

Catalytic activity of $\text{Mo}(\text{NO})_2(\text{HSO}_4)_2\text{L}_2$ and $[\text{Mo}(\text{NO})_2\text{L}_4](\text{HSO}_4)_2$ ($\text{L} = \text{MeCN}, \text{EtOH}$) in reaction of metathesis and epoxidation of olefins

A. Keller^{*}, J.M. Sobczak, R. Matusiak

Faculty of Chemistry, University of Wrocław, 14 Joliot-Curie, 50-383 Wrocław, Poland

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Abstract

The dinitrosylmolybdenum complexes $\text{Mo}(\text{NO})_2(\text{HSO}_4)_2\text{L}_2$ and $[\text{Mo}(\text{NO})_2\text{L}_4](\text{HSO}_4)_2$ ($\text{L} = \text{MeCN}, \text{EtOH}$) are reported and their use as precatalysts in the presence of ethylaluminium-dichloride for metathesis of olefins discussed. Upon treatment with EtAlCl_2 the formation of an alkylidene-molybdenum complexes has been observed, isolated and spectroscopically characterized. The title complexes (for $\text{L} = \text{MeCN}$) are also precursors of very effective catalysts of the organic hydroperoxide decomposition and olefine epoxidation reactions. The metathesis as well as epoxidation data indicate an important influence of the ligand sphere of the catalysts on their activity and product distribution. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Dinitrosylmolybdenum complexes; Alkylidene complexes; Catalysis; Metathesis; Polymerization; Epoxidation

1. Introduction

Carbene complexes play a key role in many important catalytic organic processes as cyclopropanation [1–3], polymerization of alkenes [4–6] and alkynes [7–10], Fischer–Tropsch reaction [11,12], biochemical oxidation [13], and metathesis of olefins [14–16]. For this last process, among the variety of carbene complexes synthesized so far [17–30], only those associated with Group IV–VI metals (particularly Mo and W) in relatively high oxidation states promote efficiently olefin metathesis in homogeneous solution [23–30]. Exceptions are dinitrosylmolybdenum complexes in low oxidation state but with nucleophilic carbene (alkylidene) ligands [31–34]. The requirement for stability of these complexes is the presence of ligands coordinated through oxygen atom(s) in the coordination sphere of the metal. As far, they were obtained using carboxylic and alkoxy ligands. Ethylidene complexes were obtained from respective precursors, i.e., $\{\text{Mo}(\text{NO})_2(\text{OR})_2\}_n$ and $\text{Mo}(\text{NO})_2(\text{O}_2\text{CR})_2$, in reaction with EtAlCl_2 , and can be used in syntheses of other complexes of this type in reaction with olefins [32].

^{*} Corresponding author.

As it was stated in the case of chloro-nitrosyl-molybdenum-complexes, the dinitrosylmolybdenum complexes are also very efficient and selective catalysts in epoxidation of olefins by organic hydroperoxides [35,36].

The present paper deals with the interaction of the new dinitrosylmolybdenum complexes $\text{Mo}(\text{NO})_2(\text{HSO}_2)_2(\text{L})_2$ and the dicationic complexes $[\text{Mo}(\text{NO})_2(\text{L})_4](\text{HSO}_4)_2$ ($\text{L} = \text{MeCN}$ and EtOH) with ethylaluminium-dichloride and their catalytic activity in reaction of metathesis and epoxidation of olefin.

2. Experimental

All procedures were carried out under argon atmosphere, with purified and dried reagents. $\text{Mo}(\text{NO})_3(\text{HSO}_4)_3$ (**1**), $[\text{Mo}(\text{NO})_4(\text{HSO}_4)_2](\text{HSO}_4)$ (**2**) and $\text{Mo}(\text{CO})_3(\text{MeCN})_3$ (**3**) were prepared by published methods [37–39]. IR spectra were measured using Specord M80 and Impact 400 (Nicolet) spectrophotometers. ^1H NMR spectra were recorded using Tesla BS567A and Bruker 300 spectrometers.

Metathesis reactions of olefins and polymerization of phenylacetylene were monitored by gas chromatography. A Hewlett Packard 5890 II series gas chromatograph coupled with Hewlett Packard Model mass selective detector was used for the GC–MS analyses.

Catalytic decomposition of cumene hydroperoxide (CHP) and epoxidation reaction were performed in a thermostated glass vessel with reflux condenser under argon atmosphere. Hydroperoxide concentration was determined iodometrically. Epoxide was determined potentiometrically [40]. Other products were identified spectroscopically and by gas chromatography.

