ISSN 1070-3632, Russian Journal of General Chemistry, 2010, Vol. 80, No. 10, pp. 1945–1953. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © Yu.P. Barinova, A.L. Bochkarev, Yu.E. Begantsova, L.N. Bochkarev, Yu.A. Kurskii, G.K. Fukin, A.V. Cherkasov, G.A. Abakumov, 2010, published in Zhurnal Obshchei Khimii, 2010, Vol. 80, No. 10, pp. 1634–1642.

Carbene Complexes of Molybdenum and Tungsten $Et_3E–CH=M(NAr)(OR)_2$ (M = Mo, W; E = Si, Ge) and π-Complex of Molybdenum $(RO)_2(ArN)Mo(CH_2=CH–GeEt_3)$. Synthesis and Catalytic Properties

Yu. P. Barinova, A. L. Bochkarev, Yu. E. Begantsova, L. N. Bochkarev,
Yu. A. Kurskii, G. K. Fukin, A. V. Cherkasov, and G. A. Abakumov

Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,
ul. Tropinina 49, Nizhni Novgorod, 603950 Russia
e-mail: lnb@iomc.ras.ru

Received December 16, 2009

Abstract—The heteroelement-containing alkylidene imide complexes with molybdenum and tungsten $Et_3SiCH=Mo(NAr)(OR)_2$ (**I**), Et_3 $ECH=W(NAr)(OR)_2$ (E = Si (**II**), Ge (**III**); Ar = 2,6-*i*-$Pr_2C_6H_3$; R=CMe_2 CF_3) and π-complex $(RO)_2(ArN)Mo(CH_2=CH–GeEt_3)$ (**IV**) were synthesized by the reaction of Alkyl–CH=M(NAr)$(OR)_2$ (M=Mo, W; Alkyl = *t*-Bu, $PhMe_2C$) with organosilicon and organogermanium vinyl reagents $Et_3ECH=CH_2$ (E = Si, Ge). The structure of compounds **I–III** was determined by X-ray diffraction (XRD). The complexes **I–IV** are active initiators of metathesis polymerization of cycloolefins.

DOI: 10.1134/S1070363210100129

Alkylidene Schrock complexes of the Alkyl–CH=M(NAr)$(OR')_2$ type (Alkyl = *t*-Bu, $PhMe_2C$; M = Mo, W; Ar = 2,6-Pr-$i_2C_6H_3$, R' = Alkyl, Aryl) [1–4] belong to the group of the most active catalysts of olefin metathesis reactions. Their catalytic properties as well as the composition and structure of products of metathesis reactions involving molybdenum and tungsten catalysts essentially depend on the nature of their ligand environment. The vast majority of the catalysts of this type include hydrocarbon carbene fragments. Less studied are similar complexes of molybdenum and tungsten with heteroelement-containing carbene fragments [5–11]. We have previously shown that carbene complexes with silicon and germanium substituents in the carbene fragments $Me_3ECH=M(NAr)(OR)_2$, $Me_2PhSi–CH=M(NAr)(OR)_2$ (M = Mo, W; E = Si, Ge) are catalysts for some reactions of olefin metathesis, and their catalytic activity is markedly different from the activity of the corresponding hydrocarbon analogs [8–11].

