



# A new versatile binuclear seven-coordinate complex of molybdenum(II), $[(\mu\text{-Cl})_2\{\text{Mo}(\mu\text{-Cl})(\text{SnCl}_3)(\text{CO})_3\}_2]^{2-}$

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## ABSTRACT

The two new seven-coordinate anionic complexes of molybdenum(II), binuclear  $[(\mu\text{-Cl})_2\{\text{Mo}(\mu\text{-Cl})(\text{SnCl}_3)(\text{CO})_3\}_2]^{2-}$  and mononuclear  $[\text{MoCl}_3(\text{GeCl}_3)(\text{CO})_3]^{2-}$ , have been synthesized and characterized by single-crystal X-ray diffraction studies. The binuclear complex exhibits a unique mode of reactivity towards norbornene. In a strictly anhydrous atmosphere the binuclear complex effectively initiates the ring-opening metathesis polymerization reaction of norbornene, but in the presence of water norbornene is efficiently transformed to the binorbornyl ether ( $\text{C}_7\text{H}_{11}\text{O}$ ).

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## 1. Introduction

The activation of the M–Cl  $\sigma$ -bond of tin or germanium tetrachlorides due to oxidative addition to electron-rich molybdenum(0) or tungsten(0) carbonyl complexes has previously been shown to be a valuable route to Mo(II) and W(II) seven-coordinate complexes [1–3]. Oxidative decarbonylation of low-oxidation-state tungsten and molybdenum carbonyl complexes such as  $[\text{M}(\text{CO})_4\text{L}_2]$  (L = nitrogen or phosphorous donor ligands) with  $\text{SnCl}_4$  or  $\text{GeCl}_4$  gave complexes of the type  $[\text{MCl}(\text{M}'\text{Cl}_3)(\text{CO})_3\text{L}_2]$  ( $\text{M}' = \text{Sn}, \text{Ge}$ ) [1–3]. However, we have recently shown that during the oxidative addition reaction of the tungsten(0) compound  $[\text{W}(\text{CO})_4(\text{pip})_2]$  (pip = piperidine,  $\text{C}_5\text{H}_{10}\text{NH}$ ) with Lewis acids such as tin or germanium tetrachlorides, the piperidine ligands are removed from the coordination sphere of tungsten, and seven-coordinate anionic complexes, dinuclear  $[(\mu\text{-Cl})_3\{\text{W}(\text{SnCl}_3)(\text{CO})_3\}_2]^-$  and mononuclear  $[\text{WCl}_3(\text{GeCl}_3)(\text{CO})_3]^{2-}$ , are formed [4,5].

In our previous investigations, we have shown that seven-coordinate complexes of molybdenum(II) and tungsten(II) readily react with norbornene (nbe) and vinylnorbornene to initiate the ring-opening metathesis polymerization (ROMP) reaction in dichloromethane solution at room temperature [3–8]. In the case of a binuclear initiator, the yield of the ROMP reaction of nbe declines due

to a concurrent reaction which under special condition can give a high yield of 2,2'-binorbornylidene (bi-nbe) [6]. However, the yield of bi-nbe is greatly influenced by the presence of water, and under non-strictly anhydrous conditions the formation of an nbe:HCl (1:1) adduct ( $\text{C}_7\text{H}_{11}\text{Cl}$ ,  $M_r = 130.61$ ) and an nbe:H<sub>2</sub>O (2:1) adduct ( $\text{C}_{14}\text{H}_{22}\text{O}$ ,  $M_r = 206.32$ ) have previously been detected by GC–MS. Although the 1:1 adduct of nbe and HCl was easily identified by NMR spectroscopy as *exo*-2-chloronorbornane, the nature of the bi-nbe-H<sub>2</sub>O adduct has remained unresolved even if we initially used the name 3-hydroxyl-2,2'-binorbornyl for the latter undesirable side product [4,6]. Therefore it seemed interesting to explain the nature of the bi-nbe-H<sub>2</sub>O adduct formed in reaction of nbe initiated by binuclear complexes of tungsten(II) and also of molybdenum(II) containing chloride bridges. To that end we looked for new binuclear complexes of molybdenum(II), similar to the previously described complex  $[(\mu\text{-Cl})_3\{\text{Mo}_2(\text{SnCl}_3)(\text{CO})_7\}]$  [9].

In these studies, using the molybdenum(0) complex  $[\text{Mo}(\text{CO})_4(\text{pip})_2]$  [10,11] as a precursor, we synthesized a new binuclear complex of molybdenum(II),  $[(\text{C}_3\text{H}_5)\text{pip}]_2[(\mu\text{-Cl})_2\{\text{Mo}(\mu\text{-Cl})(\text{SnCl}_3)(\text{CO})_3\}_2]$  (**1**), and a mononuclear complex,  $[\text{Hpip}]_2[\text{MoCl}_3(\text{GeCl}_3)(\text{CO})_3]^{2-}$  (**2**), and described their crystal and molecular structures. The chemical properties of complexes **1** and **2** were investigated by IR and NMR spectroscopy and their catalytic activity was checked in reaction with norbornene. The properties of the new binuclear compound **1** were compared with those of the photochemically synthesized  $\mu$ -trichloro-bridged dimer of molybdenum(II), the complex  $[(\mu\text{-Cl})_3\{\text{Mo}_2(\text{SnCl}_3)(\text{CO})_7\}]$  (**3**) [9].

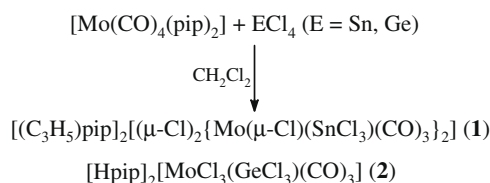
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## 2. Results and discussion