2.1. Preparation of $\text{Mo}(\text{NO})_2(\text{MeCN})_2(\text{HSO}_2)_2$ (**4**)

2.1.1. Procedure A

MeCN (1.2 ml, 22.80 mmol) and NOHSO_4 (1.92 g, 15.12 mmol) were added to a solution of $\text{Mo}(\text{CO})_6$ (2.0 g, 7.56 mmol) in $(\text{ClCH}_2)_2$ (ca. 60 ml) while stirring. Next, the reaction mixture was heated to 60°C . After 6 h the mixture was cooled to room temperature. Yellow-brown solid was collected by filtration, washed with CH_2Cl_2 and dried in vacuo (yield ca. 95%).

2.1.2. Procedure B

Solid NOHSO_4 (1.03 g, 8.38 mmol) was added to a stirred solution of **3** (2.0 g, 4.19 mmol) in $(\text{ClCH}_2)_2$ (50 ml), whereupon gas evolution and precipitation of **4** occurred. After about 6 h the yellow-brown complex was isolated by filtration, washed with CH_2Cl_2 and dried in vacuo (yield ca. 95%).

Anal.: Calcd. for $\text{C}_4\text{H}_8\text{N}_4\text{MoO}_{10}\text{S}_2$: C 11.12, H 1.87, N 12.96, S 14.84%. Found: C 11.03, H 1.92, N 12.80, S 14.70%. IR (Nujol mulls): $\nu(\text{CN})$ 2298 w, 2265 w; $\nu(\text{NO})$ 1820 s, 1698 vs; $\nu(\text{SO})$ 1135 vs, 1110 vs, 1030 vs, 960 s cm^{-1} . ^1H NMR ($\text{DMSO}-d_6$, at 25°C): δ 2.11 (s, 6H, CH_3), 7.80 (s, 2H, OH) ppm.

2.2. Preparation of $[\text{Mo}(\text{NO})_2(\text{MeCN})_4](\text{HSO}_4)_2$ (**5**)

To a stirred suspension of $\text{Mo}(\text{CO})_6$ (2.0 g, 7.56 mmol) in MeCN (30 ml) a solid NOHSO_4 (1.92 g, 15.12 mmol) was added. When the evolution of CO finished, the green solution was filtered and

concentrated to half of its original volume in vacuo before being treated with diethyl ether to induce the precipitation of a dark green solid. The solid was collected by filtration, washed with CH_2Cl_2 and dried in vacuo (yield ca. 90%).

Anal.: Calcd. for $\text{C}_8\text{H}_{14}\text{N}_6\text{MoO}_{10}\text{S}_2$: C 18.68, H 2.74, N 16.34, S 12.47%. Found: C 18.52, H 2.79, N 16.14, S 12.39%. IR (Nujol mulls): $\nu(\text{CN})$ 2280 m, 2260 w; $\nu(\text{NO})$ 1835 s, 1720 vs; $\nu(\text{SO})$ 1135 vs, 1025 vs, 950 s cm^{-1} . ^1H NMR ($\text{DMSO}-d_6$, at 25°C): δ 1.80 (s, 6H, CH_3), 2.10 (s, 6H, CH_3), 8.70 (s, 2H, OH) ppm.

2.3. Preparation of $\text{Mo}(\text{NO})_2(\text{EtOH})_2(\text{HSO}_2)_2$ (**6**)

Suspension of **1** (1.0 g, 2.25 mmol) in $(\text{ClCH}_2)_2$ (30 ml) and EtOH (1.0 ml, 17.0 mmol) was stirred for 8 h at 60°C. After that time the reaction mixture was cooled to room temperature and a green solid was collected by filtration. It was washed several times with a cool (about 0°C) EtOH and diethyl ether then dried in vacuo (yield ca. 65%).

Anal.: Calcd. for $\text{C}_4\text{H}_{14}\text{N}_2\text{MoO}_{12}\text{S}_2$: C 10.86, H 3.19, N 6.33, S 14.50%. Found: C 10.77, H 3.26, N 6.18, S 14.41%. IR (Nujol mulls): $\nu(\text{NO})$ 1810 s, 1685 vs; $\nu(\text{SO})$ 1125 vs, 1115 vs, 1025 vs, 960 s cm^{-1} . ^1H NMR ($\text{DMSO}-d_6$, at 25°C): δ 1.27 (br, 6H, CH_3), 4.18 (br, 4H, CH_2), 8.60 (s br, 4H, OH) ppm.

