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Dinitrosylmolybdenum alkylidene complexes containing n-alkyl alkoxy ligands: synthesis, spectroscopic characterization and metathesis activity

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Abstract

Reactions of $\{Mo(NO)_2(OR)_2S\}_n$ and $\{Mo(NO)_2(OR)_2\}_2$ (R = Me, Et) with $EtAlCl_2$ at room temperature yield the ethylidene $[(AlCl_2)_2(\mu\text{-}OR)_2Mo(NO)_2(CHMe)]$ complexes. They were characterized by ^1H NMR and IR spectroscopy. They are examples of low-valent ethylidene complexes with nucleophilic =CHMe ligands.

These ethylidene complexes are the products of transformation of the adducts $[(EtAlCl_2)_2(\mu\text{-}OR)_2Mo(NO)_2]$ into diethyl-complexes, followed by α-hydrogen elimination. These adducts were also obtained and characterized. Reactions of the ethylidene complexes with hex-3-ene yield the respective propylidene complexes. In this way the complex $[(AlCl_2)_2(\mu\text{-}OEt)_2Mo(NO)_2(CHEt)]$ was obtained.

The alkylidene complexes are active catalysts for olefin metathesis. Addition of $AlCl_3$ to $([EtAlCl_2)_2(\mu\text{-}OR)_2Mo(NO)_2]$ also converted them into active catalysts.

Introduction

It has been widely demonstrated that many catalytic organic reactions are propagated by metal carbene complexes [1]. The catalysts could be either the low-valent (d^n) metal carbene complexes (Fisher type [2] and Casey type [3]) or the high-valent (d^0) alkylidene type [4]. The basic difference between those two types of complexes was that the carbon atom bonds to the metal were electrophilic in the metal carbene complexes and nucleophilic in the alkylidene complexes. Quite recently the first example of a low-valent dinitrosyl ethylidene molybdenum complex $\{Mo(NO_2)\}^6$ (the superscript denotes number of metal *d*-electrons) where the ethylidene ligand was nucleophilic in nature, was synthetized and characterized spectroscopically [5].

Here the synthesis, characterization and metathesis activity of new alkylidene dinitrosyl molybdenum complexes of the type $[(AlCl_2)_2(\mu\text{-}OR)_2Mo(NO)_2(CHR)]$ (R = Me, Et) are reported.

Experimental

All procedures were carried out in a dried and purified argon atmosphere. Solvents were purified and distilled under argon from appropriate drying agents.

$EtAlCl_2$ was purified by vacuum distillation (115 °C/50 mm). $\{Mo(NO)_2(OMe)_2MeCN\}_n$ (**1**), $\{Mo(NO)_2(OEt)_2EtOH\}_n$ (**2**), $\{Mo(NO)_2(OEt)_2\}_n$ (**3**) and $\{Mo(NO)_2(OEt)_2MeNO_2\}_n$ (**4**) were prepared by a published method [6].

IR spectra were measured on Specord M80 and Perkin Elmer 180 spectrophotometers. ^1H NMR spectra were recorded on a Tesla BS567A spectrometer and were referenced to Me_4Si. Solutions in CD_3CN of the complexes were prepared for ^1H NMR spectra measurements with the temperature lowered at least to −10 °C. GLC analyses were performed on a N-503(Elpo) chromatograph.

Preparation of $[(EtAlCl_2)_2(\mu\text{-}OMe)_2Mo(NO)_2]$ *(5)*

A vigorously stirred mixture of **1** (1.5 mmol) in PhCl (10 cm^3) was cooled to −40 °C. A solution of $EtAlCl_2$ in hexane (5.0 mmol in 5.0 cm^3), cooled to −60 °C was added dropwise. Next, about 15–20 cm^3 of hexane was added at the same temperature. The green precipitate of an adduct settled down. It was filtered off, repeatedly washed with hexane and dried *in vacuo*.

Analysis. Found: C, 15.01; H, 3.85; N, 5.68; Al, 11.28; Cl, 30.12; Mo, 20.51. $C_6H_{16}N_1Al_2Cl_4MoO_4$ calc.: C, 15.27; H, 3.42; N, 5.94; Al, 11.43; Cl, 30.05; Mo, 20.33%. IR (Nujol mulls): 1820vs, 1710vs, 1150w, 1025m, br, 1000sh, 965sh, 930w, 850w, 825sh, 740m, 680m, 630m, 520sh, 492m, 410sh, 376m, 310sh, 300s, 250m.

