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Alkylidenedinitrosylmolybdenum complexes. Preparation, characteristics and metathesis activity of dicarboxylatoethylidenedinitrosylmolybdenum complexes

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Abstract

New examples of ethylidenedinitrosylmolybdenum complexes $\{(AlCl_2)_2(O_2CR)_2Mo(NO)_2(CHMe)\}_n$ and $[(EtAlCl_2)_2(AlCl_2)_2(O_2CR)_2Mo(NO)_2(CHMe)]$ (R = Me, Ph) are characterized by IR and ^{1}H NMR spectroscopy. These complexes are the products of reaction of dicarboxylatodinitrosylmolybdenum precursors with $EtAlCl_2$. They are successive examples of low-valent nucleophilic alkylidene complexes. $[(EtAlCl_2)_2(AlCl_2)_2(O_2CR)_2Mo(NO)_2(CHMe)]$ complexes are active catalysts for olefin metathesis. $\{(AlCl_2)_2(O_2CR)_2Mo(NO)_2(CHMe)\}_n$ complexes catalysed this reaction only in the presence of $AlCl_3$. The dicarboxylatodinitrosylmolybdenum precatalysts also form active catalysts for olefin metathesis with Et_4Sn and $AlCl_3$. The ethylidene catalysts formed in these systems are also characterized by IR and ^{1}H NMR spectroscopy.

Introduction

The alkoxydinitrosylmolybdenum complexes $\{Mo(NO)_2(OR)_2\}_n$ (R = Et, ^{i}Pr) and $\{Mo(NO)_2(OR)_2S\}_n$ (R = Me, S = MeCN; R = Et, S = EtOH or $MeNO_2$) form 1:2 adducts $[(EtAlCl_2)_2(\mu\text{-}OR)_2Mo(NO)_2]$ with $EtAlCl_2$, which next undergo intramolecular ethylation followed by α-hydrogen elimination to produce the ethylidene complexes $[(AlCl_2)_2(\mu\text{-}OR)_2Mo(NO)_2(CHMe)]$ [1–3]. They are the first examples of stable alkylidene complexes in the low oxidation state with nucleophilic =CHR ligands. These ethylidene complexes react with olefins, *e.g.* hex-3-ene, yielding $[(AlCl_2)_2(\mu\text{-}OR)_2Mo(NO)_2(CHEt)]$ [3].

The alkoxydinitrosylmolybdenum precursors, with Et_4Sn and $AlCl_3$, form catalytically active systems for olefin metathesis [4]. The ethylidene catalysts formed in these systems were isolated as $\{(AlCl_3 \cdot Et_3Sn)_2(\mu\text{-}OR)_2Mo(NO)_2(CHMe)\}_n$ and spectroscopically characterized [5].

Alkylidenedialkoxydinitrosylmolybdenum complexes catalyse the metathesis of olefins [2,3] including functionalized olefins [6]. Dicarboxylatodinitrosylmolybdenum complexes also form highly active catalyst systems for olefin metathesis [7,8].

The goal of this work was the synthesis and characterization of new alkylidenedinitrosylmolybdenum complexes containing carboxylate ligands. Their olefin metathesis activity is also reported.

Experimental

All experiments were performed under an argon atmosphere with standard Schlenk techniques and vacuum-line procedures. Solvents were dried and purified under argon by standard techniques. $EtAlCl_2$ was purified by vacuum distillation. $AlCl_3$ was sublimed prior to use.

$[Mo(NO)_2(MeX)_4](BF_4)_2$ (**1**, X = CN [9]; **2**, X = NO_2 [10]) were prepared according to published methods. $\{Mo(NO)_2(O_2CMe)_2\}_n$ (**3**) resulted from reaction of **1** with $Na(O_2CMe)$ in MeCN solution [7]. $Mo(NO)_2(O_2CPh)_2$ (**4**), $[Mo(NO)_2(O_2CMe)_2] \cdot MeOH$ (**5**) and $Na_2[Mo(NO)_2(O_2CMe)_4]$ (**6**) were synthesized in $MeNO_2$/MeOH (1 : 1) solutions, by treatment of **2** with $Li(O_2CPh)$ and $Na(O_2CMe)$ in molar ratios of 1 : 2 and 1 : 4 respectively [8].

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 of the complexes for ^1H NMR spectra measurements were prepared at a temperature not exceeding −10°C. GLC analyses were performed on an N-504 (Elpo) chromatograph.

