## Effect of the nature of carbene fragments in the tungsten complexes $PhMe_2E-CH=W(NAr)(OR')_2$ and $Me_3E-CH=W(NAr)(OR')_2$ (E = C, Si) on their catalytic properties in olefin metathesis reactions

A. L. Bochkarev, Yu. E. Begantsova, E. O. Platonova, G. V. Basova, I. K. Grigor ´eva, N. E. Stolyarova, I. P. Malysheva, G. K. Fukin, E. V. Baranov, Yu. A. Kurskii, L. N. Bochkarev, \* and G. A. Abakumov

G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, 49 ul. Tropinina, 603950 Nizhnii Novgorod, Russian Federation. Fax: +7 (831) 462 1497. E-mail: lnb@iomc.ras.ru

Catalytic properties of the silicon-containing carbene complexes of tungsten  $Me_3Si-CH=W(NAr)(OR')_2(1)$  and  $PhMe_2Si-CH=W(NAr)(OR')_2(2)$  and their hydrocarbon analogs  $Me_3C-CH=W(NAr)(OR')_2(3)$  and  $PhMe_2C-CH=W(NAr)(OR')_2(4)$  $(Ar = 2,6-Pr^i_2C_6H_3, R' = CMe_2CF_3)$  were studied in homometathesis of hex-1-ene, metathesis polycondensation of deca-1,9-diene, and ring opening metathesis polymerization of cyclooctene. The nature of the carbene fragment in the tungsten catalysts substantially affects their catalytic activity. Silicon-containing catalysts 1 and 2 were found to be 3-5 times less active than their hydrocarbon analogs 3 and 4. Metathesis polymerization of cyclooctene in the bulk with initiators 1-4 completed within a few minutes to form a block. Stereoregularity of the formed polyoctenamers depends to a considerable extent on the nature of the carbene fragments in the starting initiators. Initiators 1-2 lead to polyoctenamers mainly containing the *cis*-units, whereas the use of complexes 3 and 4 affords polyoctenamers mainly containing the *trans*-units. The structures of novel compound 2 and known complexes 1, 3, and 4 were determined by X-ray diffraction analysis.

**Key words:** carbene complexes, tungsten, silicon, synthesis, X-ray diffraction analysis, metathesis, polymerization.

Carbene complexes of tungsten of the type  $R-CH=W(NAr)(OR')_2$  ( $R = Bu^t$ ,  $PhMe_2C$ ,  $Ar = 2,6-Pr_{2}^{i}C_{6}H_{3}$ , R' = Alk, Aryl), along with analogous molybdenum compounds, are widely used as catalysts for the metathesis of olefins and their numerous functional derivatives.<sup>1-4</sup> The catalytic activity of the tungsten and molybdenum catalysts is determined, to a considerable extent, by the nature of the alkoxide groups and imide ligands.<sup>4</sup> The influence of the nature of the carbene fragments in the tungsten and molybdenum complexes on their catalytic properties in olefin metathesis reactions remain poorly studied. We have recently<sup>5,6</sup> found that the composition and structure of the organoelement substituent at the carbene carbon atom in the  $R_3E$ -CH=Mo(NAr)(OR')<sub>2</sub> molybdenum complexes  $(E = Si, Ge; R = Alk, Aryl; Ar = 2,6-Pr_{2}^{i}C_{6}H_{3},$  $R' = CMe_2CF_3$ ) exert a substantial effect on their catalytic activity and determine, to a great extent, stereoregularity of polyoctenamers obtained by the ring opening metathesis polymerization of cyclooctene involving these complexes. Therefore, it seemed reasonable to elucidate the effect of the carbene fragments on the catalytic properties of the silicon-containing carbene complexes

of tungsten Me<sub>3</sub>Si–CH=W(NAr)(OR')<sub>2</sub> (1) and PhMe<sub>2</sub>Si–CH=W(NAr)(OR')<sub>2</sub> (2) and their hydrocarbon analogs Bu<sup>t</sup>–CH=W(NAr)(OR')<sub>2</sub> (3) and PhMe<sub>2</sub>C–CH=W(NAr)(OR')<sub>2</sub> (4) (Ar = 2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>, R' = CMe<sub>2</sub>CF<sub>3</sub>) in the homometathesis of hex-1-ene, metathesis polycondensation of deca-1,9-diene, and ring opening metathesis polymerization of cyclooctene chosen as test reactions.

