

Catalytic activity of the $[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2]\text{Cl}$ and $[\text{Mo}(\text{NO})_2\text{Cl}_3(i\text{PrOH})]\cdot 3^i\text{PrOH}$ complexes in metathesis and polymerization of alkenes and alkynes

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Abstract

New dinitrosylmolybdenum complexes *cis*- $[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2]\text{Cl}$ and *cis*- $[\text{Mo}(\text{NO})_2\text{Cl}_3(i\text{PrOH})]\cdot 3^i\text{PrOH}$ were synthesized and their catalytic activity was investigated. The cationic complex $[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2]^+$ was found to catalyze the polymerization of norbornene. However, with EtAlCl_2 both the complexes form systems catalytically very active in metathesis (pent-2-ene), polymer degradation by cross-metathesis (polynorbornene and polyphenylacetylene by hex-3-ene), ROMP (norbornene) and polymerization of substituted acetylenes (phenylacetylene, hex-2-yne and *tert*-butylacetylene). The obtained results indicate that polymerization reaction of *tert*-butylacetylene is living polymerization. In these catalytic systems, vinyltrimethoxysilane copolymerizes with poly-*tert*-butylacetylene and parallelly induces its partial degradation. The interaction of the precatalysts with EtAlCl_2 was also studied.

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Keywords: Dinitrosyl complexes; Molybdenum; Metathesis; ROMP; Olefin; Acetylene; Living polymerization

1. Introduction

Chemistry of nitrosyl metal complexes is of special interest because of the relevance of nitric oxide in biological systems [1–8], the possibility of their application as reactive intermediates in organic and organometallic synthesis as well as in catalytic processes [9–14].

In many of these reactions, important role is played by carbene nitrosyl complexes [15–20], in particular dinitrosyl complexes of molybdenum and tungsten [12,18,21,22]. Dinitrosyl complexes

of the sixth group have the electron structure of $\{\text{M}(\text{NO})_2\}^6$ [23,24]; the products of their reduction are also known [25–27]. The dinitrosylmolybdenum complexes with $\{\text{Mo}(\text{NO})_2\}^6$ electronic structure belong to the most active catalysts of acyclic and cyclic olefin metathesis [18,28]. They are also very active catalyst of polymerization of acetylenes [29].

The aim of this study was to test the catalytic activity of new dinitrosylmolybdenum complexes with $\{\text{Mo}(\text{NO})_2\}^5$ electronic structure, i.e. $[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2]\text{Cl}$ and $[\text{Mo}(\text{NO})_2\text{Cl}_3(i\text{PrOH})]\cdot 3^i\text{PrOH}$, and to define the compound that is the real catalyst. Activity was examined in metathesis reaction of pent-2-ene, ROMP of norbornene, polymerization of phenylacetylene, hex-2-yne and *tert*-butylacetylene

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and in reaction of vinyltrimethoxysilane with poly-*tert*-butylacetylene.

2. Experimental

2.1. General data

All experiments were performed under argon atmosphere with standard Schlenk techniques and vacuum-line procedure. Solvents were purified and distilled under argon from appropriate agents. Norbornene was purified according to the literature [30]. The complexes, $\{\text{Mo}(\text{NO})_2(\text{OEt})_2\text{EtOH}\}_n$, $\{\text{MoNO}_2(\text{O}^i\text{Pr})_2\}_n$ [31] $\{\text{CrNO}_2(\text{OEt})_2\}_n$ [12] and $\{\text{W}(\text{NO})_2(\text{OEt})_2\text{EtOH}\}_n$, [13] were prepared according to the published procedure. IR spectra were measured using an Impact 400 (Nicolet) spectrophotometer. ^1H and ^{13}C NMR spectra were recorded using a Bruker ARX 300 spectrometer. Magnetic susceptibility measurements were made by the Gouy method over the temperature range 77–295 K. EPR spectra were recorded using a Bruker ESP 300E spectrometer.

2.2. Metathesis and polymerization reaction of alkenes and alkynes

Detailed procedures for performing metathesis and polymerization reactions were described elsewhere [13,32]. $[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2]\text{Cl}$ is not soluble in PhCl, but when EtAlCl_2 was added (at -10°C) to its suspension and the mixture was next heated to room temperature, a homogeneous system was formed. The catalytic reaction were quenched by methanol. In the case of polymerization reactions, methanol insoluble products were dried in vacuo, and polymer yields were determined gravimetrically.

The investigated catalytic reactions were monitored by gas chromatography, and the products were identified by GC–MS analysis (HP-5809II + 5971A). The weight-average molecular weight (\bar{M}_w) of the obtained methanol-insoluble polymers was determined by gel permeation chromatography (GPC) using polystyrene calibration (HPLC-HP-10990II with DAD-UV/VIS and RJ detector HP-1047A).

2.3. Synthesis of $[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2]\text{Cl}$

EtSiCl_3 in CH_2Cl_2 was added to a stirred solution of $\{\text{M}(\text{NO})_2(\text{OEt})_2\text{EtOH}\}_n$ in CH_2Cl_2 in 1/3 molar ratio. After about 3 h the solvent was removed under vacuum. The remainder was dissolved in MeCN and stored at room temperature during 24 h and next 24 h in refrigerator. The obtained green crystals were filtered off, washed with MeCN and CH_2Cl_2 and dried in vacuo (yield 33%).

