

# Reaction of alkylidenedinitrosylmolybdenum complexes with vinyl trisubstituted silanes and substituted acetylenes

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## Abstract

Reaction of  $\text{Mo}(\text{NO})_2(\text{CHMe})(\text{OR})_2(\text{AlCl}_2)(\text{EtAlCl}_2)$  ( $\text{R} = \text{Et}, \text{O-i-Pr}$ ) with vinyl silanes (vinyltrimethoxysilane and vinyltrimethylsilane) with substituted acetylenes (phenylacetylene and hex-2-yne) are studied. The ethylidene complex has been found to be an efficient catalyst for metathesis reaction of vinyl silanes. 1,2-Bis(trimethoxysilyl)ethene and ethylene are formed, via metathesis of vinyltrimethoxysilane, with a yield of above 80%. Similarly, the self-metathesis of vinyltrimethylsilane in the presence of this complex occurs, yielding 1,2-bis(trimethylsilyl)ethene and ethylene (yield below 20%). The latter reaction was accompanied by a dimerization leading to 1,4-bis(trimethylsilyl)butene-2 which was the prevailing product (above 30%). Trans-cisoidal poly(phenyl acetylene) with low molecular weight, as well as a polymer of hex-2-yne with high molecular weight are produced using this ethylidenemolybdenum complexes. Degradation of the poly(phenylacetylene) by cross-metathesis with vinyltrimethoxysilane was studied, too.

**Keywords:** Molybdenum; Nitrosyl; Alkylidene; Metathesis; Vinyl silanes; Acetylenes

## 1. Introduction

Reactions of dialkoxydinitrosylmolybdenum complexes with  $\text{EtAlCl}_2$  yield ethylidene  $\text{Mo}(\text{NO})_2(\text{CHMe})(\text{OR})_2(\text{AlCl}_2)_2$  complexes [1]. Reactions of such complexes with olefins give the respective alkylidene complexes; for example, in this way the propylidene  $\text{Mo}(\text{NO})_2(\text{CHEt})(\text{OEt})_2(\text{AlCl}_2)_2$  complex was obtained [1]c.

Dialkoxydinitrosylethylidenemolybdenum complexes are also formed in the reactions of  $(\text{Mo}(\text{NO})_2(\text{OR})_2)_n$  with  $\text{AlCl}_3$  (as Lewis acid), and  $\text{Et}_4\text{Sn}$  (as alkylating agent) [2]. The dicar-

boxylatodinitrosylethylidenemolybdenum complexes were prepared [3] in a similar way.

The low-valent metal centre, as well as the nucleophilic character of the carbene  $\text{C}_\alpha$ , cause that alkylidenedinitrosylmolybdenum complexes should be considered as a group of compounds different from Fisher-type carbenes (low-valent metals and electrophilic  $\text{C}_\alpha$ ) or Schrock-type carbenes (high-valent metal and nucleophilic  $\text{C}_\alpha$ ). The alkylidenedinitrosylmolybdenum complexes have been found to be highly active catalysts of metathesis of terminal, internal, and functionalized olefins, as well as cycloolefins [1–4].

In this paper we investigated reactions of alkylidenedialkoxydinitrosylmolybdenum complexes with vinyl trisubstituted silanes (vinyltrimethoxysilane and vinyltrimethylsilane) and with sub-

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stituted acetylene (phenylacetylene and hex-2-ene). The degradation of poly(phenylacetylene) by cross-metathesis with vinyltrimethoxysilane is reported too.

## 2. Experimental

All the experiments were performed under nitrogen atmosphere using standard Schlenk techniques and vacuum-line procedure. Reagents were purified by standard methods. Solvents were distilled from appropriate drying agents, i.e. sodium benzophenone ketyl or calcium hydride under nitrogen.  $(\text{Mo}(\text{NO})_2(\text{OEt})_2(\text{EtOH}))_n$  and  $(\text{Mo}(\text{NO})_2(\text{O-}i\text{-Pr})_2)_n$  were prepared according the published procedure [5]. IR spectra were measured by an Impact 400 (Nicolet) spectrophotometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR results are listed in ppm relative to TMS (Bruker 300). Metathesis oligomerization and polymerization reactions of olefins and acetylenes were monitored by gas chromatography, and the products were identified by GC-MS analysis (HP-5890II + 5971A).