Preparation of $[(EtAlCl_2)_2(\mu\text{-}OEt)_2Mo(NO)_2]$ *(6)*

This adduct was obtained in a manner similar to that described above, i.e. in the reaction of **2** or **4** with $EtAlCl_2$, at a temperature not exceeding −40 °C.

Analysis. Found: C, 19.31; H, 4.18; N, 5.03; Al, 10.85; Cl, 28.11; Mo, 18.98. $C_8H_{20}N_2Al_2Cl_4MoO_4$ calc.: C, 19.22; H, 4.03; N, 5.60; Al, 10.79; Cl 28.36; Mo, 19.19%. IR (Nujol mulls): 1822s, 1700vs, 1170w, 1040m, 995m, 960w, 925w, 895w, 840m, 810sh, 680m, 625m, 530w, 410m, br, 385w, 346m, 305m, 280m, 256.

Preparation of $[(AlCl_2)_2(\mu\text{-}OMe)_2Mo(NO)_2(CHMe)]$ *(7)*

To the solution of **1** in PhCl (1.5 mmol in 15 cm^3), the $EtAlCl_2$ in PhCl (4.5 mmol in 4.5 cm^3) was added dropwise, at about −5 °C, with vigorous stirring. The solution was heated to room temperature. When the reaction was completed (the reaction course was followed by IR spectra measurements in the ν(NO) range [7]) the solution was cooled to −40 °C. **7** was precipitated with hexane and pentane (at temperature not exceeding −40 °C) from this solution. The green product was filtered off, repeatedly washed with hexane and dried *in vacuo*.

Analysis. Found: C, 10.55; H, 2.63; N, 6.00; Al, 12.42; Cl, 32.80; Mo, 21.66. $C_4H_{10}N_2Al_2Cl_4MoO_4$ calc.: C, 10.87; H, 2.28; N, 6.34; Al, 12.21; Cl, 32.10; Mo, 21.71%. IR (Nujol mulls): 1840s, 1740s, 1160m, 1120w, 995m, 970m, 940m, 892w, 825m, 680m, 645sh, 560m, 530sh, 410m, 356m, 302s, 260m.

Preparation of $\{(AlCl_2)_2(\mu\text{-}OMe)_2Mo(NO)_2(CHMe)\}_n$ *(7a)*

To the solution of **1** and $EtAlCl_2$ in PhCl (25 cm^3) heated to room temperature (see above) hexane (5 cm^3) was added 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*.

Analysis. Found: C, 11.05; H, 2.43; N, 6.12; Al, 12.63; Cl, 32.22; Mo, 21.82. $C_4H_{10}N_2Al_2Cl_4MoO_4$ calc.: C, 10.87; H, 2.28; N, 6.34; Al, 12.21; Cl, 32.10; Mo, 21.71%. IR (Nujol mulls): 1830vs, 1820vs, 1152w, 1020m, br, 995sh, 845m, 820sh, 725sh, 680m, 630m, 550m, 422m, 382w, 315m, 300sh, 260m.

Preparation of $[(AlCl_2)_2(\mu\text{-}OEt)_2Mo(NO)_2(CHMe)]$ *(8) and* $\{(AlCl_2)_2(\mu\text{-}OEt)_2Mo(NO)_2(CHMe)\}_n$ *(8a)*

8 and **8a** were obtained following the procedures described for **7** and **7a**. The complexes **3** or **4** and $EtAlCl_2$ in PhCl at 1 : 2.5 and 1 : 3 molar ratios, respectively, were used as substrates.

Analysis for **8**. Found: C, 15.51; H, 3.21; N, 5.61; Al, 11.12; Cl, 30.42; Mo, 20.22. $C_6H_{14}N_2Al_2Cl_4MoO_4$ calc.: C, 15.34; H, 3.00; N, 5.96; Al, 11.48; Cl, 30.18; Mo, 20.42%. IR (Nujol mulls): 1844vs, 1740vs, 1165w, 1110m, 1020sh, 990m, 963sh, 935w, 820s, 780sh, 740sh, 700s, 632m, 568m, 420, 349m, 305s, 255m.