2.4. Preparation of $[\text{Mo}(\text{NO})_2(\text{EtOH})_4](\text{HSO}_4)_2$ (**7**)

1 (1.0 g, 2.25 mmol) was dissolved in EtOH and the solution was stirred for 15 min at room temperature. After that time the solution was filtered and the remainder (green solid which was identified as complex **6**) was washed with ethanol. Addition of diethyl ether to the filtrate gives a green solid appearance. Repeated dissolution of the crude product in EtOH, precipitation with diethyl ether and dried in vacuo at 80°C gave the pure product (yield ca. 75%).

Anal.: Calcd. for $\text{C}_8\text{H}_{26}\text{N}_2\text{MoO}_{14}\text{S}_2$: C 17.98, H 4.90, N 5.24, S 12.00%. Found: C 18.07, H 4.94, N 5.16, S 12.18%. IR (Nujol mulls): $\nu(\text{NO})$ 1820 s, 1690 vs; $\nu(\text{SO})$ 1145 vs, 1060 vs, 967 s cm^{-1} . ^1H NMR (acetone- d_6 , at 25°C): δ 1.25 (br, 12H, CH_3), 3.70 (br, 4H, CH_2), 4.20 (br, 4H, CH_2) ppm.

2.5. Preparation of $\{\text{Mo}(\text{NO})_2(\text{OEt})_2L\}_n$ ($L = \text{MeCN}$ (**8**); EtOH (**9**))

NaOEt (0.26 g, 3.88 mmol and 0.25 g, 3.74 mmol) was slowly added to rapidly stirred solution of **5** (1 g, 1.94 mmol) in MeCN (20 ml) and **7** (1 g, 1.87 mmol) in EtOH (20 ml), respectively at -5°C . The resulting reaction mixture was stirred for 30 min at room temperature, filtered and evaporated under vacuum. The complex (**8** or **9**) was extracted from the remainder with a small amount of CH_2Cl_2 and precipitated with hexane.

Anal. for **8**: Calcd. for $\text{C}_6\text{H}_{13}\text{N}_3\text{MoO}_4$: C 25.10, H 4.56, N 14.63%. Found: C 25.25, H 4.52, N 14.34%. IR (Nujol mulls): $\nu(\text{CN})$ 2270 w; $\nu(\text{NO})$ 1750 s, 1625 vs; $\nu(\text{CO})$ 1080 s, 1025 s cm^{-1} . ^1H NMR (CDCl_3 , at 25°C): δ 1.27 (br, 6H, CH_2CH_3), 2.09 (s, 3H, CH_3), 4.16, 4.27 (br, 4H, CH_2CH_3) ppm.

Anal. for **9**: Calcd. for $\text{C}_6\text{H}_{16}\text{N}_2\text{MoO}_5$: C 24.67, H 5.52, N 9.59%. Found: C 24.78, H 5.48, N 9.29%. IR (Nujol mulls): $\nu(\text{NO})$ 1740 vs, 1616 vs; $\nu(\text{CO})$ 1083 s, 1050 sh, 1027 s cm^{-1} . ^1H NMR (CDCl_3 , at 25°C): δ 1.22 (br, 9H CH_3), 4.23 (br, 6H, CH_2) ppm.

2.6. Preparation of $\text{Mo}(\text{NO})_2(\text{SO}_4)_2(\text{AlCl}_2)_2(\text{MeCN})_2$ (**10**)

A vigorously stirred suspension of **4** (0.5 g, 1.15 mmol) in PhCl (15 ml) was cooled down to -40°C . A solution of EtAlCl_2 in PhCl (2.30 mmol), cooled to -40°C was added dropwise. The reaction mixture was heated to room temperature. The brown product was filtered off, repeatedly washed with hexane and dried in vacuo.

Anal.: Calcd. for $\text{C}_4\text{H}_6\text{N}_4\text{Al}_2\text{Cl}_4\text{MoO}_{10}\text{S}_2$: C 7.68, H 0.97, N 8.95%, Cl 22.66, S 10.24%. Found: C 7.44, H 1.02, N 8.69, Cl 22.81, S 10.08%. IR (Nujol mulls): $\nu(\text{CN})$ 2320 w, 2300 sh; $\nu(\text{NO})$ 1829 s, 1704 vs; $\nu(\text{SO})$ 1117 vs, 1080 vs, 1034 vs, 890 m; $\nu(\text{MoClAl})$ 306 m, 293 m, cm^{-1} .