Schrock catalysts 1, 3, and 4 were synthesized as described earlier.<sup>7,8</sup> New tungsten derivative 2 containing the dimethylphenylsilyl substituent at the carbenic carbon atom was synthesized by the reaction of neopentylidene complex 3 with vinyldimethylphenylsilane (Scheme 1).

## Scheme 1

Bu<sup>t</sup>HC=W(NAr)(OR')<sub>2</sub> + PhMe<sub>2</sub>SiCH=CH<sub>2</sub> 
$$\xrightarrow{C_6H_6}_{20 \circ C}$$
  
**3**  
 $\longrightarrow$  PhMe<sub>2</sub>SiCH=W(NAr)(OR')<sub>2</sub> + CH<sub>2</sub>=CHBu<sup>t</sup>  
**2**

Published in Russian in Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 9, pp. 1840-1845, September, 2008.

1066-5285/08/5709-1874 © 2008 Springer Science+Business Media, Inc.

According to the data of <sup>1</sup>H NMR spectroscopy, the reaction between the reactants is accomplished within 3.5 h to form complex **2** in nearly quantitative yield. After removal of the solvent and volatile products, compound **2** is isolated as a viscous oily substance unstable in air and highly soluble in usual organic solvents. In the crystalline state complex **2** was isolated in 33% yield after crystallization from a minimum amount of ether at -20 °C.

The structures of complexes 1-4 were determined by X-ray diffraction analysis (Figs 1-4, Table 1). Complex 2 is isostructural to the earlier<sup>6</sup> described complex PhMe<sub>2</sub>Si-CH=Mo(NAr)(OR')<sub>2</sub> (Ar = 2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>,  $R' = CMe_2CF_3$ ,<sup>6</sup> and complex 1 is isostructural to  $Me_3E-CH=Mo(NAr)(OR')_2$  (E = Si, Ge) and  $Me_3Ge-CH=W(NAr)(OR')_2$  (Ar = 2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>,  $R' = CMe_2CF_3$ ).<sup>6,9,10</sup> The tungsten atoms in structures 1-4 have a distorted tetrahedral coordination. The W(1)-C(1) distances are 1.877(4) (1), 1.888(3) (2), 1.891(3) (3), and 1.880(1) Å (4), which is comparable with similar distances of 1.877(1) - 1.889(2) Å in  $PhMe_2E-CH=Mo(NAr)(OR')_2$  (E = Si (2a), C (2b)),  $Me_3E$ -CH=Mo(NAr)(OR')<sub>2</sub> (E = Si (1a), Ge (1b)), and  $Me_3Ge-CH=W(NAr)(OR')_2$  (1c). The Si(1)-C(1) distances in molecules 1 and 2 are 1.828(4) and 1.852(3) Å, respectively, which is insignificantly shorter than similar distances in compounds 1a (1.862(2) Å) and 2a (1.856(2) Å). Note that the Si(1)-C(1) distances in structures 1 and 2 lie in the interval typical of ordinary bonds Si(1)-C(Me,Ph): 1.840(4) - 1.881(4) Å. The R<sub>3</sub>C-C(H) distances in complexes **3** and **4** are 1.522(4) and 1.530(1) Å, respectively, which is close to the value for the ordinary bond  $C_{sp_3}-C_{sp_2}$  (1.507 Å).<sup>11</sup> It is most likely that this indicates the absence of electron density delocalization in the  $W=C(H)-Si(Me_2Ph)$ ,  $W=C(H)-Si(Me_3)$ ,  $W=C(H)-C(Me_3)$ , and  $W=C(H)-C(Me_2Ph)$  fragments. Similar situation is observed for complexes 1a-c and 2a,b. The values of the W(1)-C(1)-Si(1) angles in compounds 1 and 2 are 139.1(2) and  $138.9(2)^\circ$ , which are close to the values of analogous angles in structures **1a-c** and **2a**. In the complex  $Ph_3Si-CH=Mo(NAr)(OR')_2$  (Ar = =2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>, R' = CMe<sub>2</sub>CF<sub>3</sub>),<sup>5</sup> the angle Mo–C(H)–Si is equal to  $144.8(2)^{\circ}$ , which characterizes the large steric size of the SiPh<sub>3</sub> group compared to the groups SiMe<sub>2</sub>Ph and SiMe<sub>3</sub>. However, in complexes 3, 4, and 2b containing the neopentyl (3) and neophenyl (4, 2b) ligands the M-C(H)-C angles (M = W (3, 4), Mo (2b)) are  $144.3(2) - 144.79(8)^{\circ}$ . Evidently, since the C(H)-CR<sub>3</sub> (1.514(4)-1.530(1) Å) distances in structures 3, 4, and 2b are shorter than C(H)-Si(Me<sub>2</sub>Ph) in compounds 2 and 2a and C(H)-Si(Me<sub>3</sub>) in complexes 1 and 1a (1.828(4)-1.862(2) Å), the nonvalent interactions between the C(H)- $CR_3$  fragment and the ligands OR' and NAr are stronger, which increases the M-C(H)-C angle in structures 3, 4, and 2b.