IR (nujol mulls): $\nu(\text{CN})$ 2326 m, 2297 m, $\nu_s(\text{NO})$ 1823 versus $\nu_{\text{as}}(\text{NO})$ 1708 versus $\nu(\text{MoCl})$ 315 m, 289 m, cm^{-1} . Anal.: Calc. for $\text{C}_4\text{H}_6\text{N}_4\text{Cl}_3\text{Mo}$: C 13.95, H 1.76, N 16.27%. Found: C 14.00, H 1.82, N 16.19%.

2.4. Synthesis of $[\text{Mo}(\text{NO})_2\text{Cl}_3(\text{O}^i\text{Pr})]\cdot 3^i\text{PrOH}$

EtSiCl_3 in CH_2Cl_2 was added to a stirred solution of the complex $\{\text{MoNO}_2(\text{O}^i\text{Pr})_2\}_n$ in CH_2Cl_2 in 1/2 molar ratio. After about 3 h, CH_2Cl_2 was removed under vacuo. The remainder was dissolved in $^i\text{PrOH}$ and stored at room temperature during 24 h. The solution was removed under vacuum. The remainder was dissolved in CH_2Cl_2 , filtered off and the product was precipitated with pentane. The green complex was filtered off, washed with hexane and dried in vacuo (yield 29%).

IR (nujol mulls): $\nu_s(\text{NO})$ 1838 s, $\nu_{\text{as}}(\text{NO})$ 1710 versus $\nu(\text{OR})$ 1091 s, 921 m, $\nu(\text{MoCl})$ 315 m, 296 w, cm^{-1} . Anal.: Calc. for $\text{C}_{12}\text{H}_{32}\text{N}_2\text{Cl}_3\text{MoO}_6$: C 28.67, H 6.42, N 5.57%. Found: C 28.72, H 6.49, N 5.45%.

3. Results and discussion

3.1. Synthesis

Reaction of $\{\text{Mo}(\text{NO})_2(\text{OEt})_2(\text{EtOH})\}_n$ and $\{\text{Mo}(\text{NO})_2(\text{O}^i\text{Pr})_2\}_n$ complexes with Me_3SiCl in PhCl produces the appropriate alkylidene complexes, stable in MeCN [33], which induce olefins to polymerize. However, reaction of these dialkoxydinitrosylmolybdenum complexes (electronic structure of $\{\text{Mo}(\text{NO})_2\}^6$) with Et_3SiCl in coordinating solvents, e.g. MeCN and $^i\text{PrOH}$, leads to formation of paramagnetic complexes, $[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2]\text{Cl}$ ($\mu_{\text{eff}} = 2.07 \text{ MB}$, $\Theta = -28 \text{ K}$) and $[\text{Mo}(\text{NO})_2\text{Cl}_3(^i\text{PrOH})]\cdot 3^i\text{PrOH}$ ($\mu_{\text{eff}} = 2.12 \text{ MB}$, $\Theta = -31 \text{ K}$), respectively.

The mechanisms of these reactions is not clear yet. Analogical dialkoxynitrosyl tungsten and chromium complexes, in reaction with Et_3SiCl in coordinating solvents, undergo completely destruction which products do not contain nitrosyl ligands. In the case of chromium complex, decomposition process passes through mononitrosyl intermediate compound ($\nu(\text{NO}) = 1659 \text{ cm}^{-1}$).

The $\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2\text{Cl}$ complex is crystalline, green, weakly soluble in MeCN, MeNO_2 and alcohol and insoluble in CH_2Cl_2 , PhCl and toluene. Preliminary crystallographic investigations (Kuma M4) showed that it crystallizes in rhombic crystal system (space group Pnma, $Z = 4$). The cation $[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{CH}_3\text{CN})_2]^+$ is situated on the plane of symmetry. The NO and Cl^- ligands are coordinated in *cis* positions, while MeCN in *trans* positions with respect to them (Fig. 1). The non-coordinated chloride anion is situated along the MeCN–Mo–NCMe axis. The character of its IR spectrum is consistent with this model ($\nu_s(\text{NO}) = 1823 \text{ cm}^{-1}$, $\nu_{\text{as}}(\text{NO}) = 1708 \text{ cm}^{-1}$, $\nu(\text{CN}) = 2326$ and 2297 cm^{-1} ; $\nu(\text{MoCl}) = 315$ and 288 cm^{-1}). The IR spectrum of the complex $[\text{Mo}(\text{NO})_2\text{Cl}_3(i\text{PrOH})]\cdot 3i\text{PrOH}$ also contains two

$\nu(\text{NO})$ bands (1838 and 1710 cm^{-1}) and $\nu(\text{MoCl})$ (316 and 296 cm^{-1}). The nitrosyl-stretching frequencies are not much higher than $\nu(\text{NO})$ of their 18-electron analogs ($\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2$ ($\nu_s = 1805 \text{ cm}^{-1}$, $\nu_{\text{as}} = 1685 \text{ cm}^{-1}$) [34] and $\text{Mo}(\text{NO})_2\text{Cl}_2(i\text{PrOH})_x$ ($\nu_s = 1805 \text{ cm}^{-1}$, $\nu_{\text{as}} = 1692 \text{ cm}^{-1}$) [35]. The $[\text{Mo}(\text{NO})_2\text{Cl}_3(i\text{PrOH})]\cdot 3i\text{PrOH}$ complex is green, too, and soluble in alcohols, diethyl ether, PhCl and CH_2Cl_2 . Its solubility confirms the assumed structure, i.e. existence of three coordinated chloride ligands.