Analysis for **8a**. Found: C, 15.12; H, 3.53; N, 5.50; Al, 11.29; Cl, 30.68; Mo, 20.71. $C_6H_{14}N_2Al_2Cl_4MoO_4$ calc.: C, 15.34; H, 3.00; N, 5.96; Al, 11.48; Cl, 30.18; Mo, 20.42%. IR (Nujol mulls): 1826vs, 1721vs, 1150w, 1085w, 1060sh, 1022m, 990m, 950sh, 925w, 815s, 678m, 660sh, 640sh, 622w, 570sh, 540, 520sh, 475w, 306m, 255m.

Preparation of $[AlCl_2)_2(\mu\text{-}OEt)_2Mo(NO)_2(CHEt)]$ *(9)*

To the solution of **3** or **4** with $EtAlCl_2$ in PhCl, prepared as described for **8** and heated to the room temperature, hex-3-ene was added (Mo : hex-3-ene = 1 : 50). After about 10 min the solution was cooled to −40 ° C. Subsequent procedure was as described for **7** and **8**.

Analysis. Found: C, 17.42; H, 3.48; N, 5.28; Al, 11.30; Cl, 29.41; Mo, 20.01. $C_7H_{16}N_2Al_2Cl_4MoO_4$ calc.: C, 17.37; H, 3.33 N, 5.79; Al, 11.15; Cl, 29.30; Mo, 19.83%. IR (Nujol mulls): 1842vs, 1740vs, 1170w, 1095m, 1040sh, 995s, 960sh, 930w, 822s, 750sh, 700s, 630m, 565s, 423m, 349w, 306s, 256m.

Preparation of $\{(AlCl_2)_2(\mu\text{-}OEt)_2Mo(NO)_2(CHEt)\}_n$ *(9a)*

Method A. To the solution of **3** or **4** with $EtAlCl_2$ in PhCl and hex-3-ene (see above), after 1 h 5 cm^3 hexene was added. The solution was left until the brown precipitate settled down.

Method B. To the solution of **8** in PhCl (0.5 mmol in 10 cm^3) hex-3-ene (10 mmol) was added. The brown precipitate, which settled down after about 24 h, was filtered off, washed with hexane and dried *in vacuo*.

Analysis. Found: C, 17.50; H, 3.60; N, 5.12; Al, 11.01; Cl, 29.12; Mo, 19.92. $C_7H_{16}N_2Al_2Cl_4MoO_4$ calc.: C, 17.37; H, 3.33; N, 5.79; Al, 11.15; Cl, 29.30; Mo, 19.83%. IR (Nujol mulls): 1825vs, 1721vs, 1165w, 1100m, 1020m, 990m, 960sh, 930w, 815m, 680m, 660sh, 640sh, 620w, 570sh, 540m, 520sh, 482w, 305m, 255m.

Results and discussion

High-valent (d^0) alkylidene complexes are usually formed after abstraction of the intramolecular α-hydrogen atom from alkyl ligands [8]. The pathway of the alkylidene dinitrosyl molybdenum complexes formation is similar [5,7]. Alkoxy dinitrosyl molybdenum complexes form, with $EtAlCl_2$, the 1 : 2 adducts,

$$\left.\begin{array}{l} Mo(NO)_2(OR)_2 \longrightarrow \\ Mo(NO)_2(OR)_2L \xrightarrow{-L} \end{array}\right] \xrightarrow{2EtAlCl_2} [(EtAlCl_2)_2(\mu\text{-}OR)_2Mo(NO)_2] \qquad (1)$$

(**5**: R = Me; **6**: R = Et; **10**: R = ^iPr)

Table 1

^{1}H NMR data [a] and ν(NO) frequencies [b] for **5**, **6** and **10**

Complex	δ (ppm), J(HH) (Hz)					ν(NO) (cm^{-1})
	CH$_3$	CH$_2$	OR			
			CH$_3$	CH$_2$	CH	
5	0.90 (t, 3H) J(HH) = 7.3	−0.2 (q, 2H) J(HH) = 7.3	3.42 (s, 3H)			1820 1710
6	0.93 (t, 3H) J(HH) = 7.9	−0.15 (q, 2H) J(HH) = 7.9	1.10 (t br, 3H) J(HH) = 8.0	4.15 (br, 2H)		1822 1700
10 [c]	0.98 (t, 3H) J(HH) = 7.5	−0.03 (q, 2H) J(HH) = 7.5	1.25 (d, 6H) J(HH) = 7.4		4.25 (q, 1H) J(HH) = 7.4	1836 1723