2.7. Preparation of $\text{Mo}(\text{NO})_2(=\text{CHMe})(\text{SO}_4)_2(\text{AlCl}_2)_4(\text{EtAlCl}_2)_2$ (**11a**)

To a vigorously stirred suspension of **4** (1.0 g, 2.31 mmol) in PhCl (30 ml) the EtAlCl_2 in PhCl (18.00 mmol) was added dropwise, at -5°C . The reaction mixture was heated to room temperature. After about 30 min, the green product was filtered off, washed with hexane and dried in vacuo.

Anal.: Calcd. for $\text{C}_6\text{H}_{14}\text{N}_2\text{Al}_6\text{Cl}_{12}\text{MoO}_{10}\text{S}_2$: C 7.05, H 1.38, N 2.74, Cl 41.65, S 6.28%. Found: C 7.27, H 1.42, N 2.50, Cl 41.76, S 6.10%. IR (Nujol mulls): $\nu(\text{NO})$ 1835 s, 1725 vs; $\nu(\text{SO})$ 1145 vs, 1115 sh, 1025 vs, 950 vs, 920 vs, 885 sh, cm^{-1} .

2.8. Preparation of $\{\text{Mo}(\text{NO})_2(=\text{CHMe})(\mu\text{-OEt})_2(\text{AlCl}_2)_2(\text{EtAlCl}_2)_n\}_n$ (**14a**)

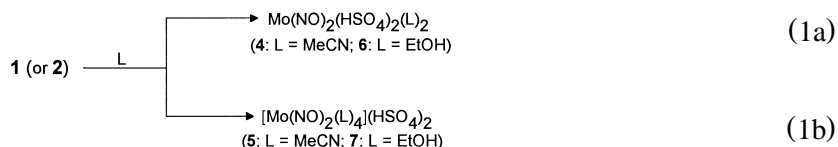
To a vigorously stirred suspension of **7** (0.5 g, 0.94 mmol) in PhCl (20 ml), the EtAlCl_2 in PhCl solution (9.40 mmol) was added dropwise at -5°C . The reaction mixture was heated to room temperature. After about 30 min, the remaining solution was filtered. A total of 5 ml of hexane was added to the filtrate and the solution was left until the brown precipitate settled down. The isolated complex was filtered off, repeatedly washed with hexane and dried in vacuo.

Anal.: Calcd. for $\text{C}_8\text{H}_{19}\text{N}_2\text{Al}_2\text{Cl}_6\text{MoO}_4$: C 15.34, H 3.00, N 5.96, Cl 30.18%. Found: C 15.57, H 3.21, N 5.48, Cl 30.27%. IR (Nujol mulls): $\nu(\text{NO})$ 1826 vs, 1721 vs; $\nu(\text{CO})$ 1022 m cm^{-1} . $^1\text{H NMR}$ (CD_3CN , at -40°C): δ 7.44 (q, 1H, $J(\text{HH}) = 10.0$ Hz, CHCH_3), 4.00 (br, 4H, OCH_2CH_3), 1.29 (t, 6H, $J(\text{HH}) = 7.9$ Hz, OCH_2CH_3), 0.95 (d, 3H, $J(\text{HH}) = 10.0$ Hz, CHCH_3) ppm.

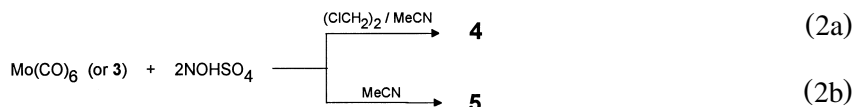
3. Results and discussion

3.1. Catalyst precursors

Treatment of **1** or **2** with donor solvents, e.g., MeCN and/or EtOH results in the transformation:



Reaction between Mo(CO)_6 (or **3**) and NOHSO_4 also produced **4** or **5** depending on concentration of MeCN:



Reaction 2b is another method for synthesis of solvated $[\text{M(NO)}_2]^{2+}$ cations [41–44].

5 and **7** in MeCN and EtOH react with NaOEt to give **8** and **9**, respectively. Complexes of this type have been previously described [45]. They were found to be precursors of stable alkylidenedinitrosyl catalysts of the olefin metathesis reaction [31,33]. The IR spectra of all of the complexes exhibit two strong bands in the $\nu(\text{NO})$ region attributable to *cis*- $\{\text{Mo(NO)}_2\}^6$ unit [46,47]. Nature of these spectra in the region of $\nu(\text{SO})$ vibrations points to the ionic nature of HSO_4^- group (C_{3v} symmetry) in complexes **5** and **7** and its coordination to molybdenum in complexes **4** and **6** (symmetry of the HSO_4^- group is C_s) [48]. Two $\nu(\text{CN})$ bands existing in the IR spectrum of the complex **4** could suggest that the MeCN ligands are mutually coordinated in the *cis* position to each other.