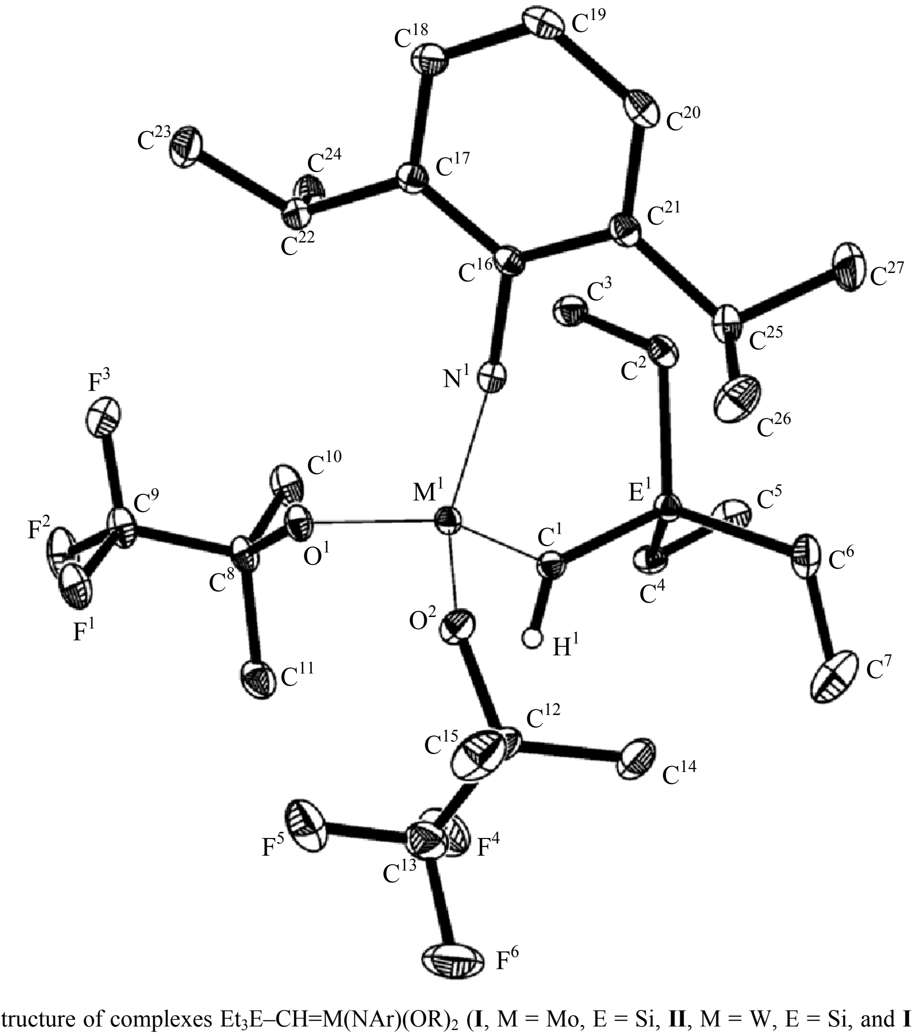
In this work new representatives of the heteroelement-containing carbene complexes of molybdenum and tungsten were synthesized, compounds with triethylsilyl and triethylgermyl substituents in the carbene fragments, $Et_3SiCH=Mo(NAr)(OR)_2$ (**I**) and $Et_3ECH=W(NAr)(OR)_2$, E = Si (**II**) or Ge (**III**). The complexes **I–III** were prepared by the reaction of alkylidene compounds $PhMe_2C–CH=Mo(NAr)(OR)_2$ [5] or *t*-Bu–CH=W(NAr)$(OR)_2$ [6] with organosilicon or organogermanium vinyl reagents $Et_3ECH=CH_2$ (E = Si, Ge):

$$\text{Alkyl–CH=M(NAr)(OR)}_2 + \text{Et}_3\text{ECH=CH}_2 \xrightarrow[-\,\text{Alkyl–CH=CH}_2]{\text{pentane, 20°C}} \textbf{I–III}$$

M = Mo, Alkyl = $PhMe_2C$; M = W, Alkyl = *t*-Bu.

According to the ^{1}H NMR spectroscopy, the formation of complex **I** is completed within 20 h, complex **II**, in 5 h, complex **III**, in 3 days. Yield of crude products is almost quantitative, however, the complexes are well soluble in the common organic solvents and could be separated in an individual state in 25–46% yield only. The complexes **I–III** are unstable in air crystalline compounds of orange (Mo) or yellow (W) color. As in the previously studied silicon- and germanium-containing alkylidene molybdenum and tungsten complexes [5–11] the signals of H_α atoms in the ^{1}H NMR spectra of complexes **I** (13.22 ppm), **II** (9.30 ppm), and **III** (9.49 ppm) appear as broad singlets shifted downfield approximately by 1.5 ppm in comparison with similar signals of these metals complexes with hydrocarbon carbene fragments [5, 6].