[a] In CD$_3$CN at −40 °C. [b] In Nujol mulls. [c] Ref. 5.

which next undergo intramolecular ethylation followed by α-hydrogen atom elimination to produce the alkylidene complexes:

$$[(\mathrm{EtAlCl_2})_2(\mu\text{-OR})_2\mathrm{Mo(NO)_2}] \rightarrow [(\mathrm{AlCl_2})_2(\mu\text{-OR})_2\mathrm{Mo(NO)_2Et_2}] \xrightarrow[-\mathrm{EtH}]{}$$

$$[(\mathrm{AlCl_2})_2(\mu\text{-OR})_2\mathrm{Mo(NO)_2(CHMe)}] \xrightarrow{\text{time}}$$

$$(\mathbf{7}\text{: R} = \text{Me; } \mathbf{8}\text{: R} = \text{Et; } \mathbf{11}\text{: R} = {}^{i}\text{Pr})$$

$$\{(\mathrm{AlCl_2})_2(\mu\text{-OR})_2\mathrm{Mo(NO)_2(CHMe)}\}_n$$

$$(\mathbf{7a}\text{: R} = \text{Me; } \mathbf{8a}\text{: R} = \text{Et; } \mathbf{11a}\text{: R} = {}^{i}\text{Pr}) \qquad (2)$$

10 and **11** were synthesized and spectrally characterized [5]. **5** and **6** were obtained from complexes **1** and **2** or **4**, respectively (reaction 1). These adducts are green precipitates reacting with oxygen and moisture. They are insoluble in alkanes and soluble to a certain extent in PhCl and CH$_2$Cl$_2$. Their IR spectra (see Experimental Section) display two ν(NO) bands (Table 1) typical for *cis*-$\{\mathrm{Mo(NO)_2}\}^6$ cores [9]. The character of these spectra in the ν(OR) region (ν(CO) < 1050 cm^{-1}) indicates bridge (Mo–OR–Al) coordination of the alkoxy-ligands [10].

The ^{1}H NMR data for the adducts in CD$_3$CN at −40 °C are presented in Table 1. Temperature increase (to 30 °C) has no effect on the character of the spectrum of **5**, but is responsible for the trace H$_\alpha$ resonance of the ethylidene group. Instead, in the case of **6**, besides giving rise to trace H$_\alpha$ resonances of =CHMe, the temperature increase results in decay of the multiplicity of signals of the CH$_2$ and CH$_3$ of ethoxy ligands in the ^{1}H NMR spectrum. This phenomenon, as well as the broad nature of the CH$_2$ resonance at −40 °C is due to the dynamic exchange process, e.g. bridge ↔ terminal OEt ligands exchange. Some effect could be exercised here by the basic character of the solvent.

Quite recently, for **10** the structure [5] was postulated where two EtAlCl$_2$ molecules are attached to the OR ligands to form simultaneously the Mo–Et–Al bridges. Such a structure could also be proposed for **5** and **6**. It is very favourable for their subsequent intramolecular transformation, leading to the formation of the respective alkylidene complexes (reaction 2).

In the solid phase, however, these adducts have most likely a polymeric, or at least dimeric, structure. Their IR bands in the range 350–250 cm^{-1}, which should be assigned to the valence vibration of Al–Cl–M (M = Al, Mo) bridges, suggest the bonding mode of monomeric forms. Such a polymeric structure would stabilize the adduct, making difficult the intramolecular transformation which could lead to the formation of the respective ethylidene complexes (reaction 2). Hence, their ^1H NMR spectra at 30 °C display only trace H_α signals of ethylidene ligands. This is followed by the trace catalytic activity of these adducts in metathesis of pent-2-ene. The activity increases remarkably in the presence of $AlCl_3$ (2×10^2 molar equivalent of pent-2-ene converts into but-2-ene and hex-3-ene after about 1.5 and 2 h for **5** and **6**, respectively). $AlCl_3$ is undoubtedly responsible for degradation of polymeric structures and allows the formation of the dialkyl intermediates, and then of the alkylidene complexes.

