

MCM-41 anchored Schrock catalyst $\text{Mo}(=\text{CHCMe}_2\text{Ph})(=\text{N}-2,6-i\text{-Pr}_2\text{C}_6\text{H}_3)[\text{OCMe}(\text{CF}_3)_2]_2$ -activity in 1-heptene metathesis and cross-metathesis reactions

Hynek Balcar^{a,*}, Naděžda Žilková^a, Jan Sedláček^b, Jiří Zedník^b

^a J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, CZ-18223 Prague 8, Czech Republic

^b Department of Physical and Macromolecular Chemistry, Laboratory of Specialty Polymers, Faculty of Science, Charles University, Albertov 2030, CZ-12840, Prague 2, Czech Republic

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Abstract

Schrock carbene complex $\text{Mo}(=\text{CHCMe}_2\text{Ph})(=\text{N}-2,6-i\text{-Pr}_2\text{C}_6\text{H}_3)[\text{OCMe}(\text{CF}_3)_2]_2$ was immobilized on mesoporous molecular sieves MCM-41 via a ligand exchange reaction with OH surface groups. The heterogeneous catalyst prepared in this way was Mo-leaching resistant and exhibited high activity and selectivity in metathesis of neat 1-heptene. The catalyst activity in cross-metathesis of 1-heptene with norbornene and cyclooctene was also studied.

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Keywords: Heterogenized catalyst; Schrock carbene; Olefin metathesis; Norbornene and cyclooctene telomerization; MCM-41

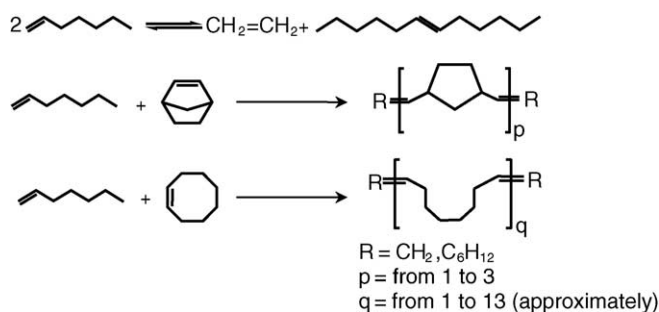
1. Introduction

The carbene complex $\text{Mo}(=\text{CHCMe}_2\text{Ph})(=\text{N}-2,6-i\text{-Pr}_2\text{C}_6\text{H}_3)[\text{OCMe}(\text{CF}_3)_2]_2$ prepared by Schrock in 1990 [1] is one of the highly efficient well-defined catalysts of olefin metathesis and metathesis polymerization. Its special attraction consists in its controllable activity and its tolerance to some functionalities. Solutions of this complex in organic solvents initiate metathesis of both internal and terminal olefins with high selectivity [2]. The ring opening metathesis polymerization (ROMP) of cycloalkenes with this catalyst proceeds in a living manner that allows to prepare polymers of a desirable molecular weight [3,4]. A series of similar four coordinate Mo-imino alkylidene complexes have been prepared later by variation of both alkoxy and imino ligands, some of them exhibiting remarkable catalytic properties, especially high stereoselectivity and enantioselectivity [5–8]. Nevertheless, because of its activity

and versatility, the complex $\text{Mo}(=\text{CHCMe}_2\text{Ph})(=\text{N}-2,6-i\text{-Pr}_2\text{C}_6\text{H}_3)[\text{OCMe}(\text{CF}_3)_2]_2$ is still the most frequently used Schrock Mo-alkylidene catalyst.

To increase practical applicability of Schrock Mo-alkylidene complexes as metathesis catalysts attempts have been done to immobilize them on polymeric as well as inorganic supports [9]. Well-defined polymer-supported catalysts were prepared via reaction of Mo catalyst precursors with chiral phenoxy groups on polystyrene- or polynorbornene-type cross-linked polymers [10,11]. These catalysts were successfully used in an enantioselective ring closing metathesis with good yields and excellent enantioselectivity. The low extent of cross-linking of polymeric support and its high swelling by the proper solvent were necessary to achieve an effective access of substrate molecules to the anchored catalytic sites. As high flexibility of segments of polymeric support seems to contribute to the catalyst decay by facilitating the bimolecular decomposition of reactive methylidene intermediates, more rigid porous materials (e.g. inorganic ones) are more promising as supports for anchoring Mo-carbene complexes. According

* Corresponding author. Tel.: +420 266053715; fax: +420 286582307.
E-mail address: balcar@jh-inst.cas.cz (H. Balcar).