Preparation of $[(EtAlCl_2)_2(O_2CR)_2Mo(NO)_2]$ *(7, R = Me; 8, R = Ph)*

Compounds **7** and **8** were obtained from **5** (dried *in vacuo* at 100°C) and **4**, respectively, in a similar manner and under similar reaction conditions to those described for adducts $[(EtAlCl_2)_2(\mu\text{-}OR)_2Mo(NO)_2]$ [3].

7: Anal. Found: C, 18.98; H, 3.48; N, 3.48; N, 4.99; Al, 10.50; Cl, 27.11; Mo, 17.85. $C_8H_{16}N_2Al_2Cl_4MoO_6$ calc.: C, 18.20; H, 3.05; N, 5.31; Al, 10.22; Cl, 26,86; Mo, 18.17%.

8: Anal. Found: C, 33.01; H, 3.60; N, 3.98; Al, 8.49; Cl, 22.02; Mo, 15.00. $C_{18}H_{20}N_2Al_2Cl_4MoO_6$ calc.: C, 33.15; H, 3.09; N, 4.30; Al, 8.27; Cl, 21,75; Mo, 14.71%.

Preparation of $\{(AlCl_2)_2(O_2CR)_2Mo(NO)_2(CHMe)\}_n$ *(9a, R = Me; 10a, R = Ph)*

Compounds **9a** and **10a** formed in the reactions of **3** or **5**, the latter being dried *in vacuo* at 100°C before use (1.5 mmol in 15 cm^3 PhCl) with $EtAlCl_2$ (3.5 mmol in 4.5 cm^3 PhCl), respectively. These reactions were carried out following the procedure described for ethylidene dialkoxydinitrosylmolybdenum complexes [3]. The procedure was changed slightly, however: the $EtAlCl_2$ was added to a solution of **3** and **5** at −10°C and the resulting solution was not heated above 0°C.

9a: Anal. Found: C, 14.90; H, 2.42; N, 5.01; Al, 11.07; Cl, 28.70; Mo, 19.00. $C_6H_{10}N_2Al_2Cl_4MoO_6$ calc.: C, 14.47; H, 2.02; N, 5.63; Al, 10.84; Cl, 28,49; Mo, 19.27%.

10a: Anal. Found: C, 30.90; H, 2.32; N, 4.03; Al, 8.17; Cl, 22.60; Mo, 15.80. $C_{16}H_{14}N_2Al_2Cl_4MoO_6$ calc.: C, 30.89; H, 2.27; N, 4.50; Al, 8.67; Cl, 22,80; Mo, 15.43%.

Preparation of [(EtAlCl$_2$)$_2$(AlCl$_2$)$_2$(O$_2$CR)$_2$Mo(NO)$_2$(CHMe)] (9b, R = Me; 10b, R = Ph)

Compounds **9b** and **10b** were prepared as described above for **9a** and **10a** but at the different molar ratio of reagents of Mo/Al = 1 : 10.

9b: Anal. Found: C, 15.52; H, 2.33; N, 3.40; Al, 14.05; Cl, 37.85; Mo, 13.00. $C_{10}H_{20}N_2Al_4Cl_8MoO_6$ calc.: C, 15.98; H, 2.68; N, 3.73; Al, 14.35; Cl, 37,73; Mo, 12.76%.

10b: Anal. Found: C, 27.10; H, 2.89; N, 2.98; Al, 12.02; Cl, 32.00; Mo, 11.07. $C_{20}H_{24}N_2Al_4Cl_8MoO_6$ calc.: C, 27.42; H, 2.76; N, 3.20; Al, 12.32; Cl, 32,38; Mo, 10.95%.

Results and discussion

The interaction of carboxylatodinitrosylmolybdenum complexes with EtAlCl$_2$

Studies of the interaction of dinitrosylmolybdenum catalyst precursors of the $\{Mo(NO)_2(OR)_2\}_n$ (R = Et, ^{i}Pr) and $\{Mo(NO)_2(OR)_2S\}_n$ (R = Me, S = MeCN; R = Et, S = EtOH) types with EtAlCl$_2$ allowed the unequivocal characterization of the main stages of the formation of carbene catalyst [1].