The monomeric species **5** and **6** in solvents (PhCl, PhMe, etc.) at room temperature, undergo rapid intramolecular conversion to diethyl complexes. Next α-hydrogen elimination leads to the formation of **7** and **8** [7] (reaction 2). These complexes were isolated as green precipitates, sensitive to air and moisture. In the solid state, they may be stored indefinitely at room temperature under an inert atmosphere. **7** and **8** are insoluble in alkanes and soluble in PhCl and CH_2Cl_2. After some time, however, the brown precipitates settle down, their quantitative composition unchanged. They are thus the polymeric species of **7** and **8**, i.e. $\{(AlCl_2)_2(\mu\text{-}OR)_2Mo(NO)_2(CHMe)\}_n$ (reaction 2). The formation of such polymeric compounds has already been suggested earlier [5,7]. Both forms of these complexes suffer decomposition under effect of H_2O and HCl:

$$\begin{aligned}&\mathbf{7},\ \mathbf{7a},\ \mathbf{8},\ \mathbf{8a},\ \mathbf{11},\ \mathbf{11a} \xrightarrow{H_2O,\ HCl}\\ &\qquad \text{Mo}^{VI}\text{-complexes} + -[CH(CH_3)CH(CH_3)]_n- + -[CH_2CH_2]-\\ &\qquad\qquad\qquad\qquad\qquad (\sim 80\%) \qquad\quad (\sim 20\%) \qquad\qquad (3)\end{aligned}$$

Decomposition products were determined by ^1H NMR and IR spectroscopy.

The alkylidene complexes **7**,**7a**, and **8**,**8a** are among the few of that type which contain β-hydrogens. They are also new examples, besides **11** and **11a** [5], of alkylidene complexes with nucleophilic α-carbon, at a low-oxidation state. The $\nu(NO)$ frequencies observed in their IR spectra (see Experimental Section and Table 2) are characteristic of *cis*-dinitrosyl molybdenum complexes of the $\{Mo(NO)_2\}^6$ electronic structure, i.e. the same as that of their precursors [6]. The character of these spectra in the $\nu(OR)$ region ($\nu(CO) < 1050$ cm^{-1}) indicates bridge coordination of the alkoxy ligands [10].

The $\nu(NO)$ frequencies for **7a** and **8a** are somewhat lower than the respective ones for **7** and **8**. This may be due to the increase of electron density on the central atoms of **7a** and **8a**, perhaps because of the formation of the additional bondings with electron donor chloride ions of the adjacent molecules. The bands in the range 350–250 cm^{-1} in the IR spectra of **7a**,**8a** and **7**,**8** are indicative for the Al–Cl–M (M = Al, Mo) interaction also in the solid phase of monomeric species. No differences were observed in the ^1H NMR spectra of the monomeric (**7**,**8**) and polymeric (**7a**,**8a**) species, respectively. The ^1H NMR spectra in CD_3CN at −40 °C of these alkylidene complexes are presented in Table 2. The high-field ^1H NMR

Table 2

^1H NMR data [a] and $\nu(NO)$ frequencies [b] for **7**, **7a**, **8**, **8a**, **8b**, **9**, **9a**, **11** and **11a**

