ($\delta 88.88$) by 42.78 ppm, yet the coupling constant stays in the range characteristic of double bond carbons (179 Hz). Thus, we assign the lower field NBD signal of **1** to the carbons of the C=C unit in the *trans* position to the CO group and the signal at higher field to the carbons of the double bond *trans* to the chlorine. With regard to the origin of this effect, the coordination shift correlates with the W–C bond distance and with the degree of metal ($d\pi$) \rightarrow olefin(π^*) back-donation.

3.2. Solid state structure of **1**

The results of an X-ray investigation of compound **1** are shown in Figs. 1 and 2 and Tables 1 and 2. The molecule $[Mo(\mu-Cl)(SnCl_3)(CO)_3(\eta^4-NBD)]$ (**1**), is shown in Fig. 1 together with the atomic numbering scheme. Table 2 contains selected bond distances and bond angles. The molybdenum atom is seven-coordinate and the tin atom is five-coordinate, with one chlorine atom occupying a bridging position between the two metal atoms. The environment of the molybdenum atom in **1** is a distorted pentagonal bipyramid (Fig. 2). In the pentagonal plane are two olefinic bonds of NBD ligand, carbonyl, $SnCl_3^-$ and chloride ligands. The Mo–Sn bond of $2.752(1)\text{ \AA}$ is supported by a chlorine bridge.

The angles subtended at the molybdenum atom by the five atoms determining the pentagonal plane are in the range $60.07(11)$ – $82.71(8)^\circ$. The major distortions from regularity of the pentagonal bipyramid appear to be associated with the presence of the chelating NBD ligand. The angles between the two alkene bonds are ca. 60° while between the alkene bonds and the neighbouring ligands ca. 80° .

The two *trans* carbonyls occupy the two axial sites with C(1)–Mo–C(3) angle of $172.41(11)^\circ$ and are in almost the same distance from Mo atom at $2.071(3)$ and $2.064(3)\text{ \AA}$, but the third CO group is in a shorter distance to Mo atom at $2.032(3)\text{ \AA}$.

The most significant feature of this complex is the fact that the coordination of NBD ligand is arranged in two types. One of the olefinic bonds is approximately *trans* to CO and the other *trans* to Cl. This gives rise to

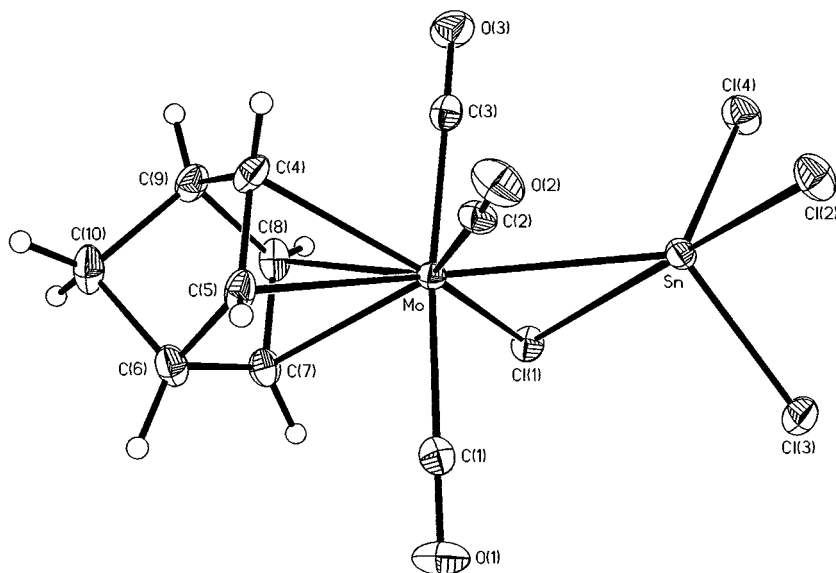


Fig. 1. Molecular structure of $[\text{Mo}(\mu\text{-Cl})(\text{SnCl}_3)(\text{CO})_3(\eta^4\text{-NBD})]$ (**1**).

a slight difference between the Mo–C distances; such that Mo–C(4) = 2.330(3) Å and Mo–C(5) = 2.335(3) Å are almost 0.1 Å shorter than Mo–C(7) = 2.431(3) Å and Mo–C(8) = 2.423(3) Å. The above bond lengths are in excellent agreement with the degree of electron back-donation from the $d\pi$ -orbitals of molybdenum to the ligands whose π acidity is taken into account. As CO is a better π acid than the olefinic bond, back-donation to CO is much preferred. For the C=C and its *trans* Cl ligand, the electron density due to back-donation is almost completely accepted by C=C, resulting in shortened Mo–C(4) and Mo–C(5) and in a lengthened C(4)–C(5) distance compared to Mo–C(7) and Mo–C(8) and C(7)–C(8) distances. The structure of **1** thus provides a good model for comparing the effect of the relative position of alkene and CO ligands on the Mo–C bond distance.