The ^1H NMR spectra of **4–6** were measured in $\text{DMSO-}d_6$ and those of **7** in acetone- d_6 , at room temperature with reference to TMS. The spectrum of **4** exhibits two singlets: one of the protons of CH_3CN and second of the protons of HSO_4^- groups, however, the spectrum of **6** (at 25°C) exhibits broad signals of CH_3 and CH_2 protons of EtOH ligands and one singlet of OH protons of EtOH and HSO_4^- ligands. There are two singlets of the CH_3CN protons in the spectrum of complex **5**, proving that the acetonitrile ligands coordinated in *trans* and *cis* positions respective to the NO group are chemical non-equivalent, and one singlet of the protons of HSO_4^- groups. A similar non-equivalency of EtOH ligands was observed in the ^1H NMR spectrum of the complex **7**.

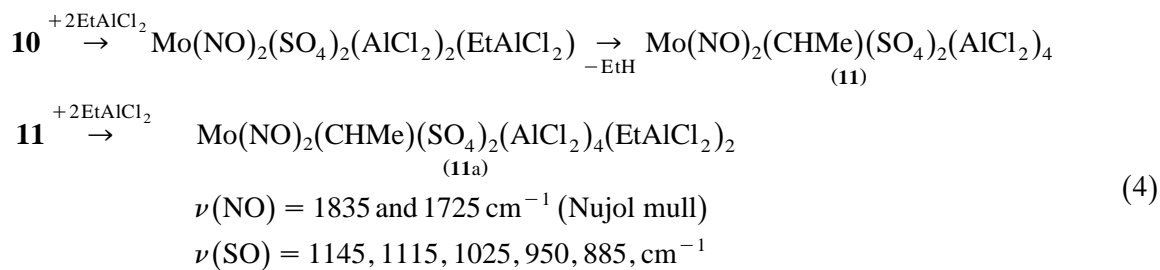
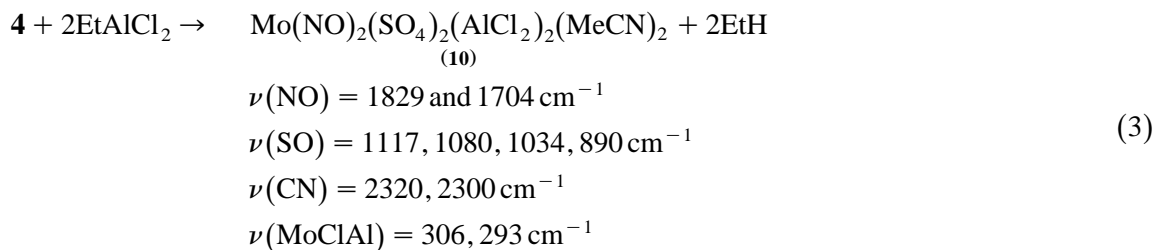
3.2. Reaction of precatalysts with EtAlCl_2

Reactions of **4–7** with EtAlCl_2 were carried out in PhCl at room temperature using different complex/ EtAlCl_2 molar ratios, for $t_a = 10 \text{ min} - 24 \text{ h}$. All the complexes are insoluble in PhCl, while the products are soluble, except the products of complex **4**. EtAlCl_2 was added at about -40°C under vigorous stirring and the heating of reaction systems at room temperature followed. These reactions were monitored by the IR method. After the appropriate time, the reaction products were isolated. Evolution of ethane was observed in all the reaction systems.

3.3. Reaction **4** with EtAlCl_2

The following reagent concentration ratios (Mo/Al) were applied: 1/2, 1/6, 1/8 and 1/10. The IR spectra, elementary analyses and catalytic activities of the solid products allow to postulate the

following reactions to proceed in the systems under examination:



10 is brown, and **11a** is green precipitate. Both are insoluble in organic solvents (alkanes, CH_2Cl_2 , PhCl and MeCN). Character of the IR spectra of these complexes in the region of $\nu(\text{SO})$ vibrations could suggest that the SO_4^{2-} ligand play a bridging role between the central metal and AlCl_2 group (symmetry of the SO_4^{2-} group is C_{2v}). The band at 306 and 293 cm^{-1} in the IR spectrum of complex **10** was attributed to $\nu(\text{MoClAl})$ vibrations. Frequencies of $\nu(\text{NO})$ in **11a** (1835, 1725 cm^{-1}) are typical of polymeric ethylidene-dinitrosylmolybdenum complexes [31,33].