The X-ray study of compounds **I–III** showed that they molecular structures are similar. Complexes **I** and **II** are isostructural. The atoms of molybdenum and tungsten, as well as of silicon and germanium in the compounds **I–III** have a distorted tetrahedral coordination (Fig. 1). The bond angles at the molybdenum and tungsten atoms are in the range 103.64(7)°–111.76(5)° and 101.7(1)°–111.9(1)°, respectively (Table 1). The bond angles at the silicon atoms in **I** and **II** [107.72(7)°–110.79(7)°] and germanium atoms in **III** [107.9(1)°–110.4(2)°] also have the values characteristic of a distorted tetrahedron. The organosilicon and organogermanium substituents at the carbene carbon atoms in the complexes **I–III** are directed toward imide ligands that corresponds to the *syn*-conformation of the complexes. The changes in the Si^1–C^1 distances in **I**, **II** and Ge^1–C^1 in **III** [1.864(2), 1.862(2) Å in **I** and **II**,



The molecular structure of complexes Et_3E–$CH{=}M(NAr)(OR)_2$ (**I**, M = Mo, E = Si, **II**, M = W, E = Si, and **III**, M = W, E = Ge). Thermal ellipsoids are given with 30% probability.

Table 1. Principal bond lengths (*d,* Å) and bond angles (ω, deg) in complexes **I–III**

Bond	**I**	**II**	**III**
M^1–C^1	1.888(2)	1.888(3)	1.892(3)
M^1–N^1	1.727(1)	1.736(2)	1.714(2)
M^1–O^1	1.9036(9)	1.893(2)	1.898(2)
M^1–O^2	1.898(1)	1.885(2)	1.891(2)
E^1–C^1	1.864(2)	1.862(3)	1.936(3)
Angle	**I**	**II**	**III**
$M^1C^1E^1$	139.75(9)	140.5(2)	139.6(2)
$M^1N^1C^{16}$	164.7(1)	166.3(2)	173.2(2)

Table 2. Characteristics of polyoctenamers obtained using initiators **I–III**[a]

Initiator	Yield, %	*trans*:*cis*, %	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
I	77	5:95	233110	147030	1.59
II	85	55:45	1437900	515500	2.79
III	83	31:69	694500	353600	1.96

[a] Polymerization in bulk, the ratio of monomer: initiator = 100:1, the reaction duration to the formation of a solid transparent block is 50 min in the case of initiator **I** and 30 min in the case of initiators **II** and **III**.

1.936(3) Å in **III**] correlate with the changes in the covalent radii of E^1 [1.13 Å (Si) in **I** and **II**, and 1.19 Å (Ge) in **III**] [12]. The distances Mo=C in complex **I** [1.888(2) Å] and W=C in **II** and **III** [1.888(3), 1.892(3) Å] are comparable with the analogous distances in the previously described silicon- and germanium-containing carbene complexes of molybdenum $Me_3SiCH{=}Mo(NAr)(OR)_2$ [1.889(2) Å] [5, 8], $PhMe_2SiCH{=}Mo(NAr)(OR)_2$ [1.877(1) Å] [10], $Ph_3SiCH{=}Mo(NAr)(OR)_2$ [1.883(3) Å] [8], $Me_3Ge\cdot CH{=}Mo(NAr)(OR)_2$ [1.889(2) Å] [7], $Ph_3GeCH{=}Mo\cdot(NAr)(OR)_2$ [1.876(2) Å] [7] and tungsten $Me_3Si\cdot CH{=}W(NAr)(OR)_2$ [1.877(4) Å] [6, 11], $PhMe_2Si\cdot CH{=}W(NAr)(OR)_2$ [1.888(3) Å] [11]. $Me_3GeCH{=}W\cdot(NAr)(OR)_2$ [1.882(3) Å] [9]. Bond angles Mo–C–Si in **I** [139.75(9)°] and WC–Si in **II** [140.5(2)°], WC–Ge in **III** [139.6(2)°] are almost of the same value. A minor difference in the structure of germanium-containing complex **III** and silicon-containing compounds **I** and **II** is the slightly larger value of the angle WNC [173.2(2)°] in **III** as compared with the MNC angles [164.7(1)°, 166.3 (2)°] in **I** and **II** [M = Mo (**I**), W (**II**)].