**Fig. 1.** Molecular structure of complex **2** (thermal ellipsoids are presented with the 30% probability).

The catalytic properties of synthesized carbene complex 2 and known catalysts 1, 3, and 4 were studied in test reactions of hex-1-ene homometathesis, metathesis polycondensation of deca-1,9-diene, and ring opening metathesis polymerization of cyclooctene.

A comparison of the reaction rate constants suggests that in hex-1-ene homometathesis (Table 2) silicon-containing catalysts 1 and 2 exhibit almost equal catalytic activity and although they are about 3 times less active than their hydrocarbon analogs 3 and 4. According to the



Fig. 2. Molecular structure of complex 1 (thermal ellipsoids are presented with the 30% probability).



Fig. 3. Molecular structure of complex 3 (thermal ellipsoids are presented with the 30% probability).

data of <sup>13</sup>C NMR spectroscopy, in all cases, dec-5-ene formed during the reactions is a mixture of the *trans*and *cis*-isomers in a ratio of ~2:1. The earlier studied analogous silicon-containing carbene complexes of molybdenum Me<sub>3</sub>Si-CH=Mo(NAr)(OR')<sub>2</sub> and PhMe<sub>2</sub>Si-CH=Mo(NAr)(OR')<sub>2</sub> are also less active in hex-1-ene metathesis than their hydrocarbon analogs Bu<sup>t</sup>-HC=Mo(NAr)(OR')<sub>2</sub> and PhMe<sub>2</sub>C-CH=Mo(NAr)(OR')<sub>2</sub>. As a whole, the molybdenum catalysts are an order of magnitude more active than analogous tungsten catalysts.<sup>5,6</sup>

In the metathesis polycondensation of deca-1,9-diene (Table 3), as well as in the homometathesis of hex-1-ene,



**Fig. 4.** Molecular structure of complex **4** (thermal ellipsoids are presented with the 30% probability).

**Table 1.** Selected bond lengths (*d*) and bond angles ( $\omega$ ) in complexes **1**–4

Parameter	1	2	3	4
Bond		d/Å	L	
W(1) - N(1)	1.730(3)	1.731(3)	1.739(2)	1.712(1)
W(1) - O(1)	1.889(3)	1.886(2)	1.889(2)	1.903(1)
W(1) - O(2)	1.897(2)	1.889(2)	1.908(2)	1.904(1)
W(1) - C(1)	1.877(4)	1.888(3)	_	_
W(1)-C(21)	_	_	1.891(3)	1.880(1)
Si(1) - C(1)	1.828(4)	1.852(3)	_	_
C(21)—C(22)	_	_	1.522(4)	1.530(1)
Angle		ω/de	g	
W(1) - C(1) - Si(1)	139.1(2)	138.9(2)	_	_
W(1)-C(21)-C(22)	_	_	144.6(2)	144.79(8)

silicon-containing complexes 1 and 2 are about 3-5 times less active than their hydrocarbon analogs 3 and 4. Under the accepted conditions (room temperature, reaction duration 60 min), the reaction products are mixture of oligomers (see Table 3). The ratio of *trans*- and *cis*-units in the formed oligomers is the same in all cases: 62 : 38.