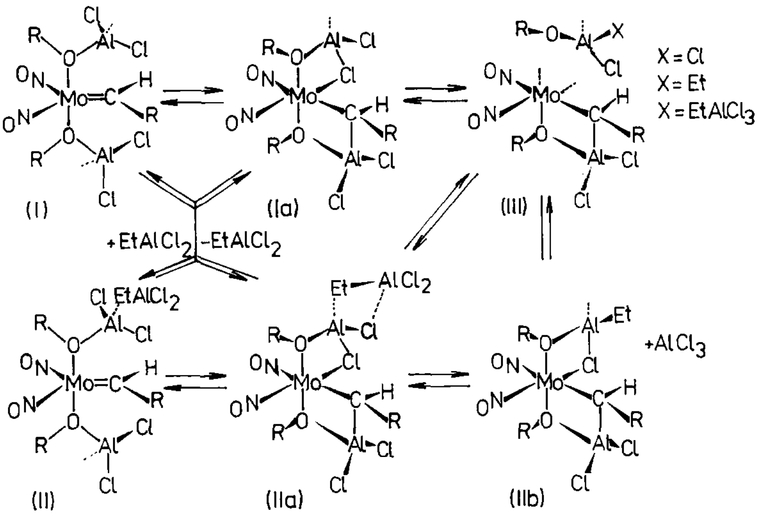
Complex	$\nu(NO)$ (cm^{-1})	δ (ppm), J(HH) (Hz)				
		=CHR		OR		
		H_α	R	CH_3	CH_2	CH
7	1840 1740	7.48 (q br, 1H) J(HH) = 10.5	0.92 (d, 3H) J(HH) = 10.5	3.52 (s, 6H)		
7a	1830 1720					
8	1844 1740	7.44 (q, 1H) J(HH) = 10.0	0.95 (d, 3H) J(HH) = 10.0	1.29 (t br, 6H) J(HH) = 7.9	4.00 (br, 4H)	
8a	1826 1721					
8b [c]	1840 1740	7.43 (q, 1H) J(HH) = 10.0	0.92 (d, 3H) J(HH) = 10.0	1.32 (t br, 6H) J(HH) = 8.0	3.98 (br, 4H)	
11	1848 1744	7.12 (q, 1H) J(HH) = 9.8	0.98 (d, 3H) J(HH) = 9.8	1.23 (d, 12H) J(HH) = 7.5		4.25 (br, 2H)
11a	1822 1720					
9	1842 1740	7.33 (t, 1H) J(HH) = 12.1	5.32 (d q, 2H) J(HH) = 12.1, 6.0	1.23 t, 6H) J(HH) = 7.9	3.93 (br, 4H)	
9a	1825 1721		1.00 (t, 3H) J(HH) = 6.0			

[a] In CD_3CN at −40 °C except **11** and **11a** that were recorded at +30 °C. [b] In Nujol mulls. [c] ^1H NMR spectrum of **8b** exhibits also CH_2 and CH_3 ($EtAlCl_2$) signals at 0.00 ppm (q, 2H, J(HH) = 8.0 Hz) and 1.04 ppm (t, 3H, J(HH) = 8.0 Hz), respectively.

resonances of α-hydrogen, typical for complex discussed here, are evidence for a nucleophilic character of alkylidene ligands [11]. The nucleophilic character is also implied by their chemical properties, for example, they do not react with nucleophilic reagents (e.g. CH_3CN).

In the complexes discussed here the $AlCl_2$ fragments attached to the alkoxy ligands keep their acidic character making it highly probable that the molybdenum and aluminum are bridged by alkylidene α-carbon (structure Ia; Scheme 1) as in Tebbe-type complexes [12].

The formation of such a bridge makes it possible for the second $AlCl_2$ group attached to alkoxy ligands to interact with the central atom of the chloride ion. This could be the reason for the lowering of the $\nu(M-Cl)$ vibration frequency in **7** and **8**. The $AlCl_2$ groups not involved in the alkylidene bridges could interact with the adjacent molecules to produce polymeric forms. They also could interact with, for instance, $EtAlCl_2$ excess, giving rise to the formation of the respective adducts (structures II, IIa; Scheme 1). Synthesis of **7**, **8** and **11** in more concentrated solutions with great $EtAlCl_2$ excess also yields such adducts; $[(AlCl_2)_2(\mu\text{-}OR)_2\text{-}$



Scheme 1

$Mo(NO)_2(CHMe)(EtAlCl_2)$] (R = Me (**7b**), R = Et (**8b**), R = ^iPr (**11b**)). Elemental analysis ($2 < Al : Mo < 3$) and the ^1H NMR examination revealed the equilibria shown in Scheme 1. The ^1H NMR data and $\nu(NO)$ frequencies of the product of reaction between **8** and $EtAlCl_2$ (**8b**) are exemplified in Table 2.

Constitution of structures I and II from Ia and IIa, respectively, (Scheme 1) by C_α–Al dissociation might be expected to provide an energetic reagent for reaction with organic compounds and might also be expected to be enhanced by the addition of a Lewis base which would complex with the aluminum atoms in structures I and II.