Scheme 1.

to our knowledge, only two attempts have so far been done to prepare a supported version of the Schrock catalyst using an inorganic support. (1) Stelzer and co-workers [12,13] used γ -alumina covered by methylalumoxane and cross-linked by various diols for supporting $\text{Mo}(=\text{CH}-t\text{-Bu})(=\text{N}-2,6-i\text{-Pr}_2\text{C}_6\text{H}_3)[\text{OCMe}_2(\text{CF}_3)_2]_2$ and $\text{Mo}(=\text{CH}-t\text{-Bu})(=\text{N}-2,6-i\text{-Pr}_2\text{C}_6\text{H}_3)(\text{OTf})_2(\text{dme})$ ($\text{Tf} = \text{CF}_3\text{SO}_2$, $\text{dme} = 1,2$ -dimethoxyethane). The catalysts prepared using this method exhibited a significant activity in ROMP, producing high molecular weight polymers. These catalysts were also successfully tested in a continuous ROMP process using linear alkenes as chain transfer agents. On the other hand, in metathesis of 1-hexene, the fast loss of the catalyst activity was observed, which was ascribed to the methylidene carbenes decomposition. The detailed character of active species remained unknown. (2) Wolke and Buffon [14] supported $\text{Mo}(=\text{CHCMe}_2\text{Ph})(=\text{N}-2,6-i\text{-Pr}_2\text{C}_6\text{H}_3)(\text{O}-t\text{-Bu})_2$ and $\text{Mo}(=\text{CHCMe}_2\text{Ph})(=\text{N}-2,6-i\text{-Pr}_2\text{C}_6\text{H}_3)[\text{OCMe}(\text{CF}_3)_2]_2$ on silica and/or silica-alumina and described their catalytic activity when heterogenized. Rapid polymerization of norbornene was observed and high molecular weight polymers were prepared in high yield. However, only low conversion was achieved in metathesis of *cis*-2-pentene. The mode of complex anchoring to the support surface was not clear.

In this paper, we report a preparation of supported version of the Schrock catalyst $\text{Mo}(=\text{CHCMe}_2\text{Ph})(=\text{N}-2,6-i\text{-Pr}_2\text{C}_6\text{H}_3)[\text{OCMe}(\text{CF}_3)_2]_2$ on siliceous mesoporous molecular sieves MCM-41 and its activity in metathesis of 1-heptene and cross-metathesis of 1-heptene with norbornene or cyclooctene (Scheme 1).

2. Experimental

2.1. Materials

$\text{Mo}(=\text{CHCMe}_2\text{Ph})(=\text{N}-2,6-i\text{-Pr}_2\text{C}_6\text{H}_3)[\text{OCMe}(\text{CF}_3)_2]_2$ was purchased by Strem and used as received. Mesoporous molecular sieves MCM-41 were synthesized using the homogeneous precipitation method with sodium silicate, hexadecyltrimethylammonium bromide and ethyl acetate. For details see [15]. 1-Heptene (Fluka, purum) was dried by NaH and distilled and degassed in vacuo; cyclooctene

(COE) (Janssen Chimica, 95%) was refluxed over NaH and distilled in vacuo; norbornene (NBE) (Fluka, purum) was distilled from NaH. Benzene (Lachema, Czech Republic) was purified by distillation with P_2O_5 , then refluxed over NaH and degassed in vacuo. Cyclohexane (Lachema, Czech Republic) was predried with CaCl_2 , rectified on a column, then refluxed over NaH and degassed in vacuo. 1,1,1,3,3,3-Hexafluoro-2-methyl-2-propanol [$(\text{CF}_3)_2\text{MeCOH}$, 95%] was purchased by Lancaster.