The appropriate carbene (alkylidene) dinitrosylmolybdenum catalysts were isolated [2,3]. Their ν(NO) frequencies ($\nu_s \approx 1850$ cm^{-1}, $\nu_{as} \approx 1750$ cm^{-1}) do not depend on the alkoxy ligands. The IR spectra of dinitrosylethylidenemolybdenum complexes formed in the system of EtAlCl$_2$ with $[Mo(NO)_2(H_2NO)X_2L_2]^{n-}$ (L = X, $n = 2$; L$_2$ = phen, $n = 0$; X = Cl$^-$, NCS$^-$ N$_3^-$), $[Mo(NO)_2(HNO)_m(NCS)_2$-$L_2]^{n-}$ ($m = 0, 1$; L = NCS$^-$, $n = 2$; L$_2$ = phen, $n = 0$) [11], Mo(NO)$_2$Cl$_2$L$_2$ (L = py, HMPT) [12], Mo(NO)$_5$(BF$_4$)$_5$ [13], **3** [7] and also **4**, **5** and **6** (Table 1) exhibit the same positions of the ν(NO) bands. The alkylidene complexes formed in these systems are much less stable in solution at room temperature compared with their dialkoxydinitrosyl counterparts. The stabilizing effect was exercised by lowering the temperature, for example the ethylidene complex formed in the system based on **3** at 0°C suffers decomposition in PhCl solution only to about 5% after 24 h [7]. The ethylidene complexes formed in the systems with **5** and **6** exhibit similar stability to the complex formed from **3**. Complexes of this type in **4**/EtAlCl$_2$ proved to be relatively stable. Their IR ν(NO) bands do not change after several hours at room temperature.

Preparation and characterization of adducts 7 and 8

The first stage of the reaction between the dialkoxydinitrosylmolybdenum complexes and EtAlCl$_2$ is the formation of the appropriate adducts in 1 : 2 molar ratio [2,3]. The data in Table 1 concerning the lower temperatures suggest the formation of similar adducts from **4** and **5**:

$$\mathbf{4},\mathbf{5} \xrightarrow{2\mathrm{EtAlCl_2}} \underset{(\mathbf{7})\ \mathrm{R = Me}\ (\mathbf{8})\ \mathrm{R = Ph}}{[(\mathrm{EtAlCl_2})_2(\mathrm{O_2CR})_2\mathrm{Mo(NO)_2}]} \qquad (1)$$

Both adducts were isolated as analytically pure precipitates. Their synthesis was carried out below −40°C, because their intramolecular changes stopped at this temperature.

Table 1

ν(NO) frequencies in IR spectra of PhCl solutions of **4**, **5** and **6** with $EtAlCl_2$ and $Et_4Sn-AlCl_3$

Ratio Mo/Al/Sn	T_a (°C)	**4**			**5**			**6**		
		t_a (min)	ν_s (cm^{-1})	ν_{as} (cm^{-1})	t_a (min)	ν_s (cm^{-1})	ν_{as} (cm^{-1})	t_a (min)	ν_s (cm^{-1})	ν_{as} (cm^{-1})
–	–	–	1790s	1680vs	–	1770s	1650vs	–	1788s	1652vs
1/*n*/–[a]	25	5	1852s	1748vs	2	1848s	1748vs			
	0	5	1830sh	1725sh	5	1835sh	1730sh			
			1852m	1748s		1848s	1748s			
		40	1852s	1748vs	20	1848s	1744vs			
	−5	5	1825m	1725sh	2	1835sh	1730sh			
			1850m	1744vs		1848s	1748s			
		45	1852s	1748vs	35	1848s	1748vs			
1/6/–	25	2	1852s	1748vs	2	1748s	1748vs	5	1850s	1748vs
	−5	2	1830sh	1725sh	2	1748s	1748vs	5	1850s	1748vs
			1850s	1744vs						
		15	1852s	1748vs	60	1748s	1744s	60	1848s	1748vs
1/10/10	25	2	1820sh	1715sh	2	1825m	1725m			
			1830m	1730m		1848m	1748m			
			1850sh	1745sh						
		10	1820sh	1720sh	10	1825m	1725m			
			1835m	1735m		1835m	1730m			
			1844m	1748m		1850sh	1750sh			
		30	1825m	1725m	30	1830sh	1725m			
			1835m	1735m		1835s	1730s			
			1850sh	1750sh		1850sh	1750sh			

[a] $n = 2$ for **4** and $n = 3$ for **5**.