EPR spectra of powdered $[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2]\text{Cl}$ and these of CH_2Cl_2 solution of $\text{Mo}(\text{NO})_2\text{Cl}_3(i\text{PrOH})\cdot 3i\text{PrOH}$ were measured at room temperature. All these spectra consist of a single, strong central resonance ($g = 1.9473$ and 1.9469 , respectively). For $\text{Mo}(\text{NO})_2\text{Cl}_3(i\text{PrOH})\cdot 3i\text{PrOH}$ in CH_2Cl_2 solution, the central resonance in the EPR spectrum clearly displays broad satellites ($A = 41.1 \text{ G}$) due to ^{95}Mo and ^{97}Mo hyperfine coupling ($I = 5/2$, natural abundance 15.9 and 9.6%, respectively). No ^{14}N hyperfine coupling is evident in these spectra, like in the respective mononitrosylmolybdenum complexes [36,37]. This observation indicates the minimum delocalization of non-paired electron density on to the nitrosyl ligands.

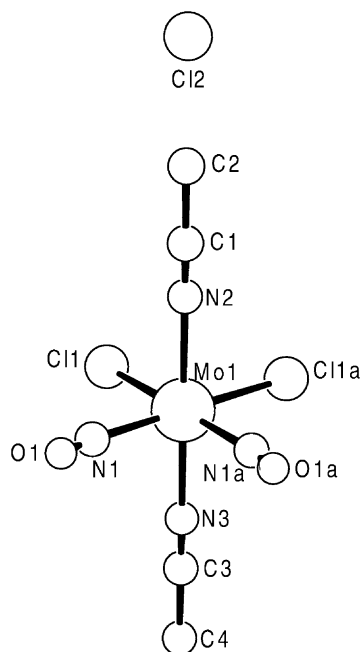


Fig. 1. Structure of the $[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{CH}_3\text{CN})_2]\text{Cl}$ molecule.

3.2. Catalytic activity

3.2.1. Cationic polymerization

The cationic compounds as well as dinitrosyl complexes $[\text{M}(\text{NO})_2(\text{MeCN})_4]^{2+}$ were found to catalyze the polymerization of acetylenes and olefins [10]. A test of the ability of these cationic compounds to generate incipient carbonium ions by interaction with olefins involved the reaction of *tert*-butylethylene with these compounds [10]. When comparing $[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2]\text{Cl}$ and $[\text{Mo}(\text{NO})_2\text{Cl}_3(i\text{PrOH})]\cdot 3i\text{PrOH}$ complexes, only $[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2]\text{Cl}$ was found to catalyze the skeletal rearrangement of *tert*-butylethylene to tetramethylethylene at room temperature in MeNO_2 . If incipient carbonium ion is generated by the reaction of $[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2]\text{Cl}$ with olefins, this complex should act as good initiator for cationic polymerization. The polynorbornene (55% yield in 24 h) obtained in the reaction of norbornene (NB) with $[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2]\text{Cl}$ (reaction conditions: MeNO_2 as solvent, room temperature, concentration

Table 1

Metathesis of pent-2-ene by $[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2]\text{Cl}$ and $[\text{Mo}(\text{NO})_2\text{Cl}_3(i\text{PrOH})]\cdot 3^i\text{PrOH}/\text{EtAlCl}_2$ systems^a

Complex	$[\text{Mo}]/[\text{EtAlCl}_2]$	t_a (min)	Conversion ^b (%)
$[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2]\text{Cl}$	6	2	54
	9	2	54
	12	2	54
	6	30	46
	9	30	51
	12	30	54
	9	60	48
	12	60	52
$[\text{Mo}(\text{NO})_2\text{Cl}_3(i\text{PrOH})]\cdot 3^i\text{PrOH}$	9	2	54
	12	2	54
	9	30	52
	12	30	54

^a Reaction conditions: solvent PhCl, $[\text{Mo}] = 2.0 \times 10^{-4}$ M, $[\text{Mo}]/[\text{olefin}] = 1/100$, $t_r = 2$ min, room temperature.^b Into but-2-ene and hex-3-ene.

of complex $[\text{Mo}] = 2.0 \times 10^6$ M; $[\text{Mo}]/[\text{NB}] = 1/100$) appears to be virtually insoluble in all common organic solvents, a feature indicative of the presence of extensive cross-linking [38].