The weight-average molecular weight ( $M_w$ ) of the obtained polymers was determined by gel permeation chromatography (GPC) using polystyrene calibration (HPLC-HP1090II with DAD-UV/VIS and RJ detector HP1047A).

### 2.1. Synthesis of $\text{Mo}(\text{NO})_2(\text{CHMe})(\text{O-}i\text{-Pr})_2(\text{AlCl}_2)_2(\text{EtAlCl}_2)$

This complex was synthesized in the same manner as described for  $\text{Mo}(\text{NO})_2(\text{CHMe})(\text{O-}i\text{-Pr})_2(\text{AlCl}_2)$  [1]b. However, the molar ratio of reacting substrates ( $(\text{Mo}(\text{NO})_2(\text{O-}i\text{-Pr})_2)_n$  and  $\text{EtAlCl}_2$ ) was 1:3 instead of 1:2.

IR (nujol mulls):  $\nu(\text{NO})$  1744 vs, 1844 vs.

$^1\text{H}$  NMR (in  $\text{CD}_3\text{CN}$  at  $-40^\circ\text{C}$ ):  $\delta$  7.12 (*q*, 1H,  $=\text{CHCH}_3$ ), 4.25 (*q*, 2H,  $\text{OCH}(\text{CH}_3)_2$ ), 1.20 (*d*, 12H,  $\text{OCH}(\text{CH}_3)_2$ ), 1.05 (*t*, 3H,  $\text{CH}_3\text{CH}_2\text{Al}$ ), 0.98 (*d*, 3H,  $=\text{CHCH}_3$ ), 0.02 (*q*, 2H,  $\text{CH}_3\text{CH}_2\text{Al}$ ).

Anal.: calc. for  $\text{C}_{10}\text{H}_{23}\text{N}_2\text{Al}_3\text{Cl}_6\text{O}_4\text{Mo}$ : C, 19.27; H, 3.85; N, 4.39; Cl, 34.10; Mo, 15.29%.

Found: C, 19.22; H, 3.71; N, 4.48; Cl, 34.04; Mo, 15.35%.

### 2.2. Metathesis of vinyl trisubstituted silanes

Detailed procedures for performing olefin metathesis reactions were described elsewhere [1]a.

### 2.3. Polymerization of phenylacetylene and hex-2-yne

Polymerization was initiated by adding a monomer solution to the catalyst solution and quenching by pouring the mixture into a large amount of methanol. Methanol-insoluble polymers were then dried in vacuo and the reaction efficiency was determined gravimetrically.

## 3. Results and discussion

### 3.1. Dialkoxydinitrosylethylidenemolybdenum complexes

Reactions of  $(\text{Mo}(\text{NO})_2(\text{OEt})_2(\text{EtOH}))_n$  and  $(\text{Mo}(\text{NO})_2(\text{O-}i\text{-Pr})_2)_n$  with  $\text{EtAlCl}_2$  at 1:3 and 1:2 molar ratio yield the appropriate ethylidene  $\text{Mo}(\text{NO})_2(\text{CHMe})(\text{OR})_2(\text{AlCl}_2)_2$  ( $\text{R} = \text{Et}, i\text{-Pr}$ ) complexes [1]bc.

An excess of  $\text{EtAlCl}_2$  causes formation of the adduct

$\text{Mo}(\text{NO})_2(\text{CHMe})(\text{OR})_2(\text{AlCl}_2)_2(\text{EtAlCl}_2)$

[1]c. This adduct, with  $\text{R} = i\text{-Pr}$ , was isolated as green precipitate. Its IR spectrum in the  $\nu(\text{NO})$  region is typical of alkylidenedinitrosylmolybdenum complexes ( $\nu_s(\text{NO}) = 1844$  and  $\nu_{\text{as}}(\text{NO}) = 1744 \text{ cm}^{-1}$ ). In a  $^1\text{H}$  NMR spectrum (see Experimental section) all proton resonances of the coordination ligands were found.