Two $EtAlCl_2$ molecules attached to the RCO_2^- ligands, simultaneously forming Mo–Et–Al bridges is the most likely structure for **7** and **8**.

The results of the theoretical calculations of the electronic structure of carboxylatodinitrosylmolybdenum complexes show that the oxygens of carboxylate ligands in *trans* positions to NO are the most pliant to electrophilic attack of Lewis acid molecules [8]. The largest negative charge gathers in the oxygen *trans* to NO and the Mo–O bonds in these positions are also the weakest.

The suggested structure of the adducts is very favourable for their subsequent intramolecular transformation, leading to the formation of the respective alkylidene complexes.

The adducts are light-green, oxygen- and moisture-sensitive precipitates unsoluble in alkanes, sparingly soluble in PhCl and soluble in MeCN.

The sparing solubility of these adducts in, *e.g.*, PhCl and CH_2Cl_2 and their IR bands in the range 350–250 cm^{-1} (Table 2), which should be assigned to the valence vibration of chloride bridges (Al–Cl–M; M = Mo or Al) bonding the monomeric forms, is proof of their polymeric structure. Such a structure, and perhaps the Mo–Cl–Al bridges instead of the Mo–Et–Al bridges, make transformation to the relative ethylidene complexes rather difficult. Their ^1H NMR spectra at 0°C and room temperature (in CD_3CN) exhibit only trace resonances of the ethylidene group.

Table 2

Selected IR bands [a] and chemical shift [b] of **7**, **8**, **9**, **9a**, **9b**, **10a** and **10b**

	7	**8**	**9a**	**9b**	**10a**	**10b**
$\nu_s(NO)$	1830s	1825s	1835s	1840s	1835s	1842s
$\nu_{as}(NO)$	1725vs	1725vs	1830vs	1740vs	1735vs	1740vs
$\nu_{as}(CO_2)$	1560s	1533s	1570s	1568s	1535s	1540s
$\nu_s(CO_2)$ [c]	1460br	1430s	1480s	1482s	1425s	1425s
			1420m	1420m		
$\nu(M-Cl)$	315m	307m	310m		303m	
	265m	280m	300sh		260m	
		256sh	265m			
$\delta(CHCH_3)$	Trace	Trace	7.49 (br,1H)	7.49 (br,1H)	7.53 (br,1H)	7.53 (br,1H)
$\delta(CHCH_3)$	Trace	Trace	1.00 (br,3H)	1.00 (br,3H)	1.02 (br,3H)	1.02 (br,3H)
$\delta(CH_2CH_3)$	−0.10 (q,2H)	−0.06 (q,2H)	Trace	−0.04 (q,4H)	Trace	−0.02 (g,4H)
$\delta(CH_2CH_3)$	0.95 (t,3H)	0.95 (t,3H)	Trace	0.90 (t,6H)	Trace	0.90 (t,6H)
$\delta(RCO_2^-)$	2.05 (s,3H)	7.75 (m,3H)	2.10 (s,6H)	2.10 (s,6H)	7.80 (m, 6H)	7.80 (m, 6H)
		7.30 (d,2H)			8.35 (d,4H)	8.35 (d,4H)

[a] In Nujol mulls. [b] In CD_3CN at −40°C. [c] In Fluorolube mulls.

The difference in the electron density distribution in **7**, **8** and their precursors **5**, **4** [8], respectively, is reflected in the appropriate shifts of the $\nu(NO)$ frequencies and in changes in the chemical shifts of the carboxylate protons (Table 2).

Compounds **7** and **8** are catalytically inactive in the olefin metathesis. They are activated by addition of $AlCl_3$, which undoubtedly is responsible for degradation of polymeric structures and consequently the formation of the active ethylidene catalysts.

Dicarboxylatodinitrosylethylidenemolybdenum complexes

Compounds **7** and **8**, when not isolated from the matrix solutions at temperatures over −30°C, undergo intramolecular transformations:

$$\mathbf{7}, \mathbf{8} \longrightarrow [(AlCl_2)_2(O_2CR)_2Mo(NO)_2(Et)_2] \xrightarrow[-EtH]{}$$

$$[(AlCl_2)_2(O_2CR)_2Mo(NO)_2(CHMe)] \quad (2)$$

$$(\mathbf{9})\ R = Me\ (\mathbf{10})\ R = Ph$$

These reactions proceed at temperatures above −30°C, as was discovered for the other nitrosyl precatalysts [14].