While studying the catalytic properties of complexes **I–III** we found that they are active initiators of metathesis bulk polymerization of cyclooctene at room temperature and cause formation of high-molecular polyoctenamers (Table 2).

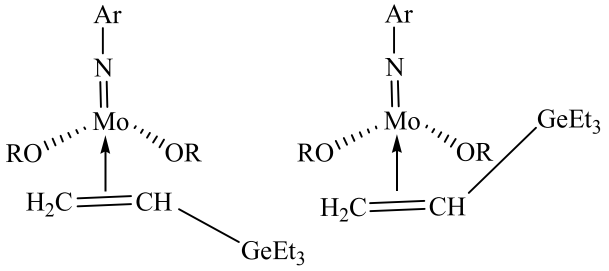
In further studies, we have attempted to synthesize a germanium-containing carbene complex of molybdenum by the reaction of $PhMe_2C{-}CH{=}Mo(NAr)(OR)_2$ with $Et_3GeCH{=}CH_2$. Unexpectedly, it was found that the reaction between these reactants proceeds by entirely different route compared with the reaction of neophylidene molybdenum complex with triethylvinylsilane. At the reagents ratio 1:1 the reaction is completed within 10 minutes affording a complex mixture of products, among which by the method of ^{1}H NMR spectroscopy the germanium-containing carbene complex $Et_3GeCH{=}Mo(NAr)(OR)_2$, (H_α, δ = 13.39 ppm) was identified, but only in ~3% yield. The main products were asymmetric olefin derivative $PhMe_2C{-}CH{=}CH{-}CH_2{-}GeEt_3$ and π-complex $(RO)_2(ArN)Mo\cdot(CH_2{=}CH{-}GeEt_3)$ (**IV**), and the reaction mixture contained unused neophylidene complex $PhMe_2C{-}CH{=}Mo(NAr)(OR)_2$ (~20% of the original amount). Reaction of $PhMe_2C{-}CH{=}Mo(NAr)(OR)_2$ with an excess of $Et_3GeCH{=}CH_2$ completed within 5 min. In the ^{1}H NMR spectrum of the reaction mixture in the alkylidene region (8.0–20.0 ppm), no signals of H_α atoms of any carbene complexes were present, the reaction products were germanium-containing olefin $PhMe_2C{-}CH{=}CH{-}CH_2{-}GeEt_3$ and π-complex **IV**:

$$PhMe_2C{-}CH{=}Mo(NAr)(OR)_2 + \underset{\text{excess}}{Et_3ECH{=}CH_2}$$

$$\xrightarrow{C_6D_6,\ 20°C} \underset{\mathbf{IV}}{(RO)_2(ArN)Mo(CH_2{=}CH{-}GeEt_3)}$$

$$+\ PhMe_2C{-}CH{=}CH{-}CH_2{-}GeEt_3$$

After removal of solvent and triethylvinylgermanium excess from the reaction mixture in a vacuum at room temperature, the unsaturated derivative $PhMe_2C{-}CH{=}CH{-}CH_2{-}GeEt_3$ was isolated in 94% yield by fractionation of the residue in a vacuum at 100–110°C. It is a colorless oily substance stable in air, which is identified using IR, ^{1}H and ^{13}C NMR spectroscopy, and elemental analysis. We failed to isolate molybdenum π-complex $(RO)_2(ArN)Mo\cdot(CH_2{=}CH{-}GeEt_3)$ in an individual state, so this compound was identified by ^{1}H and ^{13}C NMR spectroscopy as a component in a mixture with $PhMe_2C–CH=CH–CH_2–GeEt_3$. According to NMR data (see Experimental), the π-complex **IV** exists in solution at room temperature in the form of two isomers in the ratio 82:18, which seem to differ in the location of the $CH_2=CH–GeEt_3$ molecule relative to the imide and alkoxylate ligands:

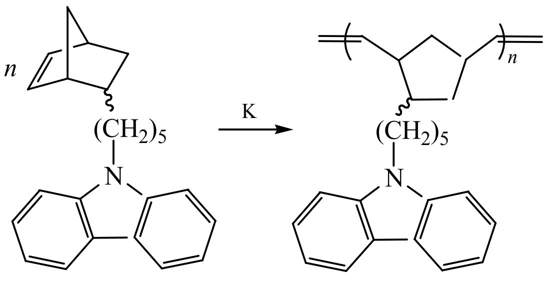


Isomer **1** Isomer **2**

It is presumable that the reaction of $PhMe_2C–CH=Mo(NAr)(OR)_2$ with $Et_3GeCH=CH_2$ proceeds in accordance with the Scheme 1.

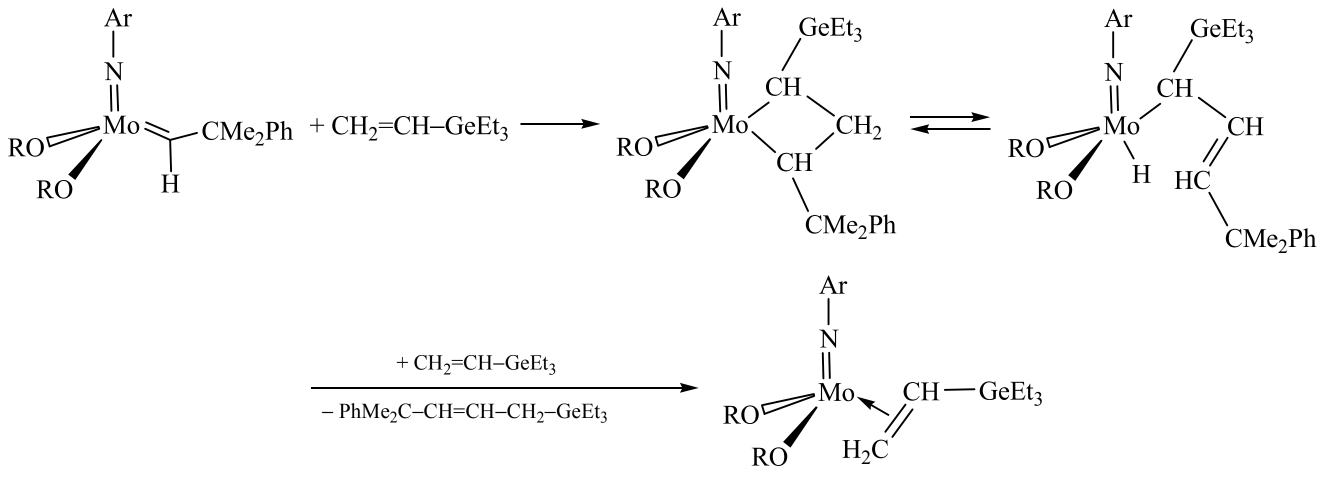
In accordance with the generally accepted mechanism of the olefin metathesis [13], in the initial stages of the reaction of the molybdenum neophylidene compounds with triethylvinylgermanium the formation occurs of a molybdocyclobutane derivative containing Et_3Ge and $PhMe_2C$ substituents at the C_α atom of the metallocycle. Then probably the β-hydride rearrangement of the molybdocyclobutane complex proceeds and its transformation into an intermediate alkyl hydride compound. In the final step, the second molecule of triethylvinylgermanium reacts with the alkyl hydride compound to form eventually the unsaturated germanium-containing compound $PhMe_2C–CH=CH–CH_2–GeEt_3$ and the molybdenum π-complex $(RO)_2(ArN)Mo(CH_2=CH–GeEt_3)$. Similar processes of β-hydride rearrangements of molybdocyclobutane derivatives and the formation of π-complexes $[(CF_3)_2MeCO]_2(ArN)Mo(CH_2=CH–SiMe_3)$, $[Benz_2Bitet](ArN)Mo(CH_2=CH–CMe_2Ph)$ ($Benz_2BitetH_2$ = 3,3'-dibenzhydryl-5,5',6,6',7,7',8,8'-octahydro-1,1'-bis-2-naphthol), $[Biphen](ArN)Mo(CH_2=CH–SnBu_3)$ ($BiphenH_2$ = 3,3'-di-*tert*-butyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diol) have been reported previously [14–16].