Tungsten carbene complexes 1-4 are active initiators of the ring opening metathesis polymerization of cyclooctene. Before block formation, the polymerization process is complished within several minutes, and a nearly complete conversion of the monomer occurs according to the NMR spectroscopy data. The study of the polymer samples showed that the ratio of the *trans*- to *cis*-units in the polyoctenamers formed depends substantially on the nature of the carbene fragment in the starting initiators (Table 4). Silicon-containing initiators 1 and 2 lead to the formation of polymers mainly containing the *cis*-units. On the contrary, in the case of hydrocarbon analogs 3 and 4, the polymers formed mainly contain the *trans*-units. We have recently found<sup>6</sup> that, when the molybdenum carbene complexes are used as the initiators of the ring opening metathesis polymerization of cyclooctene, stereoregularity of the polyoctenamers formed also depends considerably on the nature of the carbene fragment in the initial molybdenum complexes. According to the commonly accepted

 
 Table 2. Kinetic data for hex-1-ene metathesis using the tungsten catalysts\*

Cata- lyst	<i>Т</i> /°С	Conversion (%)	$k \cdot 10^{6}$ /L mol <sup>-1</sup> s <sup>-1</sup>
1	20	2.8	0.8±0.1
2	19	2.6	$0.7 \pm 0.1$
3	19	8.2	$2.8 \pm 0.2$
4	19	7.3	$2.6 \pm 0.2$

\* Conditions: [hex-1-ene]/[catalyst] = 300; in the absence of solvent; the reaction duration was 60 min.

Cata- lyst	<i>T</i> /°C	Conversion (%)	$k \cdot 10^{6}$ /L mol <sup>-1</sup> s <sup>-1</sup>	$ar{M_{ m w}}$	$\bar{M_n}$	$\bar{M}_{\rm w}/\bar{M}_{\rm n}$
1	21	4.1	1.1±0.1	600	460	1.30
2	18	2.2	0.6±0.1	450	320	1.30
3	19	9.2	2.7±0.2	760	300	2.53
4	19	11.1	3.2±0.2	750	430	1.74

 Table 3. Kinetic data for deca-1,9-diene metathesis polycondenstion using the tungsten catalysts\* and the molecular mass characteristics of the formed oligomers\*\*

\* Conditions: [deca-1,9-diene]/[catalyst] = 100; in the absence of solvent; the reaction duration was 60 min.

 $\ast\ast$  The molecular mass characteristics are given for oligomers with the 10% conversion.

mechanism of cycloolefin metathesis polymerization involving the carbene complexes of transition metals,<sup>3,12</sup> the substituent at the carbenic carbon atom of the starting initiators is transformed in the terminal group of the growing macromolecules. The studied ring opening metathesis polymerization of cyclooctene on the tungsten carbene complexes and the earlier studied polymerization of cyclooctene involving the molybdenum catalysts<sup>6</sup> were carried out under the same conditions, and the catalysts differed only by the substituent at the carbonic carbon atom. Therefore, stereoregularity of the macromolecular chain was determined by the nature of the terminal group of the growing macromolecules. As far as we know, no similar effect has previously been described in the literature. One of the possible explanations for this fact is as follows. At the stages of growth, the terminal group of the formed macromolecule is arranged in space, most likely, fairly close to the catalytic center, coordinates to the central metal atom, and, depending on the structure, determines the most favorable coordination of the next monomer molecule, which finally results in the predominant formation of the trans- or cis-unit in the growing macromolecule.

Thus, the new silicon-containing carbene complex of tungsten was synthesized. The catalytic properties of the compound synthesized and a series of the known tungsten catalysts were studied in the homometathesis of hex-1ene, metathesis polymerization of deca-1,9-diene, and ring-opening metathesis polymerization of cyclooctene.