3.2.2. Metathesis reaction

Catalytic activity of $[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2]\text{Cl}$ and $[\text{Mo}(\text{NO})_2\text{Cl}_3(i\text{PrOH})]\cdot 3^i\text{PrOH}$ complexes in metathesis reaction was examined using EtAlCl_2 as cocatalyst and pent-2-ene as the tested olefin (Table 1). Both the systems show identical catalytic activity. The metathesis equilibrium [39] was established after the reaction time (t_r) of 2 min. However, activities of both systems depend on the aging time (t_a) and on the molar ratio of $[\text{Mo}]/[\text{EtAlCl}_2]$. After $t_a \geq 30$ min and $t_r = 2$ min, for the systems with $[\text{Mo}]/[\text{EtAlCl}_2] \geq 1/9$, the metathesis equilibrium was not reached. The reason of this was instability of these systems. Stability increases with increasing concentration of cocatalyst compared to that of precatalysts (Section 3.3).

Catalytic activities of the examined systems are higher than that of appropriate systems of 18-electronic dinitrosylmolybdenum complexes [18], in which the metathesis equilibrium was established after $t_r = 5$ –15 min.

3.2.3. Cross-metathesis reaction

Degradation of unsaturated polymers by cross-metathesis with alkenes occurs in the presence of molyb-

denum and tungsten catalysts leading to oligomer [28,40–43].

Both the title complexes form also very active systems for such reaction. Degradation of polyphenylacetylene (PPA) and polynorborene (PNB) in cross-metathesis reactions with *trans*-hex-3-ene was investigated. These reactions were carried out in the presence of $[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2]\text{Cl}$ and $[\text{Mo}(\text{NO})_2\text{Cl}_3(i\text{PrOH})]\cdot 3^i\text{PrOH}/\text{EtAlCl}_2$ (1/9 and 1/12 molar ratio, respectively; $[\text{Mo}] = 2.0 \times 10^{-4}$ M, $t_a = 2$ min) catalytic systems in PhCl solutions at room temperature. The molar ratios of the polymer units ($[\text{=PU=}]$) to *trans*-hex-3-ene were 1:1 (for PPA $\bar{M}_w = 2.28 \times 10^4$, for PNB $\bar{M}_w = 4.36 \times 10^4$) and that of $[\text{Mo}]/\text{hex-3-ene}$ was 1/100. The runs of cross-metathesis reactions were monitored by determining the hex-3-ene conversion. Both the systems show also identical activity in these catalytic reactions. After 15 min, about 65% *trans*-hex-3-ene (in molar ratio to the respective polymer) was converted in each system ($[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2]\text{Cl}$: PPA 67.1%, PNB 62.9%; $[\text{Mo}(\text{NO})_2\text{Cl}_3(i\text{PrOH})]\cdot 3^i\text{PrOH}$: PPA 67.0%, PNB 63.0%). As it is usual in metathesis investigations, the units in the degradation products ($[\text{=PU=}]$) are considered from one double bond to the next. The expected units $[\text{=PU=}]_x$ ($x = 1$ –5 for PPA and 1–6 for PNB) were found. The main products (~60%) were oligomers with molecular weights corresponding to three and four polymer units.

Table 2

ROMP of norbornene by $[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2]\text{Cl}$ and $[\text{Mo}(\text{NO})_2\text{Cl}_3(i\text{-PrOH})]\cdot 3^i\text{PrOH}/\text{EtAlCl}_2$ (1/9 and 1/12 molar ratio, respectively) systems

Complex	Conversion (%)	Polymer			
		Yield (%)	$\bar{M}_w/10^5$	\bar{M}_w/\bar{M}_n	<i>cis</i> (%)
$[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2]\text{Cl}$	75.0	75.0	2.36	2.90	91.2
$[\text{Mo}(\text{NO})_2\text{Cl}_3(i\text{-PrOH})]\cdot 3^i\text{PrOH}$	75.0	74.8	2.36	2.92	91.1

3.2.4. ROMP of norbornene

No literature data on polymerization of norbornene (NB) by nitrosyl molybdenum complexes— EtAlCl_2 systems are available. Polymerization of norbornene was investigated using $[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2]\text{Cl}$ and $[\text{Mo}(\text{NO})_2\text{Cl}_3(i\text{-PrOH})]\cdot 3^i\text{PrOH}/\text{EtAlCl}_2$ (1/9 and 1/12 molar ratio, respectively; $[\text{Mo}] = 2.0 \times 10^{-4} \text{ M}$, $t_a = 2 \text{ min}$, $[\text{Mo}]/[\text{NB}] = 1/100$) systems in PhCl (5 cm^3) solutions at room temperature (Table 2). After 10 min norbornene was converted in 75% using both systems and the yield of polynorbornene was 75% ($\bar{M}_w = 2.36 \times 10^{-4}$, $\bar{M}_w/\bar{M}_n = 2.90$). These polymerization reactions of norbornene were in 100% the ring opening metathesis polymerization (characterized by IR [44,45] and NMR spectra [45–47]) and their stereoselectivity were high (91% *cis*-polymer).