One of the main reasons for the stability of these complexes is their ability to form the structures Ia and IIa (Scheme 1). The other stabilizing factors are the powerful π-acceptor properties of NO groups and the coordination of the alkylidene ligand in the Mo–NO bonding plane from the side opposite to the NO ligands [7]. Here are the most favourable conditions for the formation of the $\pi_C \rightarrow$ Mo bonding. The strong electron withdrawing ability of the NO groups means the effective charges on Mo and C_α (i.e. calculated for $[Mo(NO)_2(PH_3)(=CH_2)]$ which are $+1.17$ and -0.34, respectively [7]), are very little lower than those calculated for the alkylidene molybdenum complex at high-oxidation state (i.e. $[Cl_5Mo{=}CHMe]$, which are $+1.54$ and -0.27, respectively [13]). The alkoxy ligands also exercise some stabilizing effect. Much less stable is the similar complex with the carboxylic ligands [14]. Still less stable are the alkylidene dinitrosyl molybdenum complexes, formed from the precursors containing the non-oxygen ligands [15]. The position of $\nu(NO)$ bands (1750, 1850 cm^{-1}) in the IR spectra of $[Mo(NO)_2Cl_2L_2]$–$EtALCl_2$ (L = py, HMPT) systems [15b] could suggest the formation of the appropriate alkylidene dinitrosyl molybdenum complexes.

The brown precipitates which settled down from the catalytic systems (**1**–$EtAlCl_2$–pent-2-ene and (**2** and/or **3**)–$EtAlCl_2$–pent-2-ene) were identified as the polymeric ethylidene complexes **7a**, **8a** [7].

Kress et al. [16] claimed to have observed formation of the ethylidene and propylidene complexes in 1 : 4 molar ratio on reaction of carbene with pent-2-ene.

The ^1H NMR spectra (in CD_3CN) of **7a** and **8a** precipitated from these systems revealed the presence of small admixtures of the related propylidene complexes. **7** and **8** were treated with pent-2-ene (ca. 50 molar equivalent) in PhCl at room temperature. After $t_r = 15$ min, PhCl and olefins were removed under dynamic vacuum, and the whole dry remnant was dissolved in CD_3CN. The ^1H NMR spectra of the products displayed the ethylidene and propylidene complexes, in a ratio close to that determined experimentally by Kress et al. [16].

$[(AlCl_2)_2(\mu\text{-OEt})_2Mo(NO)_2(CHEt)]$ (**9**) was obtained by following two paths: 1. reaction of **8** with hex-3-ene; 2. isolation from the system (**3** and/or **4**)–$EtAlCl_2$–hex-3-ene. Both paths are based on the metathesis reaction:

$$Mo{=}CHMe + EtCH{=}CHEt \leftrightarrow Mo{=}CHEt + MeCH{=}CHEt$$

After prolonged reaction, the polymeric forms $\{(AlCl_2)_2(\mu\text{-OEt})_2Mo(NO)_2(CHEt)\}_n$ (**9a**) were also obtained. The ^1H NMR and IR spectra of **9** and **9a** (see Experimental Section and Table 2) point to their structures being identical to those of **8** and **8a**.

Calculations for the model alkylidene dinitrosyl molybdenum complex were carried out by the extended Hückel method, and the horizontal conformation of $=CR_2$ ligands was found to be more favourable energetically than the vertical [17].

It was suggested [5] that the strong electron withdrawing effect of the NO groups and the bulky structure of the isopropoxy ligands could stop rotation around the Mo–carbon double bond in **11**. Its ^1H NMR spectra at +30 °C and −40 °C (Table 2) show no basic difference. Another factor which could also stop the rotation is the formation of Ia type structures (Scheme 1). This reason could apply to all the alkylidene complexes discussed here.

In the ^1H NMR spectra of **7**, **7ab**, **8**, **8ab**, **9** and **9a** at about +30 °C (contrary to **11** and **11a**) the H_α resonances occurred as sharp singlets (see for example Fig. 1b) and for **7** this signal displays a broad nature at −40 °C (Fig. 1c). A similar dynamic exchange process was also observed in the tungsten carbenes [16]. The alkylidene α- or β-hydrogen exchange or migration may be the cause of these phenomena. The