 Table 4. Characteristics of polyoctenamers obtained in the bulk

 using the tungsten catalysts\*

Cata- lyst	Ratio trans : cis	$ar{M_{ m w}}$	$\bar{M_n}$	$\bar{M}_{\rm w}/\bar{M}_{\rm n}$
1	13:87	528300	238200	2.22
2	14:86	532800	283700	1.88
3	91:9	105500	64700	1.63
4	83:17	554700	291800	1.90

\* Conditions: [cyclooctene]/[catalyst] = 100; the reaction duration until the formation of a solid block in the case of catalysts **1**, **2**, and **3** was 20, 25, and 5 min, respectively. The nature of the carbene fragment in the tungsten catalysts was shown to noticeably affect their catalytic activity. The silicon-containing complexes are 3-5 times less active than their hydrocarbon analogs. It was found that the stereoregularity of the polyoctenamers formed in the ring opening metathesis polymerization of cyclooctene depended substantially on the nature of the carbene fragment in the starting tungsten initiators. When the silicon-containing carbene complexes are used, the polyoctenamers with the predominant content of the *cis*-units are formed, whereas the polyoctenamers mainly containing the *trans*-units are formed using the tungsten complexes with the hydrocarbon carbene fragment.

## **Experimental**

Experiments with compounds unstable in air were carried out in evacuated systems using the standard Schlenk technique. Thoroughly dried and degassed solvents were applied. Compounds  $1,^7 3,^7$  and 4 (Ref. 8) and PhMe<sub>2</sub>SiCH=CH<sub>2</sub> (see Ref. 13) were synthesized as described earlier.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker DPX-200 spectrometer using  $C_6D_6$  and  $CDCl_3$  as solvents and  $Me_4Si$  as the internal standard.

The experimental sets of intensities were measured on a Smart APEX automated diffractometer (graphite monochromator, Mo-K $\alpha$  radiation,  $\varphi$ — $\omega$  scan mode,  $\lambda = 0.71073$  Å). Structures 1-4 were solved by a direct method and refined by the least-squares method for  $F^2_{hkl}$  in the anisotropic approximation for all non-hydrogen atoms using the SHELXTL program package.<sup>14</sup> The SADABS program was used to apply an absorption correction.<sup>15</sup> The H atoms were placed in the geometrically calculated positions and refined in the riding model. The main crystallographic data for compound 1 (C<sub>24</sub>H<sub>39</sub>F<sub>6</sub>NO<sub>2</sub>SiW) at 100 K are the following: M = 699.50, space group P2(1)/c, a = 10.2453(4) Å, b = 30.6476(11) Å, c = 10.5719(4) Å,  $\beta = 118.179(1)^{\circ}, V = 2926.07(19) \text{ Å}^3, Z = 4, d_{\text{calc}} = 1.588 \text{ g cm}^{-3},$  $\mu = 4.047 \text{ mm}^{-1}, T_{\text{max}}/T_{\text{min}} = 0.7648/0.3486, F(000) = 1392,$  $1.33^{\circ} \le \theta \le 27.5^{\circ}$ ; 27 690 reflections were collected, of which 6685 reflections ( $R_{\text{int}} = 0.0307$ ) were independent,  $R_1 = 0.0418$ and  $wR_2 = 0.0846$  ( $\overline{I} > 2\sigma(I)$ ),  $R_1 = 0.0510$ ,  $wR_2 = 0.0874$  (by all data),  $GOF(F^2) = 1.047$ , residual electron density  $\rho_{max}/\rho_{min} =$ =  $3.007/-1.127 \text{ e} \cdot \text{Å}^{-3}$ . The main crystallographic parameters for structure 2 ( $C_{29}H_{41}F_6NO_2SiW$ ) at 100 K are the following: M = 761.57, space group P2(1)/c, a = 16.3724(4) Å,

Bochkarev et al.