3.2.5. Polymerization of phenylacetylene and hex-2-yne

Polymerization of phenylacetylene was examined using systems based on the both title complexes in the same reaction conditions (except t_r) as used for

the ROMP of norbornene (Table 3). In these conditions, phenylacetylene was converted in 88.6% after 10 min (87% yield of polymers) for both examined catalytic systems. In $\text{Mo}(\text{NO})_2(\text{O}_2\text{CPh})_2/\text{EtAlCl}_2$ system 100% conversion was observed (yield of polymer 80%) but after 4 h [29]; however, in the system with $\{\text{Mo}(\text{NO})_2(\text{OEt})_2\text{EtOH}\}_n$ after 15 min phenylacetylene was converted in 90% with the yield of polymer equal to 65% [48] (Table 3). The weight-average molecular weight \bar{M}_w of the obtained polyphenylacetylene is higher than that obtained in $\text{Mo}(\text{NO})_2(\text{O}_2\text{CPh})_2$ and $\{\text{Mo}(\text{NO})_2(\text{OEt})_2\text{EtOH}\}_n$ systems, but still rather low. This fact can be caused by kinetic effects as well as by possible degradation induced by the polymerization catalyst. The latter explanation is consistent with earlier observations that phenylacetylene, which has no substituent at *ortho* position, does not form high molecular weight polymers in the presence of Mo catalysts [49].

The structures of the obtained polyphenylacetylenes were determined by ^1H NMR and IR spectroscopies [50–53]. The polymers were identified as *trans*-cisoidal.

Table 3

Polymerization of phenylacetylene (PA) and hex-2-yne by $[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2]\text{Cl}$ and $[\text{Mo}(\text{NO})_2\text{Cl}_3(i\text{-PrOH})]\cdot 3^i\text{PrOH}/\text{EtAlCl}_2$ (1/9 and 1/12 molar ratio, respectively) systems^a

Complex	Monomer	Conversion (%)	Polymer ^b		
			Yield (%)	$\bar{M}_w/10^3$	\bar{M}_w/\bar{M}_n
$[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2]\text{Cl}$	PA	88.6	87.1	5.64	3.08
$[\text{Mo}(\text{NO})_2\text{Cl}_3(i\text{-PrOH})]\cdot 3^i\text{PrOH}$	PA	88.6	87.2	5.62	3.08
$[\text{Mo}(\text{NO})_2(\text{O}_2\text{CPh})_2]^c$	PA	100	80.0	1.0	1.15
$\{\text{Mo}(\text{NO})_2(\text{OEt})_2\text{EtOH}\}_n^d$	PA	90	65.0	2.0	
$[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2]\text{Cl}$	Hex-3-ene	32	32.0 ^e		

^a Reaction conditions: solvent PhCl , $[\text{Mo}] = 2.0 \times 10^{-4} \text{ M}$, $[\text{Mo}]/[\text{acetylene}] = 1/100$, $t_a = 2 \text{ min}$, $t_r = 10 \text{ min}$, room temperature.

^b Methanol-insoluble part.

^c [29], $t_r = 4 \text{ h}$.

^d [48], $t_r = 15 \text{ min}$.

^e Polymer insoluble in organic solvents.

When the mechanism of polymerization could be described by propagation through metal carbenes and cyclometallabutene intermediates, the polymer structure is determined by two mechanisms: (i) isomerization prior to the double bond formation—resulting in *cis*-transoidal isomer or *trans*-cisoidal isomer depending on the mode of cyclometallabutene opening [52,54–57], (ii) thermal isomerization after double bond formation—resulting in the *cis* to *trans* isomerization and cyclohexadiene sequences. The obtained results suggest that the former (i) mechanism decides on the microstructure of polyphenylacetylene formed in the tested systems.

Polymerization of hex-3-yne was carried out only with the $[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2]\text{Cl}/\text{EtAlCl}_2$ system (Table 3). Only 32% conversion of hex-3-yne was observed after $t_r = 10$ min. The yield of polymer was also 32% and the polymer was insoluble in organic solvents.

3.2.6. Living polymerization of *tert*-butylacetylene

Living polymerizations of substituted acetylenes have been achieved by using ternary catalysts based on MoOCl_4 [58–61], Schrock carbenes [62–65] and rhodium complexes [66]. We found that the tested complexes with EtAlCl_2 also cause living polymerization of *tert*-butylacetylene (Table 4). The reaction was carried out in the binary system based on $[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2]\text{Cl}$ complex in PhCl ($[\text{Mo}]/[\text{EtAlCl}_2] = 1/12$, $t_a = 2$ min). In this system, 100% yield of poly-*tert*-butylacetylene was achieved after 10 min. The *cis*-polymer content was determined by ^{13}C NMR [60]. Table 4 shows the result of so-called multistage polymerization. Monomer feeds was supplied twice repeatedly. The \bar{M}_n of the poly-*tert*-butylacetylene increased in appropriate proportion to the polymer yield. The \bar{M}_w/\bar{M}_n ratios were 1.10 and 1.15, respectively. These results clearly indicate that the

Table 4
Multistage polymerization of *tert*-butylacetylene by $[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2]\text{Cl}/\text{EtAlCl}_2$ (1/12 molar ratio) system

Polymer yield (%)	$\bar{M}_w/10^4$	\bar{M}_w/\bar{M}_n	<i>cis</i> -P- <i>t</i> -BA (%)
56	2.09	1.21	86.0
100	3.15	1.10	85.9
200	6.48	1.15	84.6

polymerization reaction of *tert*-butylacetylene using $[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2]\text{Cl}/\text{EtAlCl}_2$ system is living polymerization.