10 exhibits no catalytic activity in reactions with olefins, while **11a** is a catalyst of the olefin metathesis reaction in heterogeneous system. Catalytic activity of **11a** was tested using pent-1-ene ($\text{Mo}/\text{olefin} = 1/100$) at room temperature, in PhCl, stirred vigorously. The results are shown in Table 1.

Table 1
Catalytic activity of **4** and **5** combined with EtAlCl_2 and **11a**, **12** and **13** in metathesis reaction^a

Complex or system	t_a (min)	Olefine	Reaction time (h)	Conversion (%)
4 + 6 EtAlCl_2	15	pent-1-ene	3	33
4 + 6 EtAlCl_2	15	pent-1-ene	3 ^b	6
11a	—	pent-1-ene	5	28 (18 ^c)
11a	—	pent-1-ene	5 ^b	5
5 + 6 EtAlCl_2	10	pent-2-ene	0.5	50
5 + 6 EtAlCl_2	180	pent-2-ene	0.75	50
12 ^d	—	pent-2-ene	3	30
12 ^d	—	cyclopentene	2	50 (40 ^e)
13 ^f	—	pent-2-ene	3	28

^aReaction conditions: 25 mmol of olefine, 0.25 mmol of precatalyst or catalyst and 5 ml of chlorobenzene were stirred under argon at room temperature.

^bWithout stirring.

^cMetathesis products.

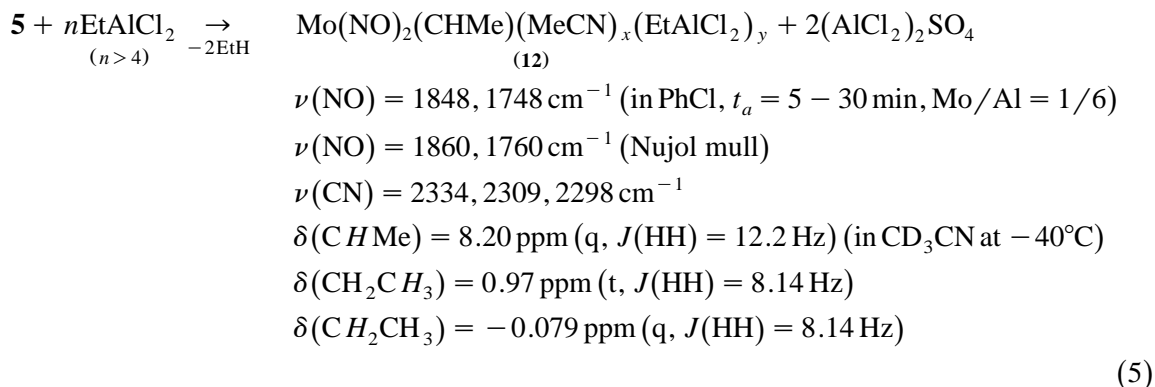
^dPrecipitated after $t_a = 10$ min.

^eYield (%) of polypentenamer insoluble in MeOH.

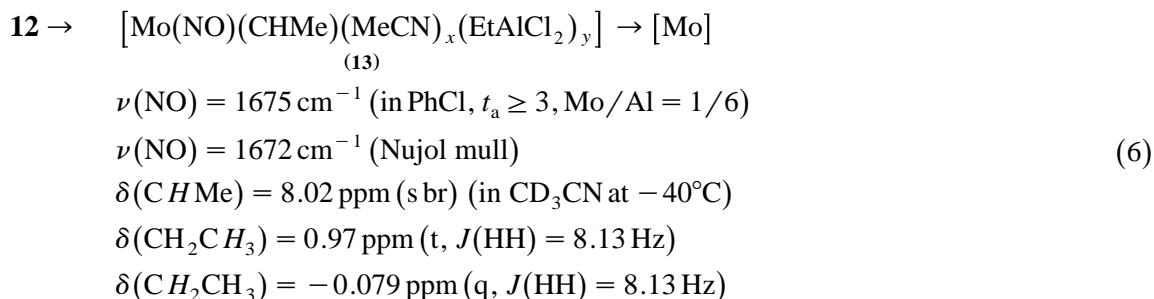
^fPrecipitated after $t_a = 3$ h.