b = 17.9479(5) Å, c = 11.3163(3) Å,  $\beta = 91.334(1)^{\circ}$ ,  $V = 3324.40(15) \text{ Å}^3$ , Z = 4,  $d_{\text{calc}} = 1.522 \text{ g cm}^{-3}$ ,  $\mu = 3.569 \text{ mm}^{-1}$ ,  $T_{\text{max}}/T_{\text{min}} = 0.7167/0.2684, F(000) = 1520, 2.44^{\circ} \le \theta \le 26.0^{\circ};$ 9695 collected reflections of which 6480 reflections  $(R_{\text{int}} = 0.0277)$  were independent,  $R_1 = 0.0344$  and  $wR_2 = 0.0857$  $(I > 2\sigma(I)), R_1 = 0.0485, wR_2 = 0.0910$  (by all data), GOF $(F^2) =$ = 1.047, residual electron density  $\rho_{max}/\rho_{min} = 1.684/-0.493 \text{ e} \cdot \text{Å}^{-3}$ . The main crystallographic parameters for structure 3  $(C_{25}H_{39}F_6NO_2W)$  at 100 K are the following: M = 683.42, space group P2(1)/c, a = 10.2190(4) Å, b = 30.4509(14) Å, c = 10.3468(4) Å,  $\beta = 117.2910(10)^{\circ}$ , V = 2861.3(2) Å<sup>3</sup>, Z = 4,  $d_{\text{calc}} = 1.586 \,\text{g cm}^{-3}, \mu = 4.097 \,\text{mm}^{-1}, T_{\text{max}}/T_{\text{min}} = 0.7352/0.4274,$  $F(000) = 1360, 1.34^{\circ} \le \theta \le 25.99^{\circ}; 24\ 182\ \text{collected\ reflections\ of}$ which 5593 reflections were independent ( $R_{int} = 0.0250$ ),  $R_1 = 0.0283$  and  $wR_2 = 0.0561$  ( $I > 2\sigma(I)$ ),  $R_1 = 0.0326$ ,  $wR_2 = 0.0574$  (by all data),  $GOF(F^2) = 1.070$ , residual electron density  $\rho_{max}/\rho_{min}$  = 1.472/–0.754  $e\cdot {\rm \AA}^{-3}.$  The main crystallographic parameters for structure 4 ( $C_{30}H_{41}F_6NO_2W$ ) at 100 K are the following: M = 745.49, space group C2, a = 18.6868(8) Å, b = 11.5698(5) Å, c = 15.8320(7) Å,  $\beta = 114.0320(10)^{\circ}$ , V = 3126.2(2) Å<sup>3</sup>, Z = 4,  $d_{calc} = 1.584$  g cm<sup>-3</sup>,  $\mu = 3.757$  mm<sup>-1</sup>,  $T_{\text{max}}/T_{\text{min}} = 0.5512/0.4535, F(000) = 1488, 2.39^{\circ} \le \theta \le 25.00^{\circ};$ 12 059 collected reflections of which 5386 reflections were independent ( $R_{int} = 0.0255$ ),  $R_1 = 0.0452$  and  $wR_2 = 0.1137$  $(I > 2\sigma(I)), R_1 = 0.0547, wR_2 = 0.1222$  (by all data), GOF $(F^2) =$ 1.106, absolute structural parameter 0.508(10), residual electron density  $\rho_{\text{max}}/\rho_{\text{min}} = 2.460/-0.949 \text{ e} \cdot \text{Å}^{-3}$ .

Hex-1-ene, deca-1,9-diene, and cyclooctene (Aldrich) were degassed before use and kept above the sodium mirror. Necessary amounts were sampled by condensation in vacuo. Kinetic experiments and the determination of the second-order reaction rate constants for hex-1-ene homometathesis and deca-1,9-diene metathesis polycondensation were conducted according to earlier described procedures.<sup>16,17</sup> Polymerization was carried out in the absence of solvent. The molecular weight distribution of the polymers was determined by gel permeation chromatography (GPC) on a Knauer chromatograph with a Smartline RID 2300 differential refractometer as a detector with a set of two Phenomenex columns (sorbent Phenogel, pore size  $10^4$  and  $10^5$  Å). The eluent was THF (2 mL min<sup>-1</sup>, 40 °C). The columns were calibrated by 13 polystyrene standards. Oligomers were analyzed on a Shimadzu chromatograph with a RID-10A differential refractometer as a detector using a Phenomenex column (sorbent Phenogel, pore size 500 Å). The eluent was THF (1 mL min<sup>-1</sup>, 40 °C). The columns were calibrated by seven polystyrene standards. The ratio of the *trans*- to *cis*-units in the polymers was determined by <sup>13</sup>C NMR spectroscopy using a known procedure.18