### 2.1. Synthesis and spectroscopic identification of complex **1**

Synthesis of compound **1** was achieved by reaction of  $[\text{Mo}(\text{CO})_4(\text{pip})_2]$  [10,11] with an excess of  $\text{SnCl}_4$  (1:7–10) in dichloromethane solution at room temperature. After keeping the reaction mixture in a refrigerator overnight, orange crystals were precipitated, which were determined through analysis by single-crystal X-ray diffraction studies to be the ionic compound **1** (Scheme 1). The IR spectrum of **1** in a KBr pellet exhibited  $\nu(\text{C}=\text{O})$  stretching modes at 2019 (m), 1947–1944 (m,sh), and 1933 (vs)  $\text{cm}^{-1}$ . Three  $\nu(\text{C}=\text{O})$  bands in the IR spectrum of **1** suggest a  $\text{C}_{3v}$  local symmetry of the  $\text{Mo}(\text{CO})_3$  carbonyl moiety. The presence of an  $\text{SnCl}_3^-$  moiety was confirmed by the IR spectrum in Nujol mull, which revealed  $\nu(\text{Sn}-\text{Cl})$  stretching modes at 350  $\text{cm}^{-1}$ . The  $^{119}\text{Sn}$  chemical shift for the trichlorostannyl  $\text{SnCl}_3^-$  ligand in **1** was observed at  $\delta = 65$  in  $\text{CD}_2\text{Cl}_2$  solution, i.e. in a region very close to  $\delta = 74$  detected here for the binuclear complex **3** [9]. What was very surprising and not seen before was the formation of the *N*-allylpiperidinium cation  $[(\text{C}_3\text{H}_5)\text{pip}]^+$  in the above reaction. However, it was proved by X-ray diffraction studies in solid state and by  $^1\text{H}$  and  $^{13}\text{C}$  NMR measurements in solution (see Section 3). Additional evidence was obtained by ESI-MS analysis, where the signal of the cation  $\text{C}_8\text{H}_{16}\text{N}^+$ , with  $M^+ = 126.1$ , was detected. The question arises how the latter cation is formed, when the only probable source of this cation is the piperidine ligand. The proposed mechanism for the formation of  $[(\text{C}_3\text{H}_5)\text{pip}]^+$  involves the splitting of the N–C and C–C bonds in one of the piperidine ligands due to synergic interactions with the molybdenum atom and the tin atom of the Lewis acid  $\text{SnCl}_4$ , leading to the creation of an allyl ligand. This process can be compared to the ring-opening polymerization of cyclic ethers such as tetrahydrofuran [12] or 1,3,5-trioxane [13] or ring-opening of 2-phenylazetidines [14]. The formation of an intermediate allyl ligand of the molybdenum complex was detected by NMR spectroscopy analysis of the crude reaction mixture. The  $^1\text{H}$  NMR spectrum shows three signals for the allyl group from three sets of protons, *central* ( $\text{H}_c$ ), *syn* ( $\text{H}_s$ ), and *anti* ( $\text{H}_a$ ) at  $\delta$  3.90 (tt,  $^3J_{\text{H}-\text{H}} = 10$  and 6.8 Hz,  $\text{H}_c$ ), 3.61 (d,  $^3J_{\text{H}-\text{H}} = 6.8$  Hz,  $\text{H}_s$ ), and 1.12 (d,  $^3J_{\text{H}-\text{H}} = 10$  Hz,  $\text{H}_a$ ) with an integral intensity ratio of 1:2:2. In the  $^{13}\text{C}$  NMR spectrum, two signals, at  $\delta = 74.4$  ( $\text{CH}_c$ ) and 58.0 ( $2\text{CH}_2$ ), can be assigned to the allyl ligand. The NMR characteristics of this allyl ligand are very similar to those of other allyl ligands in molybdenum(II) complexes [15–19]. The latter allyl ligand can take part in the creation of the  $[(\text{C}_3\text{H}_5)\text{pip}]^+$  cation, i.e. the formation of an N–C bond between the nitrogen atom of the piperidine ligand and the carbon atom of the allyl ligand. This reaction may occur at the molybdenum atom in a similar way as the formation of a C–C bond recently observed by Legzdins et al. during the reaction of an allyl complex of tungsten with cyclic amines [20].

Complex **1**, like other binuclear complexes of molybdenum(II) and tungsten(II), is highly reactive, and its reactivity toward norbornene is described below (Section 2.5).



Scheme 1.

### 2.2. X-ray crystal structure of compound **1**

The unit cell of complex **1** is built up from dimeric molybdenum anions  $[(\mu\text{-Cl})_2\{\text{Mo}(\mu\text{-Cl})(\text{SnCl}_3)(\text{CO})_3\}_2]^{2-}$  and *N*-allylpiperidinium cations  $[(\text{C}_3\text{H}_5)\text{pip}]^+$ . Crystal data and structure refinement parameters for this compound are given in Table 1. An ORTEP diagram, including the crystallographic labeling scheme of the binuclear anion in complex **1**, is shown in Fig. 1. Selected bond distances and key bond angles are given in Table 2.

The basic structural units of the anion of compound **1** are two seven-coordinate molybdenum atoms linked by two chlorine atoms occupying a bridging position between the two molybdenum atoms. The resultant geometry at each molybdenum atom is approximately a capped octahedron with the tin atom occupying the unique capping position above the center of the trigonal face defined by the chlorine atom and two carbonyl ligands with the

Table 1  
Crystal data and structure refinement parameters for compounds **1** and **2**.

	1	2
Empirical formula	$\text{C}_{22}\text{H}_{32}\text{Cl}_{10}\text{Mo}_2\text{N}_2\text{O}_6\text{Sn}_2$	$\text{C}_{19}\text{H}_{38}\text{Cl}_9\text{GeMoN}_3\text{O}_3$
Formula weight	1204.30	844.10
Crystal size (mm)	$0.10 \times 0.08 \times 0.05$	$0.10 \times 0.06 \times 0.05$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions		
<i>a</i> (Å)	9.363(2)	11.219(5)
<i>b</i> (Å)	15.357(3)	33.354(6)
<i>c</i> (Å)	13.758(3)	9.897(4)
$\beta$ (°)	100.75(2)	115.17(5)
<i>V</i> (Å <sup>3</sup> )	1943.5(7)	3352(2)
<i>Z</i>	2	4
<i>D</i> <sub>calcd</sub> (g/cm <sup>3</sup> )	2.058	1.673
Diffraction meter	Kuma KM4CCD	Kuma KM4CCD
Radiation	Mo K (= 0.71073 Å)	Mo K (= 0.71073 Å)
Temperature (K)	100(2)	100(2)
$\mu$ (mm <sup>-1</sup> )	2.625	2.015
<i>F</i> (0 0 0)	1160	1696
Number of data/parameters	8747/200	15 854/335
Index ranges	–15 ≤ <i>h</i> ≤ 15; –25 ≤ <i>k</i> ≤ 19; 22 ≤ <i>l</i> ≤ 18	–18 ≤ <i>h</i> ≤ 18; –43 ≤ <i>k</i> ≤ 55; –16 ≤ <i>l</i> ≤ 16
Number of reflections collected/unique	31 195/8747	58 667/15 854
Data collected, $\theta$ minimum/maximum (°)	2.65/36.87	2.72/36.94
<i>R</i> <sub>int</sub>	0.0619	0.0485
<i>S</i>	0.921	1.019
Final residuals: <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.0402/0.0504	0.0378/0.0663
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.678, 0.930	0.810, 0.980
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	1.147/–0.800	0.889/–0.702

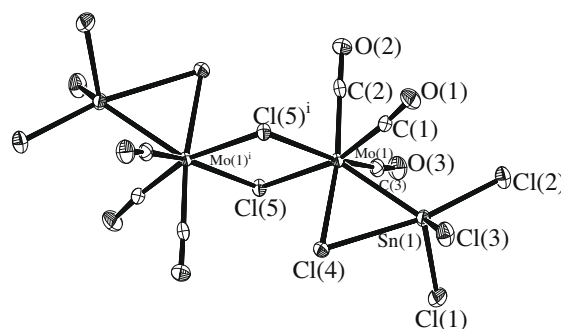


Fig. 1. The molecular structure and the atom numbering scheme of an anion of **1**. Atomic displacement ellipsoids are shown at the 50% probability level. Symmetry transformation used to generate equivalent atoms: *i* (–*x* – 1, –*y* + 1, –*z* – 1).