2.2. Hybrid catalyst preparation

MCM-41 (1 g) was dried in vacuo at 300°C for 6 h. Then it was cooled down to room temperature and suspended in a benzene solution of $\text{Mo}(=\text{CHCMe}_2\text{Ph})(=\text{N}-2,6-i\text{-Pr}_2\text{C}_6\text{H}_3)[\text{OCMe}(\text{CF}_3)_2]_2$ (78 mg of complex – i.e. 10 mg of Mo – in 10 ml of benzene) in a Schlenk vessel under Ar. The suspension was stirred over 30 min at room temperature. Within that time, MCM-41 turned yellow and the benzene phase became colourless. The solid phase was then separated by decantation, washed three times with 10 ml of benzene and dried in vacuo at room temperature. The Mo content in the prepared catalyst (Mo/MCM-41) was determined by inductively coupled plasma atomic emission spectroscopy (ICP AES). The loading found was 1 wt. % of Mo, which proved the quantitative character of immobilization process. Mo/MCM-41 was stored in sealed ampoules in vacuo.

2.3. Catalytic experiments

The metathesis of 1-heptene was carried out in Ar atmosphere in a glass batch reactor equipped with a magnetic stirring bar. In a typical experiment, Mo/MCM-41 (from 25 to 112 mg) was placed into the reactor under Ar atmosphere and then 1.5 ml of neat 1-heptene was charged under stirring. The reaction was performed at room temperature at constant pressure. The amount of ethylene evolving in the course of the reaction was continuously measured volumetrically using ideal gas approximation. When the ethylene evolution ceased, the solid catalyst was removed by decantation and the resulting supernatant was analyzed by GC and GC/MS.

The cross-metathesis of 1-heptene with NBE and COE was carried out in a sealed reactor (25 ml) under vacuo at room temperature. The reactor was filled with 30 mg of Mo/MCM-41 under Ar. After evacuation, the reactor was sealed off the vacuum line and 0.5 ml of neat 1-heptene and cyclohexane solution of NBE or COE (2.5 mmol in 1 ml) were charged simultaneously into the reactor from magnetically breakable vials. After 4 h, the reactor was opened to air and the supernatant was analyzed by GC, GC/MS and SEC techniques.

2.4. Techniques

Agilent 6890 high-resolution gas chromatograph equipped with a FID detector and a DB-5 column (length: 50 m, inner diameter: $320\ \mu\text{m}$, stationary phase thickness:

1 μm) was used. Solvent or *n*-decane were used as integration standards. GC/MS apparatuses (HP 5890 + 5971A and Carlo Erba GC 8000 with a Fisons MD 800 detector) were used for the product identification. Polymer/oligomers molecular weight characteristics were determined by SEC on TSP (Thermo Separation Products, Florida, USA) Chromatograph fitted with a refractive index detector. A series of two PL-gel columns (Mixed-B and Mixed-C, Polymer Laboratories Bristol, UK) and THF (flow rate 0.7 ml/min) were used. The weight-average molecular weight M_w and the number-average molecular weight M_n relative to polystyrene standards are reported.

^1H , ^{13}C and ^{19}F NMR spectra were recorded on a Varian Unity INOVA 400. ^1H and ^{13}C spectra were referenced to the solvent lines, ^{19}F spectrum to CFCl_3 ($\delta = 0$ ppm).

ICP AES analysis of catalyst was performed by Ecochem Co., Prague, Czech Republic. HF, HNO_3 and aqua regia were used for catalyst dissolution prior to ICP AES.

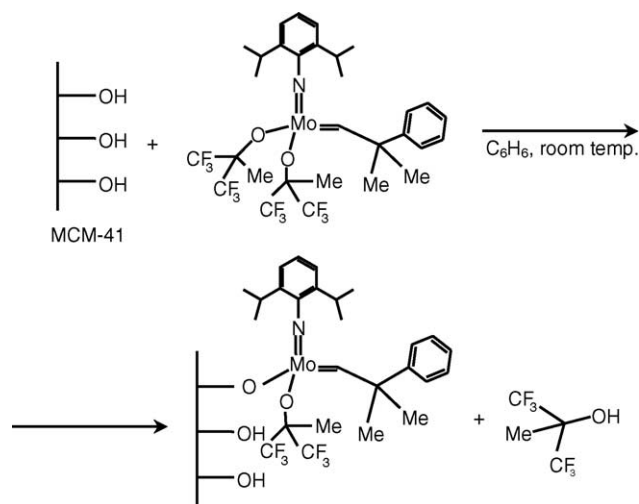
3. Results and discussion

3.1. Mo/MCM-41 preparation and characterization

MCM-41 was characterized by XRD at low angles and by nitrogen adsorption isotherms. These method confirmed high quality of support: hexagonal regular structure, BET surface area $S = 1032 \text{ m}^2/\text{g}$, mesopore volume $V = 0.718 \text{ cm}^3/\text{g}$ and mean pore diameter $d = 3.1 \text{ nm}$. For details of MCM-41 characterization see [16].