Both ethylidene complexes were isolated as yellow-green precipitates, sensitive to air and moisture. They are insoluble in alkanes, sparingly soluble in PhCl and readily soluble in CH_3CN. Such solubility, together with the presence of chloride bridge vibrations in their IR spectra in the range ~ 300 cm^{-1} is indicative of polymerization of the isolated ethylidene complexes, $\{(AlCl_2)_2(O_2CR)_2Mo(CHMe)\}_n$ (**9a**, R = Me; **10a**, R = Ph). Their $\nu(NO)$ values are lower compared to those of **9** and **10** (Table 2).

Ease of formation of the polymeric **9a** and **10a** species is due to the presence of strongly electrophilic $AlCl_2$ groups attached to the complex molecules by bridge carboxylate ligands.

The $AlCl_2$ fragments also interact with excess $EtAlCl_2$ to produce the appropriate adducts $[(EtAlCl_2)_2(AlCl_2)_2(O_2CR)_2Mo(NO)_2(CHMe)]$ (**9b**, R = Me; **10b**, R = Ph).

This is obviously the reason why the ^1H NMR spectra of **9a** and **10a** display traces of signals derived from the ethyl groups of the $EtAlCl_2$ molecules.

In the case of the alkylidenedialkoxydinitrosylmolybdenum complexes, only one $AlCl_2$ group is involved in the formation of such adducts; the second group contributes to the formation of the bridge with C_α of the ethylidene group, as in Tebbe type complexes [3].

Compounds **9b** and **10b** were also isolated as green, oxygen- and moisture-sensitive precipitates. They are insoluble in alkanes, soluble in PhCl and most readily soluble in MeCN. Their $\nu(NO)$ frequencies are not much different to those for **9a** and **10a**, respectively (Table 2). The frequencies, characteristic for $\{Mo(NO)_2\}^6$ units (the superscript denotes the number of metal *d*-electrons), should be regarded as typical for dinitrosylmolybdenum complexes with nucleophilic alkylidene ligands [2,3,5,11]. This nucleophilic character is also implied by the high-field ^1H NMR resonances of H_α (Table 2) and by the chemical properties of these ligands, *i.e.* they do not react with such nucleophilic reagents as, *e.g.* MeCN. However, such reagents could react with the $AlCl_2$ fragments to destroy the polymeric **9a** and **10a** species, and to detach $EtAlCl_2$ in the **9b** and **10b** adducts.

The only difference between the ^1H NMR spectra of **9a**, **10a** and **9b**, **10b** respectively is the presence of signals for the methyl and methylene protons of $EtAlCl_2$ in the latter (Table 2). All these spectra were taken at −40°C and 0°C, and for **10a** and **10b** at room temperature. The trend in the chemical shift of H_α in alkylidene complexes is as expected on the basis of the relative electron-withdrawing ability of the ligands [15,3]. In the series of ethylidene dinitrosylmolybdenum complexes, the $\delta(H_\alpha)$ values for **9a**, **9b** and **10a**, **10b** agree with this tendency. The H_α resonances of these complexes occur as sharp singlets at 0°C and room temperature and they display a broad nature with insufficient shaped multiplet structure at −40°C. The dynamic exchange processes inside the alkylidene ligands are also observed in other alkylidene complexes containing β-hydrogens [3,5,18]. α-Hydrogen migration may be the cause of these phenomena [3,15,19,20], but for complexes containing alkylidene ligands with β-hydrogen, this process can be more complicated.

The important factor facilitating the H_α migration is the nature of the coordinated ligands [3,15]. For complexes of the $\{Mo(NO)_2\}^6$ electronic structure, most important is the strong electron-withdrawing ability of NO ligands.

The alkylidene dinitrosyl molybdenum complexes containing carboxylate ligands, *i.e.* **9** and **10** (mainly **9**) are relatively less stable than those containing the alkoxy ligands [3]. The main reason for the stability of these complexes is the powerful π-acceptor properties of NO groups and the nature of the other ligands, *i.e.* the factors regulating the electron density on the central atom. The important stabilizing factor is the ability of alkylidene ligands to form bridge bondings with $AlCl_2$ fragments as in Tebbe-type complexes [21]. There is the possibility of the formation of such bondings in complexes with alkoxy ligands [3]. The bulky character of the coordinated ligands can stabilize the ethylidene complexes to some extent.