Catalytic activity of the above adduct in olefin metathesis reaction is higher than that of appropriate  $\text{Mo}(\text{NO})_2(\text{CHMe})(\text{OR})_2(\text{AlCl}_2)_2$  complexes and only a bit lower than that of  $(\text{Mo}(\text{NO})_2(\text{OR})_2)_n/\text{EtAlCl}_2$  systems (for example at 1:3 molar ratio,  $\text{R} = i\text{-Pr}$ ). Table 1

Table 1  
Metathesis activity of dialkoxydinitrosylethylidenemolybdenum complexes<sup>a</sup>

Catalyst	<i>t<sub>r</sub></i> (min)	Conversion (%) of pent-2-ene <sup>b</sup>	Ref.
Mo(NO) <sub>2</sub> (CHMe)(OEt) <sub>2</sub> (AlCl <sub>2</sub> ) <sub>2</sub>	35	34 <sup>c</sup>	[1c]
Mo(NO) <sub>2</sub> (CHMe)(OEt) <sub>2</sub> (AlCl <sub>2</sub> ) <sub>2</sub> /EtAlCl <sub>2</sub> (1:1)	20	50	
(Mo(NO) <sub>2</sub> (OEt) <sub>2</sub> (EtOH)) <sub>n</sub> /EtAlCl <sub>2</sub> (1:4)	20	54	
Mo(NO) <sub>2</sub> (CHMe)(O- <i>i</i> -Pr) <sub>2</sub> (AlCl <sub>2</sub> ) <sub>2</sub>	35	31 <sup>c</sup>	[1c]
Mo(NO) <sub>2</sub> (CHMe)(O- <i>i</i> -Pr) <sub>2</sub> (AlCl <sub>2</sub> ) <sub>2</sub> /EtAlCl <sub>2</sub> (1:1)	25	50	
Mo(NO) <sub>2</sub> (CHMe)(O- <i>i</i> -Pr) <sub>2</sub> (AlCl <sub>2</sub> ) <sub>2</sub> (EtAlCl <sub>2</sub> )	25	49	
(Mo(NO) <sub>2</sub> (O- <i>i</i> -Pr) <sub>2</sub> ) <sub>n</sub> /EtAlCl <sub>2</sub> (1:3)	25	54	

<sup>a</sup> Reaction conditions: solvent, chlorobenzene; concentration of catalyst [Mo] = 2.5 × 10<sup>-4</sup> mol; [Mo]:[pent-2-ene] = 1:100; room temperature.

<sup>b</sup> Into but-2-ene and hex-3-ene.

<sup>c</sup> [Mo]:[pent-2-ene] = 1:400.

shows the results of metathesis reaction of pent-2-ene, using different dialkoxydinitrosylmolybdenum catalytic systems.

### 3.2. Reactions of dinitrosylethylidenemolybdenum complexes with vinyl trisubstituted silanes

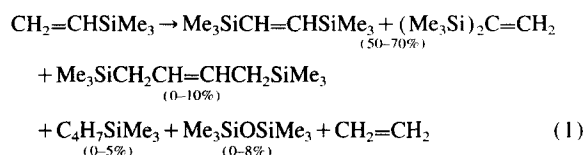
Silyl-olefins belong to a very important class of compounds widely applied in organic synthesis [6].

Alkenylsilanes, similarly to other unsaturated organosilicon compounds, do not participate easily in metathesis reactions. The first representative of the alkenylsilane series, vinyl trimethylsilane, was found inactive in self- and cross-metathesis in the presence of several catalysts [7]. This observation can be explained by the formation of metal-carbene complexes stabilized by vacant 3d orbitals of Si atoms, which are in  $\alpha$ -position relative to the carbene centre [7]b.

The imidoalkylidene tungsten and molybdenum complexes were shown to react with vinyltrimethylsilane, forming stable tungsten cyclobutanes and tungsten and molybdenum silylmethylene complexes, but not metathesis products [8].

In contrast to vinyltrimethylsilane, several vinylalkoxysilanes undergo this catalytic process [6]g,i-k,[9]. It was shown that, at 80–110°C, the homogeneous catalysts based on Ru and Rh complexes actively initiate the metathesis reaction, yielding the appropriate 1,2-bis(silyl)ethene.

Recently it was reported [10] that vinyltrimethylsilane also undergoes the self-metathesis in the presence of the catalysts based on Ru complexes, namely RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> and RuH<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>, according to the following reaction:



We studied reactions of vinyltrimethoxysilane and vinyltrimethylsilane with dinitrosylethylidenemolybdenum complexes synthesized 'in situ' from (Mo(NO)<sub>2</sub>(O-*i*-Pr)<sub>2</sub>)/EtAlCl<sub>3</sub> at 1:3 molar ratio, as well as Mo(NO)<sub>2</sub>(CHMe)(O-*i*-Pr)<sub>2</sub>(AlCl<sub>2</sub>)<sub>2</sub>(EtAlCl<sub>2</sub>) adduct. These reactions were carried out in PhCl at room temperature and monitored by gas chromatography. The products were identified by GC-MS and NMR methods by comparing their parameters with those of authentic sample [11].