3.2.7. Reaction of poly-*tert*-butylacetylene with vinyltrimethoxysilane in the presence of $[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2]\text{Cl}/\text{EtAlCl}_2$ system

Vinylsubstituted silanes, however, appeared to be inactive for degradation of unsaturated polymers as well as for their ADMET polymerization in the presence of sixth group metal carbene catalysts [67–69]. Nevertheless, vinylsilanes were used for the reduction of the molecular mass of polymers [69] and very recently were also used for the metathetical degradation of 1,4-polybutadiene by ruthenium carbene complexes [70].

We investigated the reaction of poly-*tert*-butylacetylene with vinyltrimethoxysilane in the presence of $[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{MeCN})_2]\text{Cl}/\text{EtAlCl}_2$ catalytic system (1/6 molar ratio, $[\text{Mo}] = 1.10 \times 10^{-4}$ M, $t_a = 2$ min) in PhCl at room temperature. The molar ratio of $[\text{=PU=}]$ to vinylsilane was 1:1 and that of $[\text{Mo}]/[\text{vinylsilane}] = 1/100$. The initial molecular weight of poly-*tert*-butylacetylene was 6.70×10^4 ($\bar{M}_w/\bar{M}_n = 1.41$).

After 15 min more than 70% of vinyltrimethoxysilane was consumed, where 60% contributed to the increase of polymer mass (determined gravimetrically). It was confirmed by the ^1H NMR spectrum of the obtained polymer. In effect of this copolymerization, the molecular weight of polymer also increased to 3.34×10^5 ($\bar{M}_w/\bar{M}_n = 5.16$).

A product of this reaction (~3%) was also a polymer with menaingly lower molecular weight ($\bar{M}_w = 2.84 \times 10^3$, $\bar{M}_w/\bar{M}_n = 1.20$), containing small amounts of $[\text{=Si}(\text{OCH}_3)_3]$ units (^1H NMR: δ 3.49 (OCH₃), 6.47 ($\equiv\text{SiCH=}$)). The results indicate that the copolymerization reaction is accompanied by polymer degradation by cross-metathesis.

In this catalytic system, in identical reaction conditions, vinyltrimethoxysilane undergoes polymerization with 20% yield of polymer which is insoluble in all common organic solvents.

3.3. The interaction of precatalyst with EtAlCl_2

The constant values of $\nu(\text{NO})$ ($\nu_s = 1844 \text{ cm}^{-1}$ and $\nu_{\text{as}} = 1744 \text{ cm}^{-1}$), independent on other ligands

coordinated, are characteristic for ethylenedinitrosylmolybdenum complexes with $\{\text{Mo}(\text{NO})_2\}^6$ electronic structure, formed in EtAlCl_2 systems [21,22]. In the both systems tested these frequencies are higher: $\nu_s = 1858 \text{ cm}^{-1}$, $\nu_{as} = 1757 \text{ cm}^{-1}$ (for $[\text{Mo}]/[\text{EtAlCl}_2] = 1/6:1/12$ molar ratios; in PhCl). Identical alkylidene complexes formed in these systems have limited stability depending on the $[\text{Mo}]/[\text{EtAlCl}_2]$ molar ratio. For molar ratios $\geq 1/9$ they are stable by about 30 min whereas, for molar ratios $\leq 1/12$, they are stable for almost 60 min. After this time they undergo gradual destruction. The proof of that is decay of the frequency $\nu(\text{NO})$. Its complete disappearance was observed after approximately 24 h.

ESR experiments showed that, after addition of EtAlCl_2 to the precursor, new signals appear, identical in both systems, with $g = 1.9693$, which disappear after some time, as it was observed in IR spectra. Parallely, new signals ($g = 1.9847$) appear, with evident hyperfine structure (six lines, $A = 5.0 \text{ G}$, Fig. 2), undoubtedly caused by coupling with the nucleus of ^{27}Al ($I = 5/2$).