$\text{Mo}(=\text{CHCMe}_2\text{Ph})(=\text{N}-2,6-i\text{-Pr}_2\text{C}_6\text{H}_3)[\text{OCMe}(\text{CF}_3)_2]_2$ reacts with MCM-41 in benzene smoothly and quantitatively. The content of Mo in Mo/MCM-41 (1 wt.%) determined by ICP AES was in compliance with that calculated from the amount of $\text{Mo}(=\text{CHCMe}_2\text{Ph})(=\text{N}-2,6-i\text{-Pr}_2\text{C}_6\text{H}_3)[\text{OCMe}(\text{CF}_3)_2]_2$ submitted for the immobilization.

With the aim to elucidate the mode of carbene complex anchoring on the support surface, a special experiment was performed, in which $\text{Mo}(=\text{CHCMe}_2\text{Ph})(=\text{N}-2,6-i\text{-Pr}_2\text{C}_6\text{H}_3)[\text{OCMe}(\text{CF}_3)_2]_2$ immobilization was carried out in C_6D_6 and the supernatant resulting from this process was analyzed by NMR techniques. In ^1H NMR spectra, the signals of $\text{Mo}(=\text{CHCMe}_2\text{Ph})(=\text{N}-2,6-i\text{-Pr}_2\text{C}_6\text{H}_3)[\text{OCMe}(\text{CF}_3)_2]_2$ at δ in ppm = 12.12; 7.19–6.92; 3.56; 1.52; 1.18; 1.16 (for signal assignment see [17]) completely disappeared as a result of complex anchoring while only two new signals appeared corresponding to the signals of the authentic sample of $(\text{CF}_3)_2\text{MeCOH}$ at δ in ppm = 0.96 [$\text{CH}_3(\text{CF}_3)_2$] and 1.7 (COH). The ^{13}C and ^{19}F NMR spectra of supernatant also confirmed the presence of $(\text{CF}_3)_2\text{MeCOH}$ as the only reaction product released into the liquid phase: in ^{13}C NMR spectrum, there are signals at 16.45 ppm (CH_3), about 75 ppm [$(\text{CF}_3)_2\text{MeCOH}$] and at 122.7 + 125.5 ppm (CF_3 —the remaining signals of CF_3 quadruplet were not distinguished due to their low intensity and overlap with the solvent signals); in ^{19}F NMR spectrum, there is a signal at -79.6 ppm.



Scheme 2.

The unambiguous presence of $(\text{CF}_3)_2\text{MeCOH}$ as the reaction product in the supernatant strongly suggests that the anchoring proceeded as the ligand exchange reaction in which either one or two $(\text{CF}_3)_2\text{MeCO}$ ligands of the complex were displaced by surface SiOH groups of the support (Scheme 2). As the quantitative determination of $(\text{CF}_3)_2\text{MeCOH}$ evolved was impossible we cannot specify the extent of the exchange of the second $(\text{CF}_3)_2\text{MeCO}$ ligand. In this connection, it may be noted that a Schrock's family complex having a silsesquioxane moiety bound to Mo by two Si–O–Mo bonds instead of both alkoxy ligands was prepared and reported as highly active especially in metathesis of 1-alkenes [18].

3.2. Mo/MCM-41 activity in metathesis of 1-heptene

The catalytic activity of Mo/MCM-41 was investigated in metathesis of neat 1-heptene at room temperature. Results are given in Figs. 1 and 2 and Table 1. Fig. 1 shows the time dependence of the amount of ethylene formed in

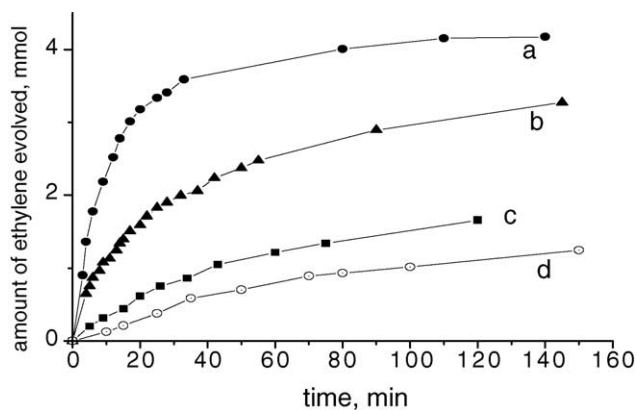


Fig. 1. Time dependence of the amount of ethylene evolved in the course of 1-heptene metathesis with Mo/MCM-41 (1 wt.% of Mo). Mo/MCM-41 = 112 mg (a), 48.5 mg (b), 25 mg (c), 112 mg—catalyst reused (d); 1-heptene = 1.5 ml, room temperature.