The catalytic activity of **9a**, **9b**, **10a** and **10b** in olefin metathesis is illustrated by

Table 3

Metathesis activity of **9a**, **9b**, **10a** and **10b**

Catalyst	t_r (min)	Conversion of pent-2-ene [a] (mol%)
9a	60	No metathesis Polymerization 12%
9a + $AlCl_3$ (1:2)	60	45
9b	45	49
9b + $AlCl_3$ (1:2)	30	40
10a	60	No metathesis Polymerization 10%
10a + $AlCl_3$ (1:2)	60	39
10b	30	30
10b + $AlCl_2$ (1:2)	30	35

[a] Into but-2-ene and hex-3-ene.

the data in Table 3. Compounds **9a** and **10a** are the active catalysts for olefin metathesis, but only in the presence of $AlCl_3$. Without $AlCl_3$, they may catalyse olefin polymerization only.

Compounds **9b** and **10b** catalyse metathesis reactions without the contribution of $AlCl_3$, but its presence increases the activity. Similar effects were also observed for other alkylidenedinitrosylmolybdenum catalysts [3].

$AlCl_3$ and $EtAlCl_2$ prevent the formation of polymeric forms of these catalysts but allow the formation of the structures most favourable for interaction with olefins.

Interaction of 4 and 5 with Et_4Sn–$AlCl_3$ co-catalysts

It was recently discovered that $\{Mo(NO)_2(OR)_2\}_n$, $\{Mo(NO)_2(OR)_2S\}_n$ and **3** form active catalytic systems for olefin metathesis with Et_4Sn as alkylating agent and $AlCl_3$ as Lewis acid [4]. The IR spectra (in the ν(NO) region) of these systems revealed that the appropriate carbene catalysts could be most efficiently generated when an Et_4Sn–$AlCl_3$ solution in Sn : Al = 1 : 1 molar ratio is introduced as precatalyst. This method was applied for the preparation of tricomponent systems with **4** and **5**. The ν(NO) bands observed in their IR spectra (Table 1) revealed that, in this case, the formation of the carbene catalysts was preceded by formation of the appropriate adducts:

$$\begin{aligned} \mathbf{3,4,5} &\xrightarrow{+2(Et_4Sn+AlCl_3)} [(Et_4Sn\cdot AlCl_3)_2(O_2CR)_2Mo(NO)_2] \xrightarrow[-EtH]{} \\ &\qquad (\mathbf{11})\ R=Me\ (\mathbf{12})\ R=Ph \\ &\qquad [(Et_3Sn\cdot AlCl_3)_2(O_2CR)_2Mo(NO)_2(CHMe)] \longrightarrow \\ &\qquad (\mathbf{13})\ R=Me\ (\mathbf{14})\ R=Ph \\ &\qquad \{(Et_3Sn\cdot AlCl_3)_2(O_2CR)_2Mo(NO)_2(CHMe)\}_n \qquad (3) \\ &\qquad (\mathbf{13a})\ R=Me\ (\mathbf{14a})\ R=Ph \end{aligned}$$

Complexes **13** and **14** undergo very fast polymerization forming **13a** and **14a**, respectively, just like their counterparts with the related alkoxy ligand [4,5]. The IR spectra (Table 1) also indicated that the formation of the ethylidene carbene complexes was not a quantitative reaction. That was the reason why attempts to prepare analytically and spectrally pure **13a** and **14a** failed. The precipitates obtained were very sparingly soluble in PhCl. They contained some impurities, *i.e.* adducts with $AlCl_3$ and/or **11** and **12**, respectively. The ^1H NMR spectra of the precipitates at −40°C in CD_3CN exhibited H_α resonances as broad singlets (**13a**, $\delta(CH) = 7.50$ ppm; **14a**, $\delta(CH) = 7.52$ ppm).

The catalytic activity of the **5**/$Et_4Sn-AlCl_3$ system is identical under the same reaction conditions, to that of the system based on **3** [4] in the metathesis reaction of both pent-2-ene and cyclopentene.

The system **4**/$Et_4Sn-AlCl_3$ is less active; the metathesis equilibrium of pent-2-ene was achieved at room temperature after 20 min and a 72% yield of polypentenamer was obtained after the same reaction time.

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