3.4. Reaction of **5** with EtAlCl₂

Reaction of **5** with EtAlCl₂ was carried using the following ratios of concentrations of the reagents: 1:6, 1:8, 1:10 i 1:12. In this range of concentrations, increasing content of EtAlCl₂ increases only its rate. Reaction is complex and leads to formation of a few unstable products, but possible for identification. Most probable course is as follows: The first step yields green dinitrosylethylidene complex (**12**):



12 decomposes to brown mononitrosyl complex, which undergoes further transitions:



IR spectra of complexes **12** and **13** were measured in PhCl solution during the reaction, as well as in solid (Nujol mull), i.e., complexes precipitated after different reaction time (t_a) (the reaction mixture was filtered, compounds were deposited using hexane). After $t_a = 3$ h, for the concentration ratio Mo/Al = 1/6, and after $t_a = 2$ h, for Mo/Al = 1/8, the $\nu(\text{NO})$ bands of **12** vanished. Moreover, ¹H NMR spectra of these precipitated complexes dissolved in CD₃CN were measured at room temperature and at -40°C, too. The H α signals of the ethylidene ligands were attributed to respective complexes by observing their decay and growth of intensity in function of time t_a . These signals at room temperature are singlets in both complexes (**12** and **13**), but at -40°C H α resonance for **12** occurred as a quartet, however, singlet of **13** display only a broad nature as a consequence of α -hydrogen migration [33]. Instability of the ethylidene complexes formed in the system under investigation undoubtedly results from the lack of ligands coordinating via oxygen in the coordination spheres. Such behaviour was observed in many other similar systems based on dinitrosyl complexes of molybdenum, which also do not contain ligands of this type [49–51]. Vanishing $\nu(\text{NO})$ frequency in the systems Mo(NO)₂Cl₂L₂–EtAlCl₂ is caused, according to Houghes [50], by migration of the NO groups to EtAlCl₂, while Seyferth and Taube [49] explains it as transformation of nitrosyl

complexes to nitrido-ethylidene compounds. These vanishing $\nu(\text{NO})$ bands in time have frequencies equal to 1850 and 1750 cm^{-1} , i.e., typical of ethylenodinitrosyl complexes of molybdenum [31–34]. The authors found that after disappearing of these frequencies, the systems conserved their catalytic properties; moreover, they document existence of nitrido ligand. Thus, the product of decomposition of complex **13** can be the nitride-ethylidene complex, as suggested by these authors [49].

Catalytic activities of these systems in olefin metathesis reaction are presented in Table 1.

3.5. Reaction of **6** and **7** with EtAlCl_2

When **1** and **2** is treated with ethanol followed with EtAlCl_2 very active homogeneous systems in olefin metathesis reaction are formed [38]. Similar catalytic activity was found in the systems **6** and/or **7**– EtAlCl_2 .

Investigations of reactions of **6** and **7** with EtAlCl_2 ($\text{Mo}:\text{Al} \leq 1:8$) showed that in both cases, well known ethylenemolybdenum complex $\text{Mo}(\text{NO})_2(=\text{CHMe})(\mu\text{-OEt})_2(\text{AlCl}_2)_2(\text{EtAlCl}_2)$ (**14**) [33] was formed ($\nu(\text{NO})$ 1740 and 1844 cm^{-1} (in PhCl); $\delta(\text{CHMe})$ 7.44 ppm (q, $J(\text{HH}) = 10.0$ Hz)). **14** polymerizes after some time forming $[\text{Mo}(\text{NO})_2(=\text{CHMe})(\mu\text{-OEt})_2(\text{AlCl}_2)_2(\text{EtAlCl}_2)]_n$ (**14a**) ($\nu(\text{NO})$ (Nujol mull) 1721 and 1826 cm^{-1}).

3.6. Catalytic activity of complexes **4** and **5** in decomposition of CHP and epoxidation of cyclohexene

During catalytic epoxidation reaction of olefins with organic hydroperoxides (reaction 7) can more or less go together with process of decomposition of ROOH.



This side-reaction usually decides about stability and selectivity of catalytic system [52,53]. From this point of view we have studied catalytic activity of complexes **4** and **5** in decomposition reaction of CHP, and results are presented in Fig. 1.