**Table 2**  
Selected bond lengths (Å) and angles (°) for anion of **1**.

Atoms	Distance	Atoms	Angle
Mo(1)–C(1)	1.974(3)	C(2)–Mo(1)–C(1)	76.22(11)
Mo(1)–C(2)	1.991(3)	C(3)–Mo(1)–C(2)	76.30(11)
Mo(1)–C(3)	1.976(3)	C(1)–Mo(1)–C(3)	104.95(11)
Mo(1)–Cl(2)	2.503(3)	C(2)–Mo(1)–Cl(5) <sup>i</sup>	88.34(8)
Mo(1)–Cl(5) <sup>i</sup>	2.527(1)	C(1)–Mo(1)–Cl(5) <sup>i</sup>	157.17(8)
Mo(1)–Cl(5)	2.552(1)	C(3)–Mo(1)–Cl(5) <sup>i</sup>	87.19(8)
Mo(1)–Cl(4)	2.565(1)	C(1)–Mo(1)–Cl(5)	84.67(8)
Mo(1)–Sn(1)	2.689(1)	C(3)–Mo(1)–Cl(5)	164.33(8)
Sn(1)–Cl(4)	2.815(1)	C(2)–Mo(1)–Cl(5)	94.48(8)
Sn(1)–Cl(3)	2.330(1)	Cl(5)–Mo(1)–Cl(5) <sup>i</sup>	79.80(3)
Sn(1)–Cl(1)	2.340(1)	C(1)–Mo(1)–Cl(4)	110.89(8)
Sn(1)–Cl(2)	2.384(1)	C(3)–Mo(1)–Cl(4)	105.32(8)
C(1)–O(1)	1.153(3)	C(2)–Mo(1)–Cl(4)	171.56(8)
C(2)–O(2)	1.144(3)	C(1)–Mo(1)–Sn(1)	70.01(8)
C(3)–O(3)	1.154(3)	C(3)–Mo(1)–Sn(1)	70.16(8)
		C(2)–Mo(1)–Sn(1)	123.05(8)
		Cl(5) <sup>i</sup> –Mo(1)–Sn(1)	132.80(2)
		Cl(5)–Mo(1)–Sn(1)	125.3(1)
		Cl(4)–Mo(1)–Sn(1)	64.75(2)
		Mo(1) <sup>i</sup> –Cl(5)–Mo(1)	100.20(3)
		Mo(1)–Sn(1)–Cl(4)	55.49(1)
		Mo(1)–Cl(4)–Sn(1)	59.76(2)

Symmetry transformation used to generate equivalent atoms: *i* (−*x*−1, −*y*+1, −*z*−1).

Cl(4)–Mo(1)–Sn(1) angle of 64.75(2)° and the C–Mo(1)–Sn(1) angles of 70.01(8)° and 70.16(8)°. The average angle between the three atoms occupying the capped face is 107.05°, while that between the three carbonyl carbons occupying the uncapped face is much smaller (85.82°). The angles between the carbonyl and the chloride ligands (C–Mo(1)–Cl), 164.33(8)° and 157.17(8)°, indicate approximately *trans* positions of these ligands. The two independent (μ-Cl)Mo(μ-Cl)(SnCl<sub>3</sub>)(CO)<sub>3</sub> moieties are joined centrosymmetrically by two bridging chlorine atoms, which are present in an edge-shared bioctahedron arrangement with an average bridging μ-Cl–Mo distance of 2.54 Å and a Cl–Mo–Cl angle of 79.80(3)°. The length of the Mo–Sn bond of 2.689(1) Å is close to the Mo–Sn bond distance of 2.707(1) Å found in the previously reported dimeric compound **3** [9].

The tin atom is five-coordinate in **1** with a geometry that is best described as distorted trigonal bipyramid. The tin-to-bridging-chlorine distance is 2.815(1) Å, considerably longer than the tin-to-nonbridging-chlorine distances (av. 2.35 Å). Similar Mo–Cl–Sn bridges had been found before in mononuclear seven-coordinate molybdenum(II) complexes [Mo(μ-Cl)(SnCl<sub>3</sub>)(CO)<sub>2</sub>(η<sup>4</sup>-C<sub>7</sub>H<sub>8</sub>)(NCMe)] (Sn–Cl of 2.897(2) Å) [21] and [Mo(μ-Cl)(SnCl<sub>3</sub>)(CO)<sub>3</sub>(NCEt<sub>2</sub>)] (Sn–Cl of 2.730(1) Å) [9], but it was the first time that such a bridge had been detected in a binuclear complex like **1**.

In the allyl moiety bonded to the nitrogen atom of the piperidinium cation, one of the C–C bond distances is shorter, at 1.314(5) Å, while the other is longer, at 1.481(4) Å. This clearly indicates the terminal position of the double C=C bond and the formulation of [(C<sub>3</sub>H<sub>5</sub>)pip]<sup>+</sup> as the *N*-(2-propenyl)piperidinium cation in **1**. This was proved by NMR data obtained in solution (see Section 3).

### 2.3. Synthesis and identification of compound **2**

The reaction of the yellow complex [Mo(CO)<sub>4</sub>(pip)<sub>2</sub>] with an excess of GeCl<sub>4</sub> (1:7) in dichloromethane solution at room temperature for 2 h gave a new compound that precipitated during overnight refrigeration to give greenish-yellow crystals that appeared to be the ionic complex **2**, as indicated by single-crystal X-ray diffraction studies (Scheme 1). The IR spectrum of **2** in a KBr pellet exhibited ν(C≡O) stretching modes at 2026 (m), 1923

(vs), 1919 (vs) cm<sup>−1</sup>. The presence of the GeCl<sub>3</sub><sup>−</sup> moiety was confirmed by the IR spectrum in Nujol mull, which revealed ν(Ge–Cl) stretching modes at 363 cm<sup>−1</sup>. Crystals of **2** were extremely insoluble, which prevented their use as a solution and purification by recrystallization. NMR studies of **2** in CD<sub>2</sub>Cl<sub>2</sub> solution were unsuccessful, the main obstacle being its very poor solubility in a non-coordinating solvent, but in a coordinating solvent such as CD<sub>3</sub>CN, the rearrangement of compound **2** was observed.