**2,6-Diisopropylphenylimido-bis(1,1-dimethyl-2,2,2-trifluoroethanolato)(dimethylphenylsilylmethylidene)tungsten (2).** A solution of PhMe<sub>2</sub>SiCH=CH<sub>2</sub> (0.094 g, 0.58 mmol) in benzene (3 mL) was added at ~20 °C to a dark yellow solution of Bu<sup>t</sup>HC=W(NAr)(OCMe<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> (0.40 g, 0.59 mmol) in benzene (5 mL). The reaction mixture was stored for 3.5 h at ~20 °C. The solvent and volatile products were removed by evaporation *in vacuo*. After the residue was recrystallized from a minimum amount of ether at -20 °C, compound **2** was obtained in a yield of 0.13 g (33%) as unstable in air light yellow-green crystals. Found (%): C, 45.95; H, 5.47. C<sub>29</sub>H<sub>41</sub>F<sub>6</sub>NO<sub>2</sub>SiW. Calculated (%): C, 45.74; H, 5.42. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>),  $\delta$ : 0.41 (s, 6 H, CHSi<u>Me<sub>2</sub>Ph); 1.22 (d, 12 H, CHMe<sub>2</sub>, J<sub>H,H</sub> = 7.0 Hz); 1.22 and </u> 1.29 (both s, 6 H each,  $OC\underline{Me}_2CF_3$ ); 3.66 (sept, 2 H,  $C\underline{H}Me_2$ ); 6.98–7.24 (m, 3 H, 2,6- $Pr^i_2C_6\underline{H}_3$  + 3 H, H(2), H(4), H(6), CHSiMe\_2<u>Ph</u>); 7.48–7.53 (m, 2 H, H(3), H(5), CHSiMe\_2<u>Ph</u>); 9.49 (s, 1 H, W=C<u>H</u>SiMe\_2Ph). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>),  $\delta$ : 0.9 (W=CHSi<u>Me</u><sub>2</sub>Ph); 23.8 (CH<u>Me</u><sub>2</sub>), 24.3, 24.4 (OC<u>Me</u><sub>2</sub>CF<sub>3</sub>); 28.3 (<u>C</u>HMe<sub>2</sub>); 80.2 (q, O<u>C</u>Me<sub>2</sub>CF<sub>3</sub>, <sup>2</sup>J<sub>C,F</sub>= 29.0 Hz); 122.9 (C(3), 2,6-Pr<sup>i</sup>\_2<u>C</u><sub>6</sub>H<sub>3</sub>); 126.9 (C(4), 2,6-Pr<sup>i</sup>\_2<u>C</u><sub>6</sub>H<sub>3</sub>); 127.0 (q, OCMe<sub>2</sub><u>C</u>F<sub>3</sub>, <sup>1</sup>J<sub>C,F</sub>= 285 Hz); 128.4 (C(3), CHSiMe\_2<u>Ph</u>); 129.1 (C(4), SiMe\_2<u>Ph</u>); 133.8 (C(2), SiMe\_2<u>Ph</u>); 141.8 (C(1), SiMe\_2<u>Ph</u>); 144.9 (C(2), 2,6-Pr<sup>i</sup>\_2<u>C</u><sub>6</sub>H<sub>3</sub>); 152.1 (C(1), 2,6-Pr<sup>i</sup>\_2<u>C</u><sub>6</sub>H<sub>3</sub>); 227.1 (W=<u>C</u>HSi).

Since no detailed quantitative characteristics were published for compound **4**, we present the NMR and elemental analysis data. Found (%): C, 48.15; H, 5.40.  $C_{30}H_{41}F_6WNO_2$ . Calculated (%): C, 48.34; H, 5.55. <sup>1</sup>H NMR ( $C_6D_6$ ),  $\delta$ : 1.18, 1.23 (both s, 6 H each, OCMe<sub>2</sub>CF<sub>3</sub>); 1.24 (d, 12 H, CHMe<sub>2</sub>, *J* = 7.0 Hz); 1.60 (s, 6 H, CMe<sub>2</sub>Ph); 3.73 (sept, 2 H, CHMe<sub>2</sub>, <sup>3</sup>*J*<sub>H,H</sub> = 6.8 Hz); 6.96–7.22 (m, 3 H, 2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub> + 3 H, H(2), H(4), H(6), CMe<sub>2</sub>Ph); 7.31–7.39 (m, 2 H, H(3), H(5), CMe<sub>2</sub>Ph); 8.53 (s, 1 H, W=CH, <sup>2</sup>*J*<sub>W,H</sub> = 13.6 Hz). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>),  $\delta$ : 23.8 (OCMe<sub>2</sub>CF<sub>3</sub>); 24.2 (CHMe<sub>2</sub>); 28.2 (CHMe<sub>2</sub>); 32.8 (CMe<sub>2</sub>Ph); 51.4 (CMe<sub>2</sub>Ph); 79.9 (q, OCMe<sub>2</sub>CF<sub>3</sub>, <sup>2</sup>*J*<sub>C,F</sub> = 29.0 Hz); 123.1 (C(3), 2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 126.08 (C(3), CMe<sub>2</sub>Ph); 126.11 (C(4), 2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 127.2 (q, OCMe<sub>2</sub>CF<sub>3</sub>, <sup>1</sup>*J*<sub>C,F</sub> = 285 Hz); 127.2, 128.4 (C arom.); 145.9 (C(2), CMe<sub>2</sub>Ph); 151.6 (C(2), 2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 151.9 (C(1), CMe<sub>2</sub>Ph); 243.2 (W=CH, <sup>1</sup>*J*<sub>W,C</sub> = 202.8 Hz).