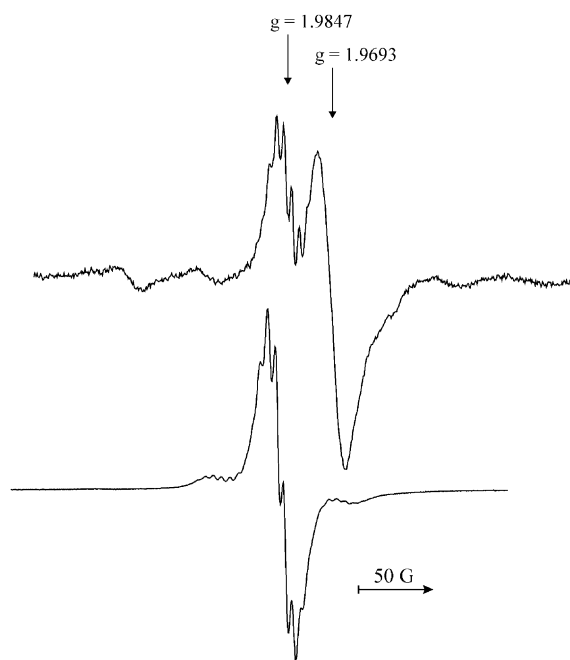


Fig. 2. EPR spectra of the $[\text{Mo}(\text{NO})_2\text{Cl}_2(\text{CH}_3\text{CN})_2]\text{Cl}/\text{EtAlCl}_2$ ($[\text{Mo}]/[\text{EtAlCl}_2] = 1/6$, in PhCl , room temperature) system after (a) 2 h, (b) 24 h.

The above results and the catalytic activities of these systems clearly indicate that identical catalyst (most probably ethylidene complex), with unaffected electronic structure, are formed in both systems and that their decomposition products are identical, too.

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References

- [1] S. Monacda, S.A. Marletta, J.B. Hibbs, M. Feelisch, in: R. Busse (Ed.), *The Biology of Nitric Oxide*, Vols. 1–4, Portland Press, Colchester, 1992–1994.
- [2] R.J.P. Williams, *Chem. Soc. Rev.* 25 (1996) 77.
- [3] G. Stochel, M. Pawelec, Z. Stasicka, *Wiad. Chem.* 51 (1997) 163.
- [4] A.R. Butler, D. Lyn, H. Williams, *Chem. Soc. Rev.* 22 (1993) 233.
- [5] P.L. Feldham, O.W. Griffith, D.J. Stuehr, *Chem. Eng.* 20 (1993) 26.
- [6] E. Cullota, D.E. Koshland Jr., *Science* 258 (1992) 18.
- [7] E.I.J. Ochiai, *Chem. Ed.* 73 (1996) 130.
- [8] G.B. Richter-Addo, P. Legzdins, *Metal Nitrosyls*, Oxford University Press, Oxford, 1992.
- [9] K.K. Pandey, *Coord. Chem. Rev.* 51 (1983) 69.
- [10] A. Sen, R.R. Thomas, *Organometallics* 1 (1982) 1251.
- [11] R. Taube, K. Seyferth, *Rev. Inorg. Chem.* 8 (1986) 31.
- [12] A. Keller, R. Matusiak, *J. Mol. Catal.* 145 (1999) 127.
- [13] R. Matusiak, A. Keller, *Polym. Bull.* 43 (1999) 199.
- [14] R. Poli, K.M. Smith, *Organometallics* 19 (2000) 2858.
- [15] G.B. Richter-Addo, P. Legzdins, *Chem. Rev.* 88 (1988) 991.
- [16] E.O. Fisher, *Rev. Pure Appl. Chem.* 24 (1970) 407.
- [17] J.A. McCleverty, J. Williams, *Transition Met. Chem.* 1 (1982) 760.
- [18] A. Keller, J.M. Sobczak, J.J. Ziółkowski, in: E.R. Braithwaite, J. Haber (Eds.), *Studies in Inorganic Chemistry*, Vol. 19, Elsevier, Amsterdam, 1994, Chapter 11, p. 618.
- [19] E. Tram, P. Legzdins, *J. Am. Chem. Soc.* 119 (1997) 5071.
- [20] C.S. Adams, P. Legzdins, E. Tram, *J. Am. Chem. Soc.* 123 (2001) 612.
- [21] A. Keller, *J. Organomet. Chem.* 407 (1991) 237.
- [22] A. Keller, *J. Organomet. Chem.* 436 (1992) 199.
- [23] J.H. Enemark, R.D. Feltham, *Coord. Chem. Rev.* 13 (1974) 339.
- [24] R.D. Feltham, J.H. Enemark, in: G.L. Geoffroy (Ed.), *Topics in Inorganic and Organometallic Stereochemistry*, Wiley/Interscience, New York, 1981 (Chapter 4).
- [25] D. Ballived-Tkachenko, A. Boughried, C. Bremard, J. *Electroanal. Chem.* 196 (1985) 315.