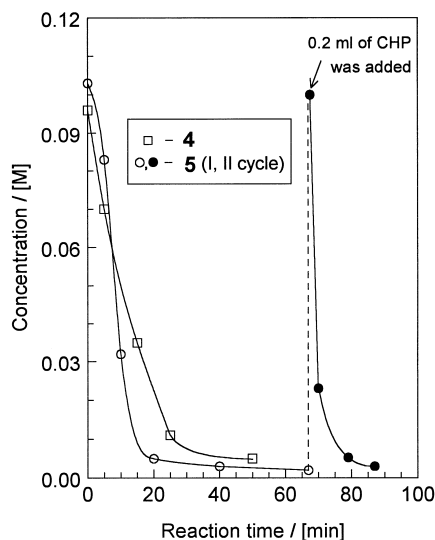


Fig. 1. Decomposition of CHP catalysed by **4** and **5**. Reaction conditions: 5.9 mg (0.014 mmol) and 5.8 mg (0.011 mmol) catalyst for **A** and **B**, respectively, 0.2 ml (1.4 mmol) CHP, 13.7 ml PhCl , $T = 50^\circ\text{C}$.

These complexes are precursors of very active catalysts. The products are phenol and acetone. Conversion of CHP are 94.8 and 98.0%, respectively for **4** and **5**. In the case of the complex **5** short induction time was observed, in this time an active complex is probably formed. It is interesting to notice that this catalyst is not deactivated in course of decomposition of CHP, because when new portion of CHP was added to a reaction mixture, very fast reaction was observed without induction period (Fig. 1). Complexes **4** and **5** are also precursors of very effective catalysts of the cyclohexene epoxidation reaction (Fig. 2).

In this case short induction period was observed for complex **5**, however the rate of epoxidation reaction is higher for **5** than **4**. Besides differences in the reaction rate, more important differences were observed in selectivities of formation of epoxycyclohexane which are 100 and 65.4% at conversion of CHP, 50 and 73.6%, respectively for complexes **4** and **5**.

In the epoxidation reaction with complex **5** by-product, *cis*-1,2-cyclohexanediol was isolated from post-reaction mixture (mp = 99.0–99.5°C, after sublimation; lit. mp = 99–101°C [54]). *cis*-Configuration was confirmed by IR and proton NMR spectra (comparable to spectra in The Aldrich Library [55]) and by comparisons with data for *trans* isomer. From the post-reaction mixture a yellow molybdenum compound was also isolated. IR spectrum of this compound shows $\nu(\text{Mo}-\text{O})$ at 935s, 910 vs and 885 vs cm^{-1} and absorption of coordinated 1,2-cyclohexanediol (2923 vs, 2845 s, 1070 vs, br cm^{-1}). Nature of the spectrum in the region $\nu(\text{Mo}-\text{O})$, could suggest mixture of *cis*-dioxo complex (two bands at 935 and 910 cm^{-1}) and dimeric species (intensive absorption at 885 cm^{-1} , characteristic for dimeric molybdenum(VI) complexes [56]). Earlier this type of complexes were isolated by Sheldon [57]. Recently, Zamaraev et al. have detected spectroscopically and characterized in situ the 1,2-diolo- molybdenum(VI) complexes, which drive the catalytic cycle of cyclohexene epoxidation [58].

Clear differences in catalytic activity of complexes **4** and **5** in epoxidation reaction can be expressed from one side in structural differences and from second side in unusual activity of **5** in decomposition reaction of CHP. The unusual activity of **5** in reaction with CHP probably causes secondary reaction of hydroperoxide and epoxycyclohexane to form *cis*-1,2-cyclohexanediol.

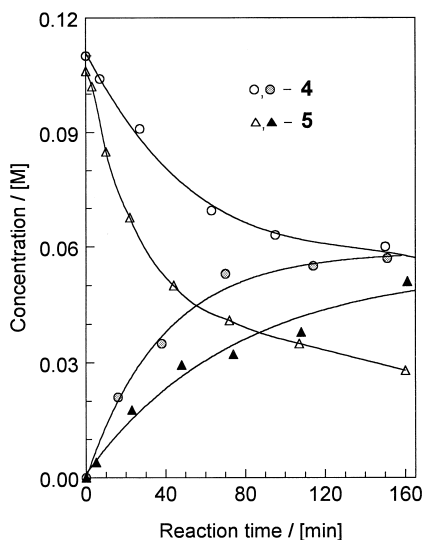


Fig. 2. Cyclohexene epoxidation with CHP catalysed by **4** and **5**. Reaction conditions: 4.6 mg (0.011 mmol) and 5.8 mg (0.011 mmol) complex **4** and **5**, respectively, 0.16 ml (1.1 mmol) CHP, 0.54 ml (5.3 mmol) cyclohexene, 10.3 ml PhCl, $T = 50^\circ\text{C}$.

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