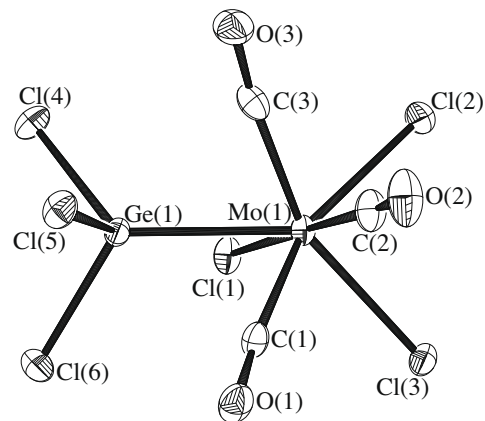
The precise mechanism for the formation of compound **2** remains uncertain, although it is clear that the complex [Mo(CO)<sub>4</sub>(pip)<sub>2</sub>] reacts differently with SnCl<sub>4</sub> and GeCl<sub>4</sub>. As can be seen in Scheme 1, the piperidine ligands were lost, and what had been the piperidine ligand had now become a piperidinium cation: [(C<sub>3</sub>H<sub>5</sub>)pip]<sup>+</sup> in **1** and [Hpip]<sup>+</sup> in **2**. The origin of the Hpip<sup>+</sup> cation is not clear, although generation of HCl under the reaction conditions is the most likely.

Complex **2** appeared totally non-reactive toward nbe. The starting material remained unchanged when complex **2** and nbe were stirred in CH<sub>2</sub>Cl<sub>2</sub> solution for 24 h.

### 2.4. X-ray crystal structure of compound **2**

The unit cell of complex **2** is built up from a molybdenum anion [MoCl<sub>3</sub>(GeCl<sub>3</sub>)(CO)<sub>3</sub>]<sub>2</sub><sup>2−</sup>, a chloride anion Cl<sup>−</sup>, a piperidinium cation [Hpip]<sup>+</sup>, and a dichloromethane molecule. Crystal data and structure refinement parameters for this mixture of compounds are given in Table 1. An ORTEP diagram, including the crystallographic labeling scheme, for the anion of compound **2** is shown in Fig. 2. Selected bond distances and key bond angles are given in Table 3.

The geometry of the seven-coordinate molybdenum atom in the anion of complex **2** is very similar to the capped octahedral structure in each half of the dimeric anion of complex **1**. The small differences that are observed result from the fact that in **2** all ligands are terminal, while in **1** three chlorine atoms are shared as μ-Cl bridges. The unique capping position above the center of the trigonal face defined by the chlorine atom and two carbonyl ligands with the Cl(1)–Mo–Ge angle of 70.21(2)° and the C–Mo–Ge angles of 69.19(6)° and 68.16(5)° is occupied by the germanium atom. The average angle between the three atoms: Cl(1), C(3) and C(1), occupying the capped face is 108.07°, while that between three carbonyl carbons occupying the uncapped face is much smaller (89.40°). The lengths of the Mo–Cl(1) bond of 2.567(2) Å is slightly longer than the two other Mo–Cl bond distances of 2.509(1) and 2.511(1) Å found for chlorine atoms occupying the uncapped face. The angles between the carbonyl and the chloride ligands (C–Mo–



**Fig. 2.** The molecular structure and the atom numbering scheme of an anion of **2**. Atomic displacement ellipsoids are shown at the 50% probability level.

**Table 3**  
Selected bond lengths (Å) and angles (°) for anion of **2**.

Atoms	Distance	Atoms	Angle
Mo(1)–C(1)	1.987(2)	C(2)–Mo(1)–C(1)	75.33(9)
Mo(1)–C(2)	1.981(3)	C(3)–Mo(1)–C(2)	74.93(9)
Mo(1)–C(3)	1.985(2)	C(1)–Mo(1)–C(3)	110.18(8)
Mo(1)–Cl(2)	2.509(1)	C(2)–Mo(1)–Cl(2)	92.42(7)
Mo(1)–Cl(3)	2.511(1)	C(3)–Mo(1)–Cl(2)	81.30(6)
Mo(1)–Cl(1)	2.567(2)	C(1)–Mo(1)–Cl(2)	159.70(5)
Mo(1)–Ge(1)	2.528(1)	C(2)–Mo(1)–Cl(3)	93.21(7)
Ge(1)–Cl(4)	2.170(1)	C(3)–Mo(1)–Cl(3)	159.47(6)
Ge(1)–Cl(6)	2.183(1)	C(1)–Mo(1)–Cl(3)	82.04(6)
Ge(1)–Cl(5)	2.183(1)	Cl(2)–Mo(1)–Cl(3)	82.57(2)
C(1)–O(1)	1.148(2)	C(2)–Mo(1)–Ge(1)	113.91(6)
C(2)–O(2)	1.136(3)	C(3)–Mo(1)–Ge(1)	69.19(6)
C(3)–O(3)	1.142(2)	C(1)–Mo(1)–Ge(1)	68.16(5)
		Cl(2)–Mo(1)–Ge(1)	132.12(2)
		Cl(3)–Mo(1)–Ge(1)	131.34(3)
		C(2)–Mo(1)–Cl(1)	175.87(6)
		C(3)–Mo(1)–Cl(1)	106.91(7)
		C(1)–Mo(1)–Cl(1)	107.12(7)
		Cl(2)–Mo(1)–Cl(1)	84.27(4)
		Cl(3)–Mo(1)–Cl(1)	83.93(2)
		Ge(1)–Mo(1)–Cl(1)	70.21(2)

Cl), of 175.87(6)°, 159.70(5)°, and 159.47(6)° (165.0° av.), indicate approximately *trans* positions of these ligands. The lengths of the Mo–Ge bond of 2.528(1) Å is almost identical as the Mo–Ge bond distance of 2.529(1) and 2.539(1) Å found in the seven-coordinate compound [Mo(GeCl<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>(NCEt)<sub>3</sub>] [22], but distinctly shorter than the 2.631(1) Å found in the compound [MoCl(GeCl<sub>3</sub>)(CO)<sub>3</sub>(η<sup>4</sup>-C<sub>7</sub>H<sub>8</sub>)] [23].

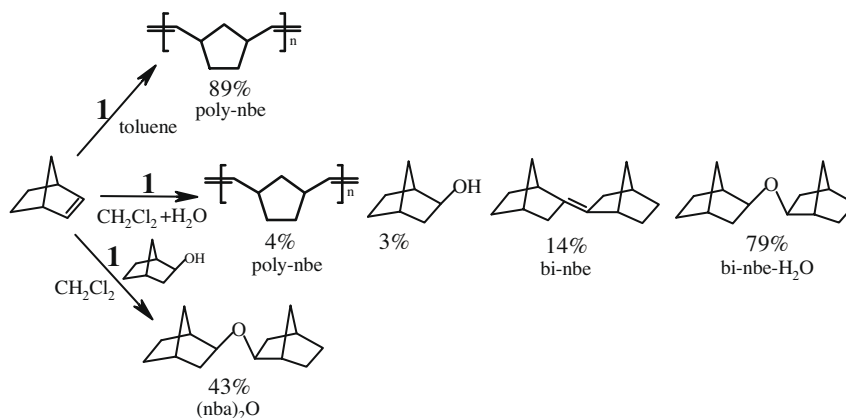
The germanium atom in the GeCl<sub>3</sub><sup>−</sup> anion is nearly tetrahedral with an average bond angle of 108.87°, varying in the range

100.14(3)–119.31(3)°. However, the Mo–Ge–Cl bond angles (117.65° av.) are much larger than the Cl–Ge–Cl angles (100.16° av.).