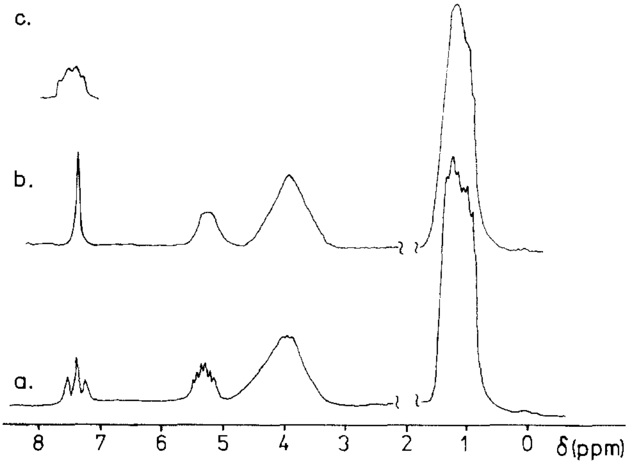


Fig. 1. ^1H NMR spectra of **9** in CD_3CN (signals of the solvent are omitted) at (a) −40 °C, (b) +30 °C and (c) H_α signal of **7** at −40 °C.

presence of $-[CH_2CH_2]-$ fragments in decomposition products of **7a**, **8**, **8a**, **11** and **11a** (reaction 3) could suggest the migration of β-hydrogens.

The nature of CH_2 resonance of propylidene ligand in the ^1H NMR spectrum of **9** at 30 °C (Fig. 1b) indicates that the observed process concerns α-hydrogen exchange (migration). This process depends markedly on the nature (π-donor strength) of the alkoxy ligands. In **11**, at room temperature this process is slow enough to show a resolved quartet for Mo=C*H*Me resonance [5] while in **7** this resonance still has a broad nature at −40 °C (Fig. 1c). It is well documented that the nature of the anionic ligands in the metal alkylidene complexes is the important factor facilitating or preventing the migration of an α-hydrogen [18].

In the alkylidene dinitrosyl molybdenum complexes with $\{Mo(NO)_2\}^6$ units so far recognized, the $\nu(NO)$ frequencies are almost independent of the kind of axial ligands [5,6b,7,14,15a]. This means that the electron density in the $\{Mo(NO)_2\}^{2+}$ moiety is stable in all complexes studied. The character of Mo=CHR bondings is thus greatly influenced by the electron-donating ability of the alkoxy ligands. The observed trends in chemical shifts of H_α (Table 2) have the same explanation. Similar trends were documented by Osborne [11ab] and Schrock [11c].

The broad singlets of methyl and ethylene resonances of ethoxy ligands in ^1H NMR spectra of **8**,**8a** and **9**,**9a** at room temperature are probably due to the bridging ↔ terminal OR ligands exchange as demonstrated in Scheme 1 (I and/or II ↔ III).

The formation of structures III (Scheme 1) could be quite an important stage in the olefin metathesis reaction mechanism.

The catalytic activity of **7**, **7a**, **8**, **8a**, **9** and **11** in pent-2-ene metathesis reactions is illustrated by the data in Table 3. The activity of monomeric species depends on the nature of the coordinated alkoxy ligands and decrease in the order **7** > **8** > **11**. The bulky character of the coordinated alkoxy ligands and the ease of getting the structure III (Scheme 1) support such an order. $AlCl_3$ facilitates the formation of

Table 3

Metathesis activity of **7**, **7a**, **8**, **8a**, **9** and **11** [a]

Catalyst	t_r (min)	Conversion of pent-2-ene [b] (mol%)
7	35	48
7+$AlCl_3$(1:1)	30	49
7a	60	no metathesis polimerization–15%
7a+$AlCl_3$	50	40
8	35	34
8+$AlCl_3$(1:1)	30	38
8a	60	no metathesis polimerization–20%
8a+$AlCl_3$	60	33
9	35	25
9+$AlCl_3$(1:1)	30	26
11	35	31
11+$AlCl_3$(1:1)	30	36

[a] Reaction conditions: solvent, chlorobenzene; concentration of catalysts $[Mo] = 2.5 \times 10^{-4}$ mol; [Mo]:[pent-2-ene] = 1:400. [b] Into but-2-ene and hex-3-ene.

active structures. As it has already been stated for W=CHR complexes [16], the reactivity for M=CHR arrangement with olefins declines in the order R = Me > Et (**8** > **9**).

The polymeric species **7a** and **8a** may catalyse the pent-2-ene polymerization reactions only, but in the presence of $AlCl_3$ they are converted into active catalysts of metathesis reactions.

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