The tin atom is five-coordinate in **1** with a geometry that is best described as distorted trigonal bipyramidal with the two chlorine atoms occupying the axial sites; the Cl(2)–Sn–Cl(1) angle is 173.64(2)°. In the trigonal plane are two chlorine atoms and Mo atom. The tin to bridging chlorine distance is 2.889(1) Å, being considerably longer than the other Sn–Cl distances (av. 2.35 Å). The molybdenum to bridging chlorine distance is 2.474(1) Å and indicates that the bridging chlorine forms a stronger bond with the molybdenum while the Sn–Cl bond is weakened.

3.3. Ring-opening metathesis polymerisation of NBD initiated by **1**

The reaction between $[(\text{CO})_4\text{M}(\mu\text{-Cl})_3\text{M}(\text{SnCl}_3)(\text{CO})_3]$ and an excess of NBD was followed by $^1\text{H-NMR}$ spectroscopy which confirmed the formation of **1** (Fig.

3). At the beginning of the reaction the olefinic protons signal of the coordinated NBD at δ 5.27 increases in intensity. Simultaneously the formation of an unsaturated poly-NBD with characteristic signals of the olefinic protons at ca. 5.6 and 5.4 ppm appear and grow. After a prolonged reaction time, signals due to **1** decay and the intensity of signals due to poly-NBD very slowly increase.

In a reaction between **1** and an excess of NBD monitored by $^1\text{H-NMR}$ spectra, the ROMP of NBD starts immediately after the reagents mixing (Fig. 4). However, only a small part of compound **1** rearranges to species initiating the polymerisation reaction. Signals due to the protons of the NBD ligand in **1** (denoted in the spectrum by black points) still remain visible in the

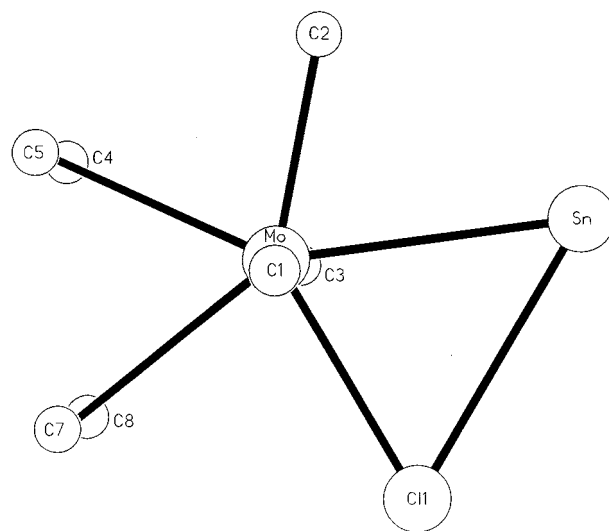


Fig. 2. Projection of the coordination sphere of Mo on the pentagonal plane illustrating the pentagonal bipyramidal geometry of **1**.

Table 2
Selected bond lengths (Å) and bond angles (°) for [Mo(μ -Cl)(SnCl₃)(CO)₃(η^4 -NBD)] (1)