**Metathesis of hex-1-ene.** The reactions were carried out without solvent at ~20 °C. Hex-1-ene (0.9091 g, 10.820 mmol) was added under an argon atmosphere to an ampule connected with a gas burette and containing catalyst **2** (27.2 mg, 0.036 mmol), and the mixture was stirred. The amount of evolved ethylene was determined volumetrically at an interval of 1 min during 1 h. The reaction was stopped by the addition of  $Al_2O_3$  to the reaction mixture. Unconverted hex-1-ene was removed by evaporation *in vacuo*, and according to the <sup>13</sup>C NMR spectroscopy data, the remaining liquid products were a mixture of *trans*- and *cis*-dec-5-enes<sup>19</sup> in a ratio of 66 : 34. The reactions of hex-1-ene metathesis using other catalysts were carried out similarly. At least five kinetic experiments were conducted for each catalyst.

Metathesis polycondensation of deca-1,9-diene. The reactions were carried out without solvent at ~20 °C. Deca-1,9-diene (1.406 g, 10.170 mmol) was added under an argon atmosphere to an ampule connected with a gas burette and containing catalyst 1 (68.6 mg, 0.098 mmol), and the mixture was stirred. The amount of evolved ethylene was determined volumetrically at an interval of 1 min during 1 h. The reaction was stopped by the addition of one droplet of benzaldehyde to the reaction mixture. The deca-1,9-diene that did not react was removed by evaporation *in vacuo* at 70 °C, and the remaining oligomers were analyzed by GPC to determine the molecular weight characteristics. The ratio of the *trans*- and *cis*-units was determined by <sup>13</sup>C NMR spectroscopy using a known procedure.<sup>18</sup> The deca-1,9-diene metathesis polycondensation reactions were carried out similarly. At least five kinetic experiments were carried out for each catalyst.

**Ring-opening metathesis polymerization of cyclooctene.** Cyclooctene (0.6352 g, 5.764 mmol) was added to an ampule filled with argon and containing catalyst **2** (43.8 mg, 0.058 mmol), and the mixture was stirred at ~20 °C. The solid transparent block was formed within 25 min. The reaction mixture was additionally kept for 1 h at ~20 °C. A polymer sample was dissolved under an argon atmosphere in CDCl<sub>3</sub> with an addition of a small amount of benzaldehyde to decompose the catalyst. <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy was used for analysis. It was found that the polyoctenamer formed contained no starting cyclooctene. Thus, the yield of the polymer was nearly quantitative. To perform the GPC analysis, a polymer sample was dissolved under an argon atmosphere in THF with an addition of benzaldehyde. The molecular weight characteristics are given in Table 4. It was shown in special experiments that the molecular weight characteristics remained unchanged after reprecipitation from methanol. The reactions of ring-opening metathesis polymerization of cyclooctene using other catalysts and analyses of the polymer products were carried out similarly.

The authors are grateful to V. D. Myakushev and S. A. Ponomarenko (N. S. Enikolopov Institute of Synthetic Materials, Russian Academy of Sciences) for help in the GPC analysis of oligomers.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos 05-03-32694, 06-03-32728, 07-03-90822-mob\_st, and 08-03-00436).

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Received November 14, 2007; in revised form April 16, 2008