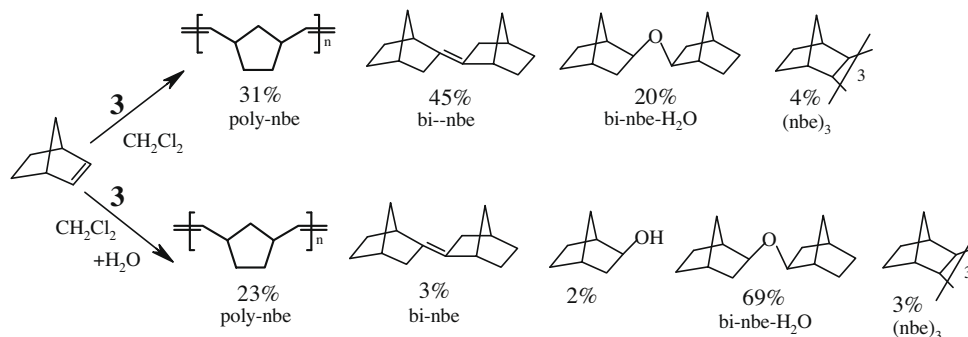
## 2.5. Reactions of norbornene initiated by binuclear complexes **1** and **3**

In reaction of nbe initiated by **1** at room temperature in toluene solution and at strictly anhydrous conditions, a ROMP polymer (poly-1,3-cyclopentylenevinylene, poly-nbe) was isolated in 89% yield by mass (Scheme 2). However, when a 1:1 mixture of nbe and water reacted in CH<sub>2</sub>Cl<sub>2</sub> solution in the presence of complex **1**, the major product detected by GC-MS was an adduct containing two molecules of nbe and H<sub>2</sub>O (bi-nbe-H<sub>2</sub>O) (ca. 82% by GC-MS in a mixture containing 15% of bi-nbe and 3% of nbe-H<sub>2</sub>O adduct), but poly-nbe was formed only in 4% yield by mass. A similar reaction course was observed in the presence of the binuclear complex **3** in CH<sub>2</sub>Cl<sub>2</sub> solution containing a 1:1 mixture of nbe and H<sub>2</sub>O (Scheme 3). Although poly-nbe was isolated in 23% yield by mass, the remaining nbe was transformed mainly to the bi-nbe-H<sub>2</sub>O adduct (90% of liquid products). Under similar conditions (CH<sub>2</sub>Cl<sub>2</sub> solution, room temperature) but without the addition of water, complex **3** gave 31% yield of poly-nbe, but the major product detected by GC-MS was bi-nbe (45%). The content of the reaction products was confirmed by <sup>1</sup>H NMR spectra, after revealing the nature of the bi-nbe-H<sub>2</sub>O adduct, which NMR analysis surprisingly identified as binorbornyl ether (C<sub>7</sub>H<sub>11</sub>)<sub>2</sub>O, (nba)<sub>2</sub>O (see below). An identical binorbornyl ether was obtained in separate experiments in which nbe reacted with *exo*-norborneol, or *exo*-norborneol alone, was subjected to etherification (dehydration) in CH<sub>2</sub>Cl<sub>2</sub> solution in the presence of a catalytic amount of complex **1** (Scheme 3).

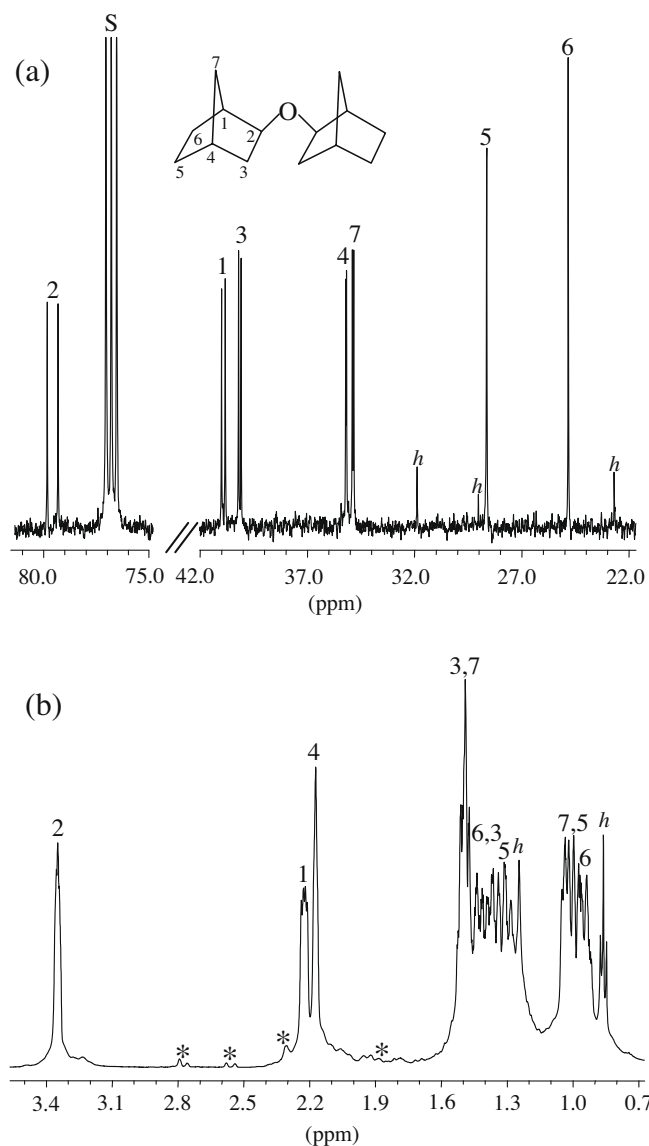
Assignment of the proton and carbon signals of (nba)<sub>2</sub>O was done by combining the NMR data from <sup>1</sup>H–<sup>1</sup>H COSY and <sup>1</sup>H–<sup>13</sup>C



**Scheme 2.**



**Scheme 3.**



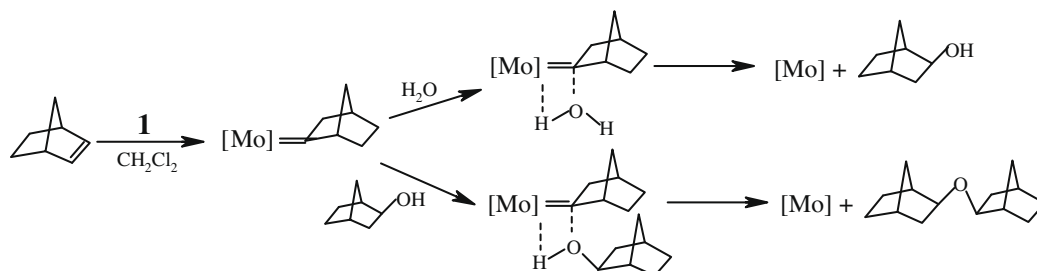
**Fig. 3.** NMR spectra of the binorbornyl ether: (a)  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (126 MHz,  $\text{CDCl}_3$ , 298 K) and (b)  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ , 293 K). The solvent signal is labeled as S. Asterisks denote the bi-nbe resonances, and *h* denotes *n*-heptane resonances.