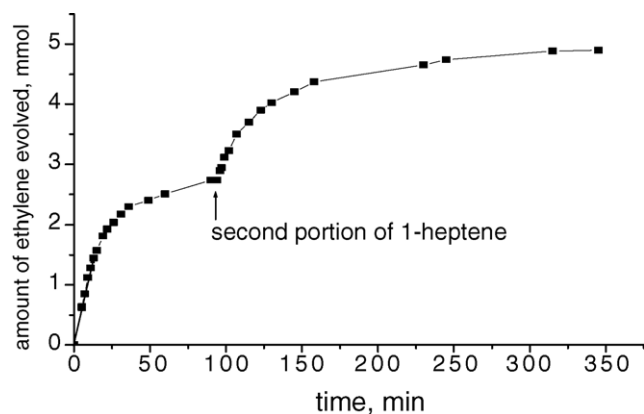


Fig. 2. Time dependence of the amount of ethylene evolved for two step substrate addition in 1-heptene metathesis with Mo/MCM-41 (1 wt.% of Mo). Mo/MCM-41 = 36 mg, 1.0 ml of 1-heptene in each portion, room temperature.

the course of the reactions performed with various initial 1-heptene to Mo mole ratios. The rapid evolution of ethylene was observed instantaneously after mixing the catalyst with 1-heptene. The initial rate of ethylene formation increased with the increasing catalyst concentration (Fig. 1, curves a, b and c). At a prolonged reaction time, this rate slowed down as a consequence of 1-heptene consumption. Nevertheless, the catalytic centres in the system remained active as indicated by the renewal of ethylene formation after charging an additional portion of 1-heptene (Fig. 2).

In Table 1, the final 1-heptene conversion, K' , determined from the total amount of ethylene formed (assuming 1-heptene conversion according to Scheme 1) is compared with the values of the conversion K given by GC analysis of the supernatant resulting after the removal of the catalyst (see Section 2). In all experiments described in Table 1, GC/MS revealed 6-dodecene (*cis* content = 32% as determined from 130.4 and 129.8 ppm signals in ^{13}C NMR spectrum) as a strongly prevailing reaction product and only traces of C_8 and C_{11} alkenes formed as a result of 1-heptene double bond shift isomerization followed by cross-metathesis. On the base of GC analysis of the supernatant, K and S values (S stands

for selectivity to 6-dodecene) shown in Table 1 were calculated from the mass balance using the following equations: $K = 2(n_D + \sum n_C)/(n_H + 2n_D + 2\sum n_C)$, $S = n_D/(n_D + \sum n_C)$, where n_H , n_D and n_C are mole amounts of 1-heptene, 6-dodecene and cross-metathesis products (C_8 and C_{11}), respectively. It is obvious from Table 1 that (i) selectivity to 6-dodecene is close to 100% in all experiments; and (ii) K and K' values calculated in the manner described above are always close to each other, i.e. the amount of ethylene dissolved in the reaction mixture is negligible. These findings make us believe that the determined amounts of ethylene evolved provide sufficiently precise values of 1-heptene conversions for any stage of the reaction, including the initial stage. The initial TOF values calculated from the curves in Fig. 1 are given in Table 1 (initial TOF = $\lim [2n_E/(n_{\text{Mo}}t)]$ for $t \rightarrow 0$, where n_E is the mole amount of ethylene evolved, n_{Mo} the mole amount of Mo in Mo/MCM-41 applied, and t stands for the reaction time). With the initial 1-heptene/Mo mole ratio ranging from 900 to 2100, the initial TOFs of about 1.0 s^{-1} were obtained regardless of the catalyst concentration. This demonstrates high activity of Mo/MCM-41 in 1-heptene metathesis. These values are lower nevertheless of the same order of magnitude as those reported (i) for parent $\text{Mo}(=\text{CHCMe}_2\text{Ph})(=\text{N}-2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)[\text{OCMe}(\text{CF}_3)_2]_2$ [2]; and (ii) for its silsesquioxane containing analogue [18], both used as homogeneous catalysts. For low Mo/MCM-41 concentration (1-heptene/Mo mole ratio of 4100), the initial TOF value decreased to 0.49 (Table 1, no. 3). The TON values shown in Table 1 (calculated for final conversions at the reaction times given in Table 1) are close to those, which can be calculated from the data reported in [2] and [18] for the above given homogeneous catalysts.