Only minor differences in activities of the applied catalytic systems were observed (Table 2).

The main products of vinyltrimethoxysilane metathesis reaction are 1,2-bis(trimethoxysilyl)ethene (yield about 80%) and ethylene (reaction 2):

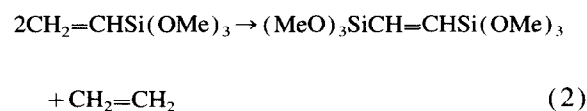


Table 2  
Metathesis of vinyltrimethoxysilane (I) and vinyltrimethylsilane (II) catalyzed by dinitrosylethylidenemolybdenum complexes<sup>a</sup>

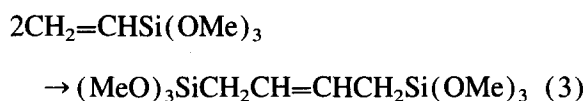
Catalyst	Olefin	<i>t<sub>r</sub></i> (h)	Conv. (%)	Yield (%)	
				III <sup>b</sup>	VI <sup>c</sup>
Mo(NO) <sub>2</sub> (CHMe)(O- <i>i</i> -Pr) <sub>2</sub> (AlCl <sub>2</sub> ) <sub>2</sub> (EtAlCl <sub>2</sub> )	I	24	86	78	8
	II	2	50	19	31
(Mo(NO) <sub>2</sub> (O- <i>i</i> -Pr) <sub>2</sub> ) <sub>n</sub> /EtAlCl <sub>2</sub> (1:3)	I	24	90	82	8
	II	2	52	12	33

<sup>a</sup> Reaction conditions: solvent, chlorobenzene; concentration of catalyst [Mo] = 2.4 × 10<sup>-4</sup> mol; [Mo]:[olefin] = 1:100, room temperature.

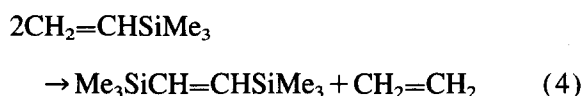
<sup>b</sup> 1,2-bis(silyl)ethene;

<sup>c</sup> 1,4-bis(silyl)-butene-2.

This process was accompanied by dimer 1,4-bis(trimethoxysilyl)butene-2 formation (yield about 8%):

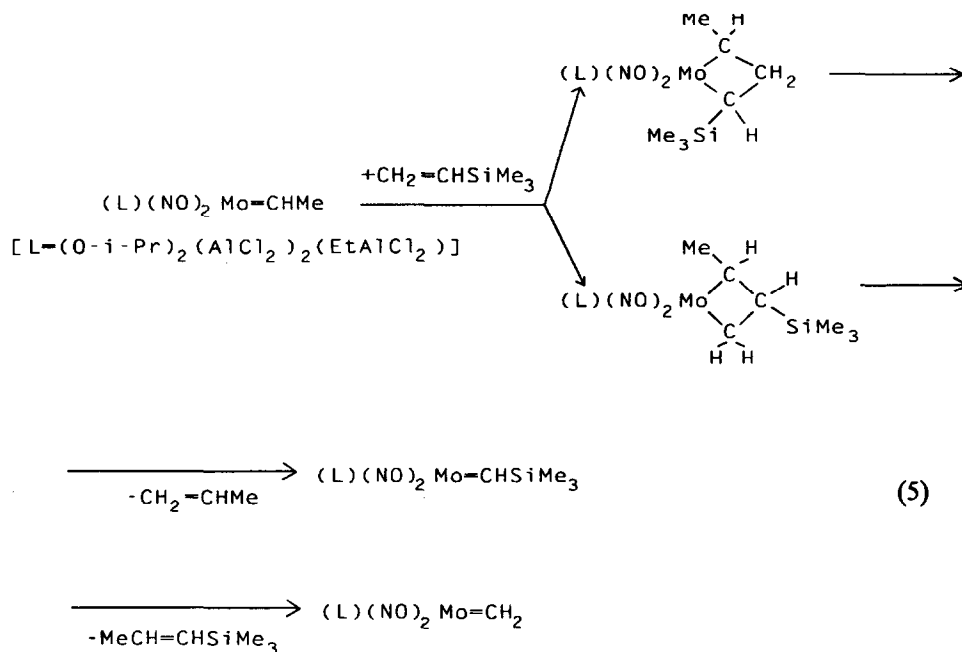


Vinyltrimethylsilane undergoes similar reactions but with different yields. In that case the dimer 1,4-bis(trimethoxysilyl)butene-2 was the main product (about 32%), while the metathesis reaction (reaction 4) product's yield was only about 19%.