HMQC correlations and DEPT experiments. The analysis of these spectra was aided considerably by the prior assignment of *exo*- and *endo*-norborneol [24–25]. The 125 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of a chloroform solution of the resulting binorbornyl ether exhibited six pairs of equal-intensity carbon signals in the range of 80–28 ppm and one higher-intensity carbon signal at

24.83 ppm (Fig. 3). This spectrum suggests the presence of a diastereomeric compound (1:1 mixture of two diastereoisomers, *rac* and *mezo*), which can be expected due to two chiral centers in a molecule of  $(\text{C}_7\text{H}_{11})_2\text{O}$ . Two signals of equal intensity, at  $\delta$  80.02 and 79.51, assigned to the chiral methine carbons HC-2, are at a higher separation, while the separation of signals in each successive pair decreases with the decrease in chemical shift. The  $^1\text{H}$  NMR spectrum shows poorly resolved multiplets due to methine protons at C-2 and C-1, at  $\delta$  3.35 and 2.23, respectively. These signals, after careful analysis of 600, 500, and 300 MHz spectra appear rather as two multiplet signals. Similar analysis of other proton signals reveals that most of them are very close double signals. Although their assignment to relevant carbons was done without difficulty by  $^1\text{H}$ - $^{13}\text{C}$  HMQC correlations, the coupling constants could not be measured accurately.

The mechanism for the formation of the binorbornyl ether  $(\text{nba})_2\text{O}$  can involve the intermediacy of a molybdanorbornylidene species which under anhydrous conditions initiates the ROMP reaction of nbe [26]. The coupling of two norbornylidene ligands leads to the formation of bi-nbe. This compound is formed as a mixture of four stereoisomers identified by NMR spectroscopy due to four proton signals at  $\delta$  2.79, 2.76, 2.58, and 2.54 ppm, characteristic of the methine protons HC-1 [4,6,27], and was observed here in all experiments, even at a 1:1 molar ratio of nbe:H<sub>2</sub>O (Fig. 3). In the presence of water, the norbornylidene ligand can be transformed to norborneol, which was detected in small amounts in our experiments as nbe-H<sub>2</sub>O adduct by GC-MS method (Scheme 2 and 3). Such formation of alcohol in reaction of a carbene ligand had been observed before [28–32]. In a similar way as with water, the carbene ligand interacts with alcohol [33–34]. Thus, the addition of the H–O bond of norborneol to the carbon atom of molybdanorbornylidene species and the formation of C–O and C–H bonds is one of the methods of the formation of  $(\text{nba})_2\text{O}$  (Scheme 4). It is important to note that in this route, for each equivalent of water present, two equivalents of norbornene are consumed, since the initially formed norborneol can react with another equivalent of norbornene to give  $(\text{nba})_2\text{O}$ . Another route that can be considered is the elimination of water from two molecules of previously formed norborneol. To determine the role of norborneol during the reaction, we also studied the reaction of a 1:1 mixture of nbe and norborneol and norborneol alone in the presence of **1** in dichloromethane solution. We were struck by the high yield of ether formation, which reached 43% after 24 h at room temperature for the 1:1 nbe/norborneol mixture and 77% for norborneol alone.

Both the chloro-bridged binuclear complexes **1** and **3** react similarly with nbe and under slightly different reaction conditions can be used as catalysts for the synthesis of poly-nbe, bi-nbe, and  $(\text{nba})_2\text{O}$ . Similar reactivity of the binuclear compounds **1** and **3** results from the similar mechanism of interaction of both compounds with olefin, i.e. the splitting of chloride bridges by olefin and the formation of a mononuclear coordinatively unsaturated



**Scheme 4.**

molybdenum species that is able to activate an olefin molecule. It is worth pointing out that the detection of bi-nbe provides direct evidence for molybdenum(II)-promoted transformation of olefin to a molybdaalkylidene ligand, which is able to initiate the ROMP reaction or disproportionate giving a new olefin as the alkylidene-alkylidene coupling product. In the presence of HCl or H<sub>2</sub>O, the molybdanorbonylidene species decomposes to give 2-chloro-norbornane or norborneol, respectively.

Although the dehydration of alcohols to ethers has been recently observed in the presence of transition metal catalysts [35–42] the formation of ether in one-pot synthesis from olefin is very scarce [43–44]. The reaction catalyzed by **1** not only proceeds under very mild conditions but is selective as well.

## 2.6. Conclusions

The studies reported in this paper were conducted in order to investigate the reactivity of molybdenum(II) complexes towards nbe and water. To that end two new seven-coordinate complexes of molybdenum(II) were synthesized. The binuclear complex of molybdenum(II) reacts readily with nbe and under the reaction conditions can be used as an efficient initiator for the ring-opening metathesis polymerization reaction, dimerization, which gives binbe, and etherification, which leads to the formation of binorbonyl ether. The mononuclear complex of molybdenum(II), synthesized in reaction between [Mo(CO)<sub>4</sub>(pip)<sub>2</sub>] and GeCl<sub>4</sub> appeared totally non-reactive toward nbe.

In conclusion, we report a very simple and efficient method of preparing a versatile binuclear anionic molybdenum(II) complex **1**, and the discovery of a molybdenum catalytic system for one-pot synthesis of binorbonyl ether from nbe and water. This is a rare example of etherification using a group 6 metal complex as catalyst.

## 3. Experimental

### 3.1. General data

The synthesis and manipulation of all chemicals were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Solvents and liquid reagents were pre-dried with CaH<sub>2</sub> and vacuum transferred into small storage flasks prior to use. Mo(CO)<sub>6</sub> and *exo*-norborneol (Aldrich) were used as received. IR spectra were measured with a Nicolet-400 FT-IR and a Bruker IF-S66 instrument. <sup>1</sup>H, <sup>13</sup>C, two-dimensional <sup>1</sup>H–<sup>1</sup>H COSY and <sup>1</sup>H–<sup>13</sup>C HMQC, and DEPT NMR spectra were recorded with Bruker 600, 500, and 300 MHz instruments. All chemical shifts are referenced to residual solvent protons for <sup>1</sup>H NMR ( $\delta$  7.24 CDCl<sub>3</sub>, 5.32 CD<sub>2</sub>Cl<sub>2</sub>, 1.98 CD<sub>3</sub>CN) and to the chemical shift of the solvent for <sup>13</sup>C NMR (77.0 CDCl<sub>3</sub>; 54.0 CD<sub>2</sub>Cl<sub>2</sub>, 118.0 CD<sub>3</sub>CN). The <sup>119</sup>Sn chemical shifts are referenced to an external standard, Ph<sub>3</sub>SnCl ( $\delta$  = –44.7 ppm [45]). Analyses of the catalytic reaction products were performed on a Hewlett-Packard GC–MS system. The organometallic compounds were analyzed on MicroOTOF-Q Bruker using the ESI method. Mo(CO)<sub>6</sub>, norbornene and *exo*-norborneol were used as received. [Mo(CO)<sub>4</sub>(pip)<sub>2</sub>] [10,11] was synthesized in photochemical reaction of Mo(CO)<sub>6</sub> with piperidine in *n*-heptane. During this reaction the molybdenum complex containing piperidine ligands was settled as a light yellow powder. The complex **3** was synthesized in photochemical reaction of Mo(CO)<sub>6</sub> with SnCl<sub>4</sub> in *n*-heptane according the familiar method [9], and its <sup>119</sup>Sn{<sup>1</sup>H} NMR (186.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum showed a signal at  $\delta$  = 74. The photolysis source was an HBO 200 W high-pressure Hg lamp.