The filtration experiment proved that catalytic activity is bound to the solid phase in the course of the metathesis reaction. Mo/MCM-41 (30 mg) was mixed with 1-heptene (1.5 ml) and after 30 min of reaction at room temperature, approximately half the volume of the liquid phase was separated from Mo/MCM-41 by filtration into the side vessel of the reactor. Both parts of the reaction mixture were allowed to react for additional 270 min at room temperature. Conversion and selectivity from GC at 30 min were $K = 0.28$

Table 1
Metathesis of 1-heptene catalysed by Mo/MCM-41 (1 wt.% of Mo) at room temperature

No.	Amount of Mo/MCM-41 (mg)	Amount of 1-heptene (ml)	Initial 1-heptene/Mo mole ratio	Initial TOF (s^{-1})	Reaction time (min)	K' ^a	K ^b	S ^c	TON ^d
1	112	1.5	900	1.07	140	0.78	0.79	0.986	710
2	48.5	1.5	2100	1.00	145	0.61	0.62	0.988	1300
3	25	1.5	4100	0.49	120	0.31	0.31	0.984	1270
4	36	1.0	1900	1.06	90	0.77	0.77	0.988	1460
5 ^e	36	1.0 + 1.0	—	—	345	0.68	0.66	0.986	2510
6 ^f	112	1.5	900	0.05	420	0.38	0.39	0.989	350

^a Final 1-heptene conversion based on C_2H_4 evolved.

^b Final 1-heptene conversion by GC.

^c Selectivity to 6-dodecene by GC.

^d TON (calculated from K).

^e Second portion of 1-heptene added after 90 min.

^f Catalyst reusing.

Table 2
Cross-metathesis of NBE or COE with 1-heptene catalysed by Mo/MCM-41 (1 wt.% of Mo)

Type of product	Composition (mmol) of the resulting reaction mixture	
	1-Heptene/NBE	1-Heptene/COE
1-Heptene	2.50	0.83
Starting cycloalkene	0.01	0.33
6-Dodecene	0.30	0.67
CH ₂ =M=CH ₂	0.02	0.23
CH ₂ =M=CH(CH ₂) ₄ CH ₃	0.37	0.44
CH ₃ (CH ₂) ₄ CH=M=CH(CH ₂) ₄ CH ₃	0.02	0.21
CH ₂ =(M) ₂ =CH ₂	<0.01	0.08
CH ₂ =(M) ₂ =CH(CH ₂) ₄ CH ₃	0.09	0.19
CH ₃ (CH ₂) ₄ CH=(M) ₂ =CH(CH ₂) ₄ CH ₃	<0.01	0.13
CH ₂ =(M) ₃ =CH ₂	<0.01	0.03
CH ₂ =(M) ₃ =CH(CH ₂) ₄ CH ₃	0.04	0.10
Low-molecular-weight polymer	Corresponds to 1.8 mmol NBE ^a	0

Mo/MCM-41 = 30 mg (0.00313 mmol Mo), 1-heptene = 3.6 mmol, NBE (COE) = 2.5 mmol, volume of reaction mixture = 1.5 ml, room temperature, cyclohexane, reaction time = 4 h.

^a $M_w = 2100$, $M_n = 1400$.

and $S = 0.987$. For the part of the reaction mixture which remained in contact with Mo/MCM-41, conversion increased during the additional 270 min to $K = 0.57$ ($S = 0.985$), while in the part of the reaction mixture without the heterogeneous phase, the K value remained unchanged.