- [26] D. Ballived-Tkatchenko, A. Boughried, C. Bremard, *Inorg. Chem.* 25 (1986) 826.
- [27] P. Legzdins, B. Wassink, *Organometallics* 7 (1988) 482.
- [28] K.J. Ivin, J.C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, San Diego, 1997.
- [29] A. Keller, R. Matusiak, *J. Mol. Catal.* 142 (1999) 317.
- [30] J. Meinwald, N.H. Hudak, *Organic Synthesis*, Vol. 37, Wiley, New York, 1952, p. 65.
- [31] A. Keller, *Inorg. Chim. Acta* 149 (1988) 165.
- [32] A. Keller, R. Matusiak, *J. Mol. Catal.* 142 (1999) 317.
- [33] A. Keller, *J. Mol. Catal.* 78 (1993) L15.
- [34] D. Ballived-Tkatchenko, *J. Chem Soc., Dalton Trans.* 6 (1983) 1137.
- [35] L. Bencze, J. Kohan, B. Mohai, *Acta Chim. Hung.* 113 (1983) 183.
- [36] F.G. Herring, P. Legzdins, G.B. Rechter-Addo, *Organometallics* 8 (1989) 1485.
- [37] N.A. Obaidi, A.J. Edwards, C.J. Jones, J.A. McCleverty, B.D. Neaves, *J. Chem Soc., Dalton Trans.* 1 (1989) 127.
- [38] J.P. Kennedy, *Cationic Polymerization of Olefins: A Critical Inventory*, Wiley/Interscience, New York, 1975, p. 192.
- [39] W.B. Hughes, *J. Am. Chem. Soc.* 92 (1970) 532.
- [40] K. Hummel, *Pure Appl. Chem.* 54 (1982) 351.
- [41] K. Hummel, *J. Mol. Catal.* 28 (1985) 381.
- [42] E. Hubmann, K. Hummel, M. Doesinger, T. Pongratz, R. Saaf, *Makromol. Chem.* 191 (1990) 1799.
- [43] J.C. Marmo, K.B. Wagener, *Macromolecules* 28 (1995) 2602.
- [44] H. Balcar, M. Pacovská, *J. Mol. Catal.* 115 (1997) 101.
- [45] T.J. Katz, S.J. Lee, N. Acton, *Tetrahedron Lett.* 47 (1976) 4247.
- [46] C. Larroche, J.P. Laval, A. Lattes, M. Leconte, F. Quignard, J.M. Basset, *J. Org. Chem.* 47 (1982) 2019.
- [47] T. Steinhäusler, W.J. Koros, *J. Polym. Sci., Part B: Polym. Phys.* 24 (1997).
- [48] A. Keller, R. Matusiak, *J. Mol. Catal.* 104 (1996) 213.
- [49] G. Costa in: G. Allen (Ed.), *Comprehensive Polymer Science*, Vol. 4, Pergamon Press, Oxford, 1989 (Chapter 9).
- [50] C. Simionescu, V. Percec, S. Dumitresku, *J. Polym. Sci., Polym. Chem. Ed.* 15 (1977) 2497.
- [51] T.J. Katz, T.H. Ho, N.-Y. Shih, C.-Y. Ying, I.W. Van Stuard, *J. Am. Chem. Soc.* 106 (1984) 2659.
- [52] J. Kunzel, V. Percec, *J. Polym. Sci., Part A: Polym. Chem.* 28 (1990) 1221.
- [53] C. Simionescu, V. Percec, *J. Polym. Sci., Polym. Chem. Ed.* 18 (1980) 147.
- [54] V. Percec, P. Rinaldi, *Polym. Bull.* 9 (1983) 548.
- [55] V. Percec, *Polym. Bull.* 10 (1983) 1.
- [56] A. Furlani, C. Napeletano, V.M. Russo, W.J. Feast, *Polym. Bull.* 16 (1986) 311.
- [57] V. Percec, P. Rinaldi, *Polym. Bull.* 9 (1983) 58.
- [58] T. Yoshimura, T. Masuda, T. Higashimura, *Macromolecules* 21 (1988) 1899.
- [59] T. Mizumoto, T. Masuda, T. Higashimura, *Macromol. Chem. Phys.* 196 (1995) 1769.
- [60] T. Masuda, H. Izumikawa, Y. Misumi, T. Higashimura, *Macromolecules* 29 (1996) 1167.
- [61] S. Hyano, T. Itoh, T. Masuda, *Polymer* 40 (1999) 4071.
- [62] H.H. Fox, R.R. Schrock, *Organometallics* 11 (1992) 2163.
- [63] H.H. Fox, M.O. Wolf, R. O'Dell, B.L. Lin, R.R. Schrock, M.S. Wrighton, *J. Am. Chem. Soc.* 116 (1994) 2827.
- [64] R.R. Schrock, S. Luo, N. Zanetti, H.H. Fox, *Organometallics* 13 (1994) 3396.
- [65] R.R. Schrock, S. Luo, J.C. Lee, N. Zanetti, M.W. Davis, *J. Am. Chem. Soc.* 118 (1996) 3883.
- [66] Y. Kishimoto, T. Miyatake, T. Ikariya, R. Noyori, *Macromolecules* 29 (1996) 5054.
- [67] D.W. Smith, K.B. Wagener, *Macromolecules* 26 (1993) 1633.
- [68] E.S. Finkelstein, B. Marciniac, in: B. Marciniac, J. Chojnowski (Eds.), *Progress in Organosilicon Chemistry*, Gordon and Breach, London, 1995, p. 445.
- [69] R. Streck, *J. Mol. Catal.* 15 (1982) 3.
- [70] B. Marciniac, M. Lewandowski, J. Guliński, A.F. Noels, A. Demonceau, E. Matecka, D. Jan, *Polymer* 41 (2000) 827.