### 3.2. Reaction of [Mo(CO)<sub>4</sub>(pip)<sub>2</sub>] with SnCl<sub>4</sub> and the formation of compound **1**

A slurry of [Mo(CO)<sub>4</sub>(pip)<sub>2</sub>] (0.045 g, 0.12 mmol) in dichloromethane (15 cm<sup>3</sup>) was treated with an excess of SnCl<sub>4</sub> (0.1 cm<sup>3</sup>, 0.85 mmol), added by means of a syringe. A color change from light yellow to deep orange and complete dissolution of the piperidine compound were observed when the solution was stirred under ambient conditions for 2 h. The solvent was evaporated in vacuum to give an orange residue, which was washed several times with *n*-heptane and dried under vacuum to give 0.086 g of an orange powder. The cation of compound **1**, [C<sub>8</sub>H<sub>16</sub>N]<sup>+</sup> (*M*<sup>+</sup> = 126.1), and anions [Mo<sub>2</sub>Sn<sub>2</sub>Cl<sub>8</sub>C<sub>4</sub>O<sub>4</sub>]<sup>–</sup> (*M*<sup>–</sup> = 823.0), and [Mo<sub>2</sub>Sn<sub>2</sub>Cl<sub>8</sub>C<sub>3</sub>O<sub>3</sub>]<sup>–</sup> (*M*<sup>–</sup> = 794.9), were detected by ESI-MS. The sample, very poorly soluble in halogenated hydrocarbons, was investigated by NMR and IR spectroscopy. Single orange crystals of compound **1** were deposited from the dichloromethane solution by keeping the crude reaction mixture at 273 K. X-ray confirmed that they contained ionic compounds: [(C<sub>3</sub>H<sub>5</sub>)pip]<sub>2</sub>[( $\mu$ -Cl)<sub>2</sub>{Mo( $\mu$ -Cl)(SnCl<sub>3</sub>)(CO)<sub>3</sub>}]<sub>2</sub> (**1**).

IR (KBr disc):  $\nu$ (CO) 2019 (s), 1947–1944 (m,sh), 1933 (vs) cm<sup>–1</sup>. IR (Nujol mull):  $\nu$ (Sn–Cl) 350 cm<sup>–1</sup>. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 253 K):  $\delta$  = 6.11 (s, 1H, NH), 5.85 (ddt, <sup>3</sup>J<sub>H–H</sub> = 16.8, 10.0, 7.3 Hz, 1H, C <sub>$\beta$</sub> H-allyl), 5.67 (d, <sup>3</sup>J<sub>H–H</sub> = 10.0 Hz, 1H, C <sub>$\gamma$</sub> H<sub>2</sub>-allyl), 5.60 (d, <sup>3</sup>J<sub>H–H</sub> = 16.8 Hz, 1H, C <sub>$\gamma$</sub> H<sub>2</sub>-allyl), 3.70 (m, 2H, C <sub>$\alpha$</sub> H<sub>2</sub>-allyl), 3.35 (s, 4H, C <sub>$\alpha$</sub> H<sub>2</sub>-pip), 1.85 (s, 4H, C <sub>$\beta$</sub> H<sub>2</sub>-pip), 1.67 (s, 2H, C <sub>$\gamma$</sub> H<sub>2</sub>-pip). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 253 K):  $\delta$  = 223.2 (CO), 129.6 (1C, C <sub>$\beta$</sub> H-allyl), 124.2 (1C, C <sub>$\gamma$</sub> H<sub>2</sub>-allyl), 54.7 (1C, C <sub>$\alpha$</sub> H<sub>2</sub>-allyl), 47.5 (2C, C <sub>$\alpha$</sub> H<sub>2</sub>-pip), 23.1 (2C, C <sub>$\beta$</sub> H<sub>2</sub>-pip), 21.7 (1C, C <sub>$\gamma$</sub> H<sub>2</sub>-pip). <sup>119</sup>Sn{<sup>1</sup>H} NMR (186.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta$  = 65.

### 3.3. Reaction of [Mo(CO)<sub>4</sub>(pip)<sub>2</sub>] with GeCl<sub>4</sub> and the formation of compound **2**

A sample of GeCl<sub>4</sub> (0.1 cm<sup>3</sup>, 0.86 mmol) was added by means of a syringe to a stirred suspension of [Mo(CO)<sub>4</sub>(pip)<sub>2</sub>] (0.045 g, 0.12 mmol) in dichloromethane (15 cm<sup>3</sup>). A color change from light yellow to greenish-yellow and complete dissolution of the piperidine compound were observed when the solution was stirred under ambient conditions for 2 h. The solvent was evaporated in vacuum to give a greenish-yellow residue, which was washed several times with *n*-heptane and dried under vacuum to give 0.030 g of a greenish-yellow powder.

(Anal. Calc. for C<sub>13</sub>H<sub>24</sub>Cl<sub>6</sub>GeMoN<sub>2</sub>O<sub>3</sub>: C, 24.29; H, 3.79; N, 4.39. Found: C, 25.34; H, 4.04; N, 4.19%). Single greenish-yellow crystals of compound **2** were deposited from the dichloromethane solution by keeping the crude reaction mixture at 273 K. X-ray confirmed that they contained ionic compounds: [Hpip]<sub>2</sub>[MoCl<sub>3</sub>(GeCl<sub>3</sub>)(CO)<sub>3</sub>] (**2**).

IR (KBr disc):  $\nu$ (CO) 2026 (m), 1923 (vs), 1919 (vs) cm<sup>–1</sup>. IR (Nujol mull):  $\nu$ (Ge–Cl) 363 cm<sup>–1</sup>. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$  = 7.39 (s, 2H, NH<sub>2</sub>), 3.01 (s, 4H, CH<sub>2</sub>), 1.94 (s, 4H, CH<sub>2</sub>), 1.77 (s, 2H, CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$  = 229.3 (2CO), 217.2 (1CO).