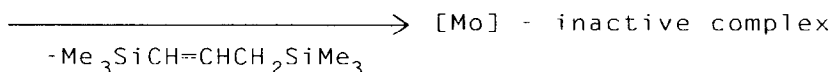
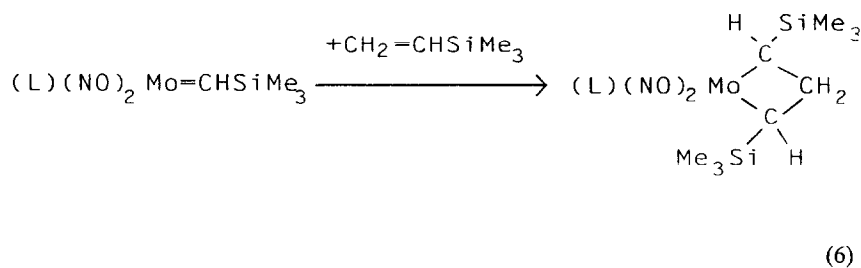


Other products, like CH<sub>3</sub>CH=CH<sub>2</sub>, CH<sub>3</sub>CH=CHSiMe and Me<sub>3</sub>SiCH=CHCH<sub>2</sub>SiMe<sub>3</sub> were found as traces.

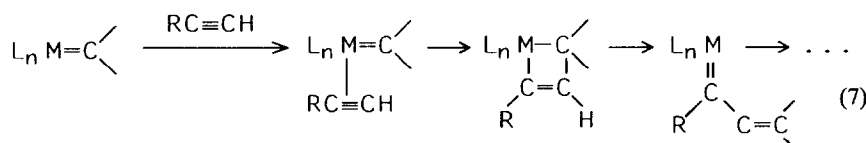
CH<sub>2</sub>=CHCH<sub>3</sub> and CH<sub>3</sub>CH=CHSiMe<sub>3</sub> were formed in a stoichiometric reaction of ethylidene catalyst with vinyltrimethylsilane (Eq. 5 – Scheme 1) with no doubt. However, Me<sub>3</sub>SiCH=CHCH<sub>2</sub>SiMe<sub>3</sub> was probably a product of deactivation reaction of the catalyst (Eq. 6 – Scheme 2). It results in vanishing of the catalytic



Scheme 1.



Scheme 2.



Scheme 3.

cal activity after about 2 hours (at 50% of the conversion of vinyltrimethylsilane; the reaction vessel open to ambient atmosphere).

### 3.3. Reaction of dinitrosylethylidenemolybdenum complexes with phenylacetylene and hex-2-yne

Polymerization of monosubstituted acetylenes takes an interest as a method for the preparation of polymers offering useful applications. It is known that the catalyst of olefin metathesis catalyze this reaction too [12]. Up to now, the alkylidenenitrosylmolybdenum complexes have not been tested in this reaction.

Mechanism of polymerization of terminal acetylenes was proposed: it was supposed to occur via metallalkylidene and metallacyclobutene intermediates [13] (Eq. 7 – Scheme 3).

Polymerization of phenylacetylene and hex-2-yne was examined using very active olefin metathesis catalysts [1,5]  $\text{Mo}(\text{NO})_2(\text{CHMe})(\text{OR})_2(\text{AlCl}_2)_2(\text{EtAlCl}_2)$  ( $\text{R} = \text{i-Pr}$  and  $\text{Et}$ ; in the latter case the compound was prepared in situ from  $(\text{Mo}(\text{NO})_2(\text{OEt})_2(\text{EtOH}))_n$  and  $\text{EtAlCl}_2$  at 1:4 molar ratio). Table 3 gives the results of this polymerization experiment carried at the molar ratio monomer:catalyst equal to 100 in  $\text{PhCl}$  at  $20^\circ\text{C}$ .

In these conditions phenylacetylene was converted in 75 and 90% after 15 min while the time of 100% conversion was 35 and 25 min, for dinitrosylethylidenemolybdenum catalysts with *O-i-Pr* and *OEt* ligands, respectively. The results were in contradiction with the conclusion that polymerization yield of phenylacetylene remains rather low when using  $\text{Mo}$  catalysts [13].