Bond lengths			
Mo–Sn	2.7519(6)	Mo–Cl(1)	2.4739(8)
Mo–C(1)	2.071(3)	C(4)–C(5)	1.388(4)
Mo–C(2)	2.032(3)	C(7)–C(8)	1.362(4)
Mo–C(3)	2.064(3)	Sn–Cl(1)	2.8886(11)
Mo–C(4)	2.330(3)	Sn–Cl(2)	2.3714(10)
Mo–C(5)	2.335(3)	Sn–Cl(3)	2.3374(8)
Mo–C(7)	2.431(3)	Sn–Cl(4)	2.3482(9)
Mo–C(8)	2.423(3)		
Bond angles			
C(1)–Mo–C(2)	87.91(11)	C(5)–Mo–C(7)	60.26(11)
C(1)–Mo–C(3)	172.41(11)	C(7)–Mo–C(8)	32.60(10)
C(1)–Mo–C(4)	112.76(11)	C(5)–Mo–Cl(1)	142.31(8)
C(1)–Mo–C(5)	78.15(11)	C(8)–Mo–Cl(1)	81.97(8)
C(1)–Mo–C(7)	75.65(11)	C(7)–Mo–Cl(1)	82.71(8)
C(1)–Mo–C(8)	108.12(11)	C(2)–Mo–Sn	72.25(8)
C(1)–Mo–Cl(1)	86.60(8)	C(3)–Mo–Sn	82.25(8)
C(1)–Mo–Sn	91.84(8)	C(4)–Mo–Sn	140.66(8)
C(2)–Mo–C(3)	94.78(11)	C(5)–Mo–Sn	146.71(8)
C(2)–Mo–C(4)	78.25(11)	C(8)–Mo–Sn	141.96(8)
C(2)–Mo–C(5)	75.69(11)	C(7)–Mo–Sn	147.86(8)
C(2)–Mo–C(7)	135.09(11)	Cl(1)–Mo–Sn	66.87(3)
C(2)–Mo–C(8)	138.31(11)	Mo–Cl(1)–Sn	61.17(3)
C(2)–Mo–Cl(1)	138.51(8)	Mo–Sn–Cl(1)	51.96(2)
C(3)–Mo–C(4)	74.77(11)	Cl(3)–Sn–Mo	120.92(3)
C(3)–Mo–C(5)	109.39(11)	Cl(4)–Sn–Mo	113.25(2)
C(3)–Mo–C(8)	74.41(11)	Cl(2)–Sn–Mo	122.96(2)
C(3)–Mo–C(7)	106.99(11)	Cl(1)–Sn–Cl(2)	173.64(2)
C(3)–Mo–Cl(1)	86.69(8)	Cl(1)–Sn–Cl(3)	84.10(3)
C(4)–Mo–C(5)	34.61(11)	Cl(1)–Sn–Cl(4)	90.15(3)
C(4)–Mo–C(8)	60.07(11)	Cl(3)–Sn–Cl(2)	96.87(4)
C(4)–Mo–Cl(1)	140.83(8)	Cl(3)–Sn–Cl(4)	102.57(3)
C(4)–Mo–C(7)	70.69(11)	Cl(4)–Sn–Cl(2)	95.75(3)
C(5)–Mo–C(8)	70.71(11)		

spectrum, even after the disappearance of free NBD. In the ¹³C{¹H}-NMR spectrum of this reaction mixture not only very well-resolved signals of poly-NBD, but also carbon signals of the NBD ligand due to residual compound **1** can still be observed (Fig. 5).

On the observed ¹H- and ¹³C-NMR spectra the microstructure of the poly-NBD formed in above reactions can be analysed [29]. From the integral ratio of signal due to protons denoted 1,4 at δ 3.64 (*cis* double bond) and δ 3.24 (*trans* double bond) the value of *cis* double bond content was calculated to be ca. 30%. A similar value of *cis* double bond content was obtained from ¹³C-NMR spectra. For this purpose the well-resolved signal of carbon denoted by 1,4 and 7 was integrated (Fig. 5). This spectrum was measured after a reaction in the NMR tube, so carbon signals of the NBD ligand due to residual compound **1** can still be observed.

The most likely process for the initiation of the ROMP of NBD involves the coordination of the diene to the metal centre followed by ring-opening, 1,2-hydrogen shift and alkylidene ligand formation (Scheme

1). Such a transformation can result from the different type of coordination of NBD ligand to the metal centre. In the presence of an excess of NBD the weakly coordinating alkene bond can be substituted by NBD molecule leading to the formation of alkylidene ligand and next metallacyclobutane unit.

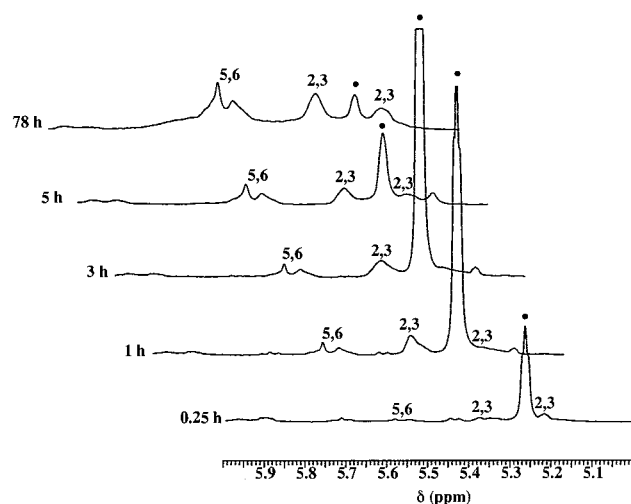


Fig. 3. The olefinic proton region of the ¹H-NMR spectra recorded at 300 MHz during the reaction of [(CO)₄Mo(μ -Cl)₃Mo(SnCl₃)(CO)₃] and NBD at 293 K in CDCl₃. The resonance at δ 5.27 denoted by (●) is due to the olefinic protons of **1**. Proton signals in the poly-NBD are labelled as follows:

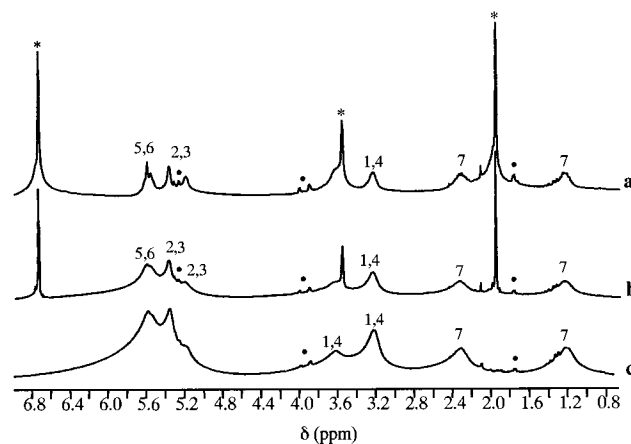
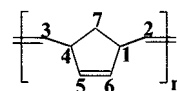
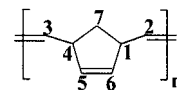


Fig. 4. ¹H-NMR spectra recorded at 300 MHz during the reaction of **1** and NBD (*) at 293 K in CD₂Cl₂; (a) after 5 h; (b) 24 h; and (c) 5 days. The resonances denoted by (●) is due to protons of the NBD ligand in **1**. Proton signals in the poly-NBD are labelled as follows:



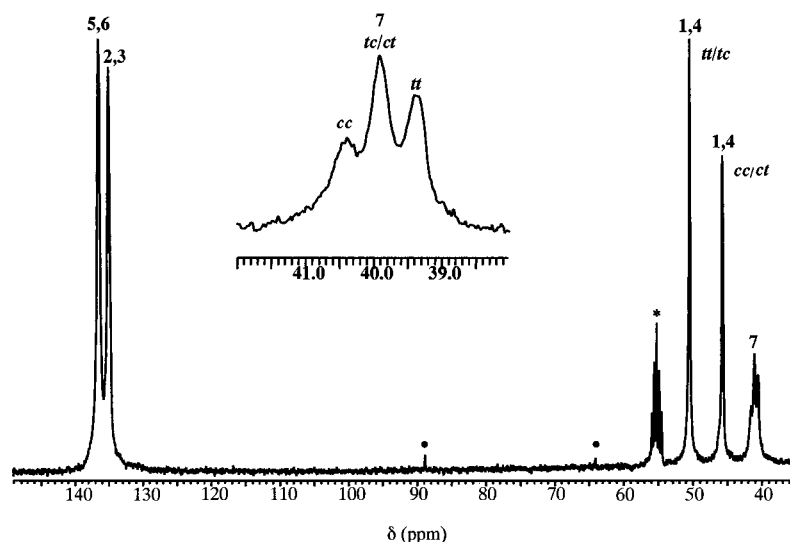
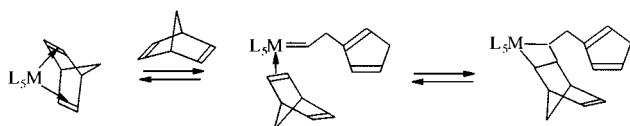
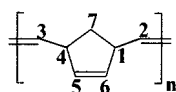


Fig. 5. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum recorded at 300 MHz after the reaction of **1** (●) and NBD at 293 K in CD_2Cl_2 (*). Carbon signals in the poly-NBD are labelled as follows:



Scheme 1. The initiation of ROMP by compound **1**.

4. Conclusions

Although many studies of seven-coordinate molybdenum(II) have been carried out to date there has been no report of these compounds reactions with a cyclic olefin as NBD. For these reasons we consider it unusually interesting that molybdenum(II) species of the $[\text{Mo}(\mu\text{-Cl})(\text{SnCl}_3)(\text{CO})_3(\eta^4\text{-NBD})]$ (**1**) type can be prepared directly from $[(\text{CO})_4\text{Mo}(\mu\text{-Cl})_3\text{Mo}(\text{SnCl}_3)(\text{CO})_3]$.

The compound **1** in the presence of an excess of NBD rearranges to species initiating the ring-opening metathesis polymerisation. The microstructure of poly-NBD formed was determined by ^1H - and ^{13}C -NMR spectroscopy.

To the best of our knowledge this paper represents the first study that has simultaneously detected the coordination of cyclic olefin to the transition metal and the initiation of the ring-opening metathesis polymerisation.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic

Data Centre, deposition no. 168181. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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