### 3.4. X-ray crystallography

The crystal data collection and refinement details for complexes **1** and **2** are summarized in Table 1. X-ray crystal structure analyses were performed using data collected at 100 K on a KM4-CCD diffractometer and graphite-monochromated Mo K $\alpha$  radiation generated from a Diffraction X-ray tube operated at 50 kV and 35 mA. The images were indexed, integrated, and scaled using the KUMA data reduction package [46]. The structure was solved by the heavy atom method using SHELXS97 [47] and refined by the full-matrix least-squares method on all *F*<sup>2</sup> data [48]. Non-H atoms were included in the refinement, with anisotropic displacement param-

ters, and H atoms were included from the geometry of the molecules and were not refined. The intensities were corrected for absorption [46]; min/max absorption coefficients: 0.678/0.930 for **1** and 0.810/0.980 for **2**.

### 3.5. General procedure for reaction of nbe in the presence of complexes **1** and **3**

In a round-bottomed flask equipped with a magnetic stirrer, complex **1** or **3** was weighed (ca. 0.03 mmol). Next, the solvent (10 cm<sup>3</sup> CH<sub>2</sub>Cl<sub>2</sub> or toluene) and the reagents: nbe, H<sub>2</sub>O, or norborneol (ca. 1.5 mmol), were added through the septum to a solution of the molybdenum complex, and the reaction mixture was stirred at room temperature for 24 h. After that time the solvent was removed in vacuum at room temperature and the residue was extracted with *n*-heptane and analyzed by GC–MS. The solid that was not dissolved in *n*-heptane was treated with CHCl<sub>3</sub> (5 cm<sup>3</sup>) and its solution with methanol (10 cm<sup>3</sup>). The precipitate (polymer) was then separated from the solution, dried under vacuum, and weighed.

The GC–MS analysis revealed the formation of the following compounds appearing as retention time increased: norborneol (C<sub>7</sub>H<sub>12</sub>O, *M*<sub>r</sub> = 112.17), chloronorbornane (C<sub>7</sub>H<sub>11</sub>Cl, *M*<sub>r</sub> = 130.61), 2,2'-binorbornylidene (C<sub>14</sub>H<sub>20</sub>, *M*<sub>r</sub> = 188.32) [6], nbe:H<sub>2</sub>O (2:1) adduct (C<sub>14</sub>H<sub>22</sub>O, *M*<sub>r</sub> = 206.32), and nbe trimer (C<sub>21</sub>H<sub>30</sub>, *M*<sub>r</sub> = 282.46). The latter compounds were formed with different yields depending upon the reaction conditions.

### 3.6. Transformation of nbe in CH<sub>2</sub>Cl<sub>2</sub> solution in the presence of in situ generated compound **1**

In a round-bottomed flask equipped with a magnetic stirrer, a solution of complex **1** was prepared in a 3 h reaction of Mo(CO)<sub>4</sub>(pip)<sub>2</sub> (0.045 g, 0.12 mmol) and SnCl<sub>4</sub> (0.1 cm<sup>3</sup>, 0.85 mmol) in dichloromethane (8 cm<sup>3</sup>) under an atmosphere of nitrogen. Next, nbe (0.28 g, 3.0 mmol) or its 1:1 molar mixture with H<sub>2</sub>O or norborneol in 2 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub> was added through the septum to a solution of **1**, and the reaction mixture was stirred at room temperature for 24 h. After that time the reaction mixture was analyzed as in Section 3.5.

### 3.7. Characterization of binorbornyl ether

The formation of a compound with molecular weight *M*<sub>r</sub> = 206.32 (C<sub>14</sub>H<sub>22</sub>O) was detected by GC–MS in a mixture of the products of all reactions of nbe carried out in non-strictly anhydrous conditions in the presence of complexes **1** and **3**. In reaction carried out at a 1:1 molar ratio of nbe and H<sub>2</sub>O, the isolated yield of the latter compound was 79% in the presence of **1** and 69% in the presence of **3**. GC–MS: C<sub>14</sub>H<sub>22</sub>O, *M*<sub>r</sub> = 206.32, *m/z* (relative intensity): 206 (*M*<sup>+</sup>, 1%), 95 (C<sub>7</sub>H<sub>11</sub>, 100%), 67 (C<sub>5</sub>H<sub>7</sub>, 20%). IR (Film/KBr, cm<sup>-1</sup>): ν = 2953 (vs), 2869 (s), 1474 (w), 1450 (m), 1438 (w), 1346 (m), 1315 (w), 1308 (w), 1289 (vw), 1221 (vw), 1175 (m), 1149 (m), 1115 (m), 1092 (s), 1040 (m), 1027 (s), 985 (w), 923 (vw), 883 (vw), 840 (w), 803 (m), 763 (m), 665 (m). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K): δ = 3.36, 3.35 (m, 1H, CH-2), 2.24, 2.22 (d, *J*<sub>H-H</sub> = 4.7 Hz, 1H, CH-1), 2.18 (s, 1H, CH-4), 1.50 (dd, <sup>2</sup>*J*<sub>H-H</sub> = 11 Hz, <sup>3</sup>*J*<sub>H-H</sub> = 11 Hz, 1H, CH<sub>2</sub>-3), 1.49 (d, <sup>2</sup>*J*<sub>H-H</sub> = 8 Hz, 1H, CH<sub>2</sub>-7), 1.43 (dd, <sup>2</sup>*J*<sub>H-H</sub> = 11 Hz, <sup>3</sup>*J*<sub>H-H</sub> = 11 Hz, 1H, CH<sub>2</sub>-6), 1.37 (dd, <sup>2</sup>*J*<sub>H-H</sub> = 11 Hz, <sup>3</sup>*J*<sub>H-H</sub> = 11 Hz, 1H, CH<sub>2</sub>-5), 1.31 (dd, <sup>2</sup>*J*<sub>H-H</sub> = 11 Hz, <sup>3</sup>*J*<sub>H-H</sub> = 11 Hz, 1H, CH<sub>2</sub>-3), 1.04 (d, <sup>2</sup>*J*<sub>H-H</sub> = 8 Hz, 1H, CH<sub>2</sub>-7), 0.99 (dd, <sup>2</sup>*J*<sub>H-H</sub> = 11 Hz, <sup>3</sup>*J*<sub>H-H</sub> = 11 Hz, 1H, CH<sub>2</sub>-5), 0.94 (dd, <sup>2</sup>*J*<sub>H-H</sub> = 11 Hz, <sup>3</sup>*J*<sub>H-H</sub> = 11 Hz, 1H, CH<sub>2</sub>-6). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>, 298 K): δ = 80.02, 79.51 (1C, CH-2), 41.00, 40.83 (1C, CH-1), 40.21, 40.09 (1C, CH<sub>2</sub>-3), 35.21, 35.17 (1C, CH-4), 34.90, 34.83 (1C, CH<sub>2</sub>-7), 28.64, 28.63 (1C, CH<sub>2</sub>-5), 24.83 (1C, CH<sub>2</sub>-6).

## 4. Supplementary material

CCDC 719774 and 719773 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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