The weight-average molecular weight  $\bar{M}_w$  of the obtained polymers was low (about 2000). 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  $\text{Mo}$  catalysts [14]. Structure of poly(phenylacetylene) was determined by IR and NMR spectroscopy [13,15]. We identified the obtained poly(phenylacetylenes) as transcisoidal ones.

The gaseous products of the reaction of dialkoxidinitrosylethylidenemolybdenum complexes with phenylacetylene, after not more than 15 min, contained traces of acetylene, while the final ones contained methanol-soluble products, among others 1,3-hexadien-5-yne. It suggests that the polymerization reaction is accompanied by

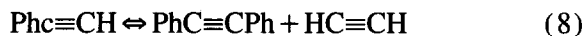
Table 3

Polymerization of phenylacetylene (PA) and hex-2-yne by dinitrosylethylidenemolybdenum catalyst<sup>a</sup>

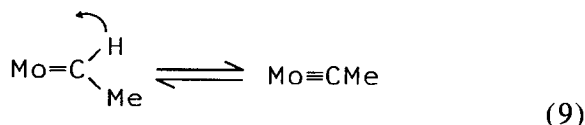
Catalyst	Monomer	<i>t<sub>r</sub></i> (min)	Conv. (%)	Polymer <sup>b</sup>	
				Yield (%)	<i>M<sub>w</sub></i> <sup>c</sup>
Mo(NO) <sub>2</sub> (CHMe)(O- <i>i</i> -Pr) <sub>2</sub> (AlCl <sub>2</sub> ) <sub>2</sub> (EtAlCl <sub>2</sub> )	PA	15	75	68	2000
		35	100		
Mo(NO) <sub>2</sub> (OEt) <sub>2</sub> /EtAlCl <sub>2</sub> (1:4)	PA	15	90	65	2000
		25	100		
	hex-2-yne	60	15	15	–

<sup>a</sup> Reaction conditions: solvent, chlorobenzene; concentration of catalyst [Mo] = 2.4 × 10<sup>-4</sup> mol, [Mo]:[monomer] = 1:100; *t<sub>r</sub>* = 20°C.<sup>b</sup> Methanol-insoluble part;<sup>c</sup> Determined by GPC.

metathesis reaction (reaction 8), which is probably only initialised by alkylidyne (carbyne) complexes.



Migration of ethylidene  $\alpha$ -hydrogen in dialkoxydinitrosylethylidenemolybdenum complexes [1]c (reaction 9) makes possible formation of the alkylidyne complexes.



Only 15% conversion of hex-2-yne was observed after 1 h, but the product was polymer of high molecular weight, insoluble in organic solvents. Its yield was 15% too.

### 3.4. Cross-metathesis of poly(phenylacetylene) with vinyltrimethoxysilane

Poly(phenylacetylene) obtained by polymerization of phenylacetylene in presence of the dinitrosylethylidenemolybdenum catalyst was degraded in cross-metathesis reaction with vinyltrimethoxysilane. This reaction was carried out in the presence of (Mo(NO)<sub>2</sub>(O-*i*-Pr))<sub>*n*</sub>/EtAlCl<sub>2</sub> (1:3 molar ratio, [Mo] = 2.5 × 10<sup>-4</sup> M) catalytic system in PhCl solution at room temperature. Molar ratio of [–PhC=CH–]<sub>*n*</sub> to CH<sub>2</sub>=CHSi(OMe)<sub>3</sub> was 1:*n* (*n* was calculated

from  $\bar{M}_w$ ), and that of [Mo]:CH<sub>2</sub>=CHSi(OMe)<sub>3</sub> was 1:100.

After 3 h 90% of CH<sub>2</sub>=CHSi(OMe)<sub>3</sub> was converted. The total number of the reaction products found was 18. The products (determined by GC-MS) were (MeO)<sub>3</sub>SiCH=CHSi(OMe)<sub>3</sub> (self-metathesis product), dienes and polydienes without silane groups CH<sub>2</sub>[=CH–CPh=]<sub>*x*</sub>CH<sub>2</sub>, containing one silane group CH<sub>2</sub>[=CH–CPh=]<sub>*x*</sub>CHSi(OMe)<sub>3</sub>, and with two silane groups (OMe)<sub>3</sub>SiCH[=CH–CPh=]<sub>*x*</sub>CHSi(OMe)<sub>3</sub>.

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