The activity of Mo/MCM-41 in repeated application was tested in following experiment. The catalyst separated after finishing the experiment no. 1 described in Table 1 (Fig. 1, curve a) was washed by benzene under Ar and dried in vacuo at room temperature. Then 1.5 ml of 1-heptene was added. The reaction proceeded with unchanged high selectivity, however, the initial TOF was about 20 times lower than that obtained with fresh Mo/MCM-41. Nevertheless, at a prolonged reaction time, 1-heptene conversion of about 40% was still achieved (Fig. 1, curve d, Table 1 No. 6). The content of Mo determined by ICP AES in Mo/MCM-41 isolated after its second application was (0.96 ± 0.09) wt.%, i.e. either no or only negligible Mo leaching occurred during the preceding catalyst treatment. Therefore, the observed decrease in Mo/MCM-41 activity should be attributed to the deactivation of anchored carbene species, occurring most probably during the catalyst isolation and drying (e.g. as a result of a reaction with accumulated impurities).

3.3. Mo/MCM-41 activity in cross-metathesis of 1-heptene with NBE and COE

Products of 1-heptene cross-metathesis with NBE and COE, respectively, are summarized in Table 2. In addition to the homometathesis product (6-dodecene), three series of telomers (mixture of *Z*-, *E*-isomers, according to GC and GC/MS), $Q^1M_nQ^1$, $Q^1M_nQ^2$ and $Q^2M_nQ^2$ ($n = 1, 2, 3$; $Q^1 = CH_2$, $Q^2 = CH_3(CH_2)_4CH$, M = repeating NBE or COE monomeric unit) were found. A low-molecular-weight polymer of $M_w = 2100$ and $M_n = 1400$ was detected by SEC among the products of the 1-heptene/NBE cross-metathesis. Its quantification from SEC was impossible, however, its

amount can be roughly estimated from the mass balance of NBE (Table 2). In the case of 1-heptene/COE system, SEC found no polymer.

The products distribution shown in Table 2 is in a qualitative accordance with literature data for the cross-metathesis of COE or NBE with 1-alkenes [19,20,21] catalysed by various homogeneous catalysts. The products are formed by the ROMP of cycloalkenes with 1-alkenes acting as chain transfer agents. The formation of a low-molecular-weight polymer in a NBE-containing system and the absence of this product in a COE-containing system reflects the higher polymerizability of NBE in the ROMP. The dominance of the unsymmetrical series $Q^1M_nQ^2$ among telomers in both systems (Table 2) is typical of a cross-metathesis of cycloalkenes with 1-alkenes [22], which reflects the different reactivity of $Mt = CH_2$ and $Mt = CHR$ carbenes in the catalytic cycle. In the 1-heptene/NBE system, a $Q^1M_1Q^1/Q^1M_1Q^2/Q^2M_1Q^2$ ratio of 1:18.5:1 was found. In the 1-heptene/COE system, this ratio was close to the statistical one, i.e. 1:2:1. The findings suggest that the system with COE was close to the equilibrium when the reaction was stopped. This is in contrast to the system with NBE, where the stronger dominance of $Q^1M_1Q^2$ telomer and low consumption of 1-heptene may indicate that the equilibrium was not achieved. This may be due to the formation of a low-molecular-weight polymer, which increased the viscosity in the reaction system, thus reducing the diffusion rate.

4. Conclusions

The Schrock carbene complex $Mo(=CHCMe_2Ph)(=N-2,6-i-Pr_2C_6H_3)[OCMe(CF_3)_2]_2$ was immobilized on MCM-41 by a ligand exchange reaction under the formation of the heterogeneous catalyst Mo/MCM-41 and 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol. Mo/MCM-41 containing 1 wt.% of Mo exhibited high activity and selectivity in

the metathesis of neat 1-heptene to 6-dodecene. The activity was found to be close to that achieved for parent $\text{Mo}(=\text{CHCMe}_2\text{Ph})(=\text{N}-2,6-i\text{-Pr}_2\text{C}_6\text{H}_3)[\text{OCMe}(\text{CF}_3)_2]_2$ used as homogeneous catalyst, however, Mo/MCM-41 can be used without any solvent and it can be easily separated from the reaction products. The catalytic activity was found to be steadily bound to the solid phase, and the catalyst was found to be resistant to Mo leaching. Mo/MCM-41 initiated the ROMP of NBE and COE with 1-heptene as the chain transfer agent. In the 1-heptene/NBE system of a roughly equimolar composition, a low-molecular-weight polymer ($M_w = 2100$ and $M_n = 1400$) results as the main product, while in the 1-heptene/COE system, low telomers are formed, with 1,9-pentadecadiene being the predominant telomer.

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