Note that the π-complex $(RO)_2(ArN)Mo(CH_2=CH–GeEt_3)$ without its isolation from a mixture with $PhMe_2C–CH=CH–CH_2–GeEt_3$ is capable to initiate the ring-opening metathesis polymerization (ROMP) of norbornene and its carbazole derivative, 9-(5-bicyclo[2.2.1]hept-5-ene-2-yl-pentyl)-9*H*-carbazole [$NBE–(CH_2)_5–Carb$]. Norbornene in benzene solution was polymerized in 2–3 min to form polynorbornene in 96% yield ($\overline{M}_w$ = 2177400, $\overline{M}_n$ = 796300, $\overline{M}_w/\overline{M}_n$ = 2.73; the content of *cis* units 74%). The functional norbornene derivative $NBE–(CH_2)_5–Carb$ [17] polymerized in benzene solution in an hour.



K = $(RO)_2(ArN)Mo(CH_2=CH–GeEt_3)$.

Scheme 1.



The carbazole-containing functionalized polynorbornene was isolated in 70% yield ($\overline{M}_w = 19000$, $\overline{M}_n = 7300$, $\overline{M}_w/\overline{M}_n = 2.60$). The resulting polymer is of practical interest, since it is known [18] that carbazole-containing polymers are used as hole-conducting materials in the manufacture of organic light-emitting diodes.

The initiating ability of the molybdenum π-complex can be explained by the probable formation of carbene complexes at the interaction of this compound with cycloolefins, which subsequently participate in the stage of the chain growth (Scheme 2).

Thus, we have synthesized and structurally characterized new molybdenum and tungsten carbene complexes with triethylsilyl and triethylgermyl substituents in the carbene fragments. These compounds actively initiate metathesis polymerization of cyclooctene in bulk at room temperature that leads to the formation of high-molecular polyoctenamers. It is shown that the reaction of a neophylidene compound $PhMe_2C–CH=Mo(NAr)(OR)_2$ with triethylvinylgermanium leads to the formation of the molybdenum π-complex $(RO)_2(ArN)Mo(CH_2=CH–GeEt_3)$ capable to initiate metathesis polymerization of norbornene and its carbazole-containing functional derivatives.

EXPERIMENTAL

All operations were performed in evacuated glass ampules using common Schlenk technique. The solvents used were thoroughly purified and degassed. $PhMe_2C–CH=Mo(NAr)(OR)_2$ [5], *t*-Bu–CH=W(NAr)OR)$_2$ [6], $Et_3ECH=CH_2$ (E = Si, Ge) [19], and NBE–$(CH_2)_5$–Carb [17] were synthesized as described in the literature. Cyclooctene (Aldrich) was degassed before use and kept over sodium mirror. Necessary amounts were measured off by condensation in a vacuum. Norbornene (Aldrich) was used without further purification.

The NMR spectra of tungsten and molybdenum complexes in deuterobenzene and of the polymer samples in deuterochloroform were obtained on a Bruker DPX-200 spectrometer (^{1}H NMR: 200 MHz, ^{13}C NMR: 50 MHz). NMR spectra of π-complex **IV** and $PhMe_2C–CH=CH–CH_2–GeEt_3$ in deuterobenzene were obtained on a Bruker Avance III-400 spectrometer (^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz), assignment of signals was carried out using a gradient 2D-spectroscopy: proton–proton correlation (GE-COSY) and proton–carbon correlation (GE-HSQC). Chemical shifts are shown in parts per million (ppm) relative to tetramethylsilane as internal reference.

IR spectrum of compound $PhMe_2C–CH=CH–CH_2–GeEt_3$ in the form of a liquid film between plates of KBr or CaF_2 were recorded on a FSM 1201 IR-Fourier spectrometer.

Molecular mass distribution in the polymers was determined by gel permeation chromatography (GPC) on a Knauer chromatograph with a Smartline RID 2300 differential refractometer as detector, with a set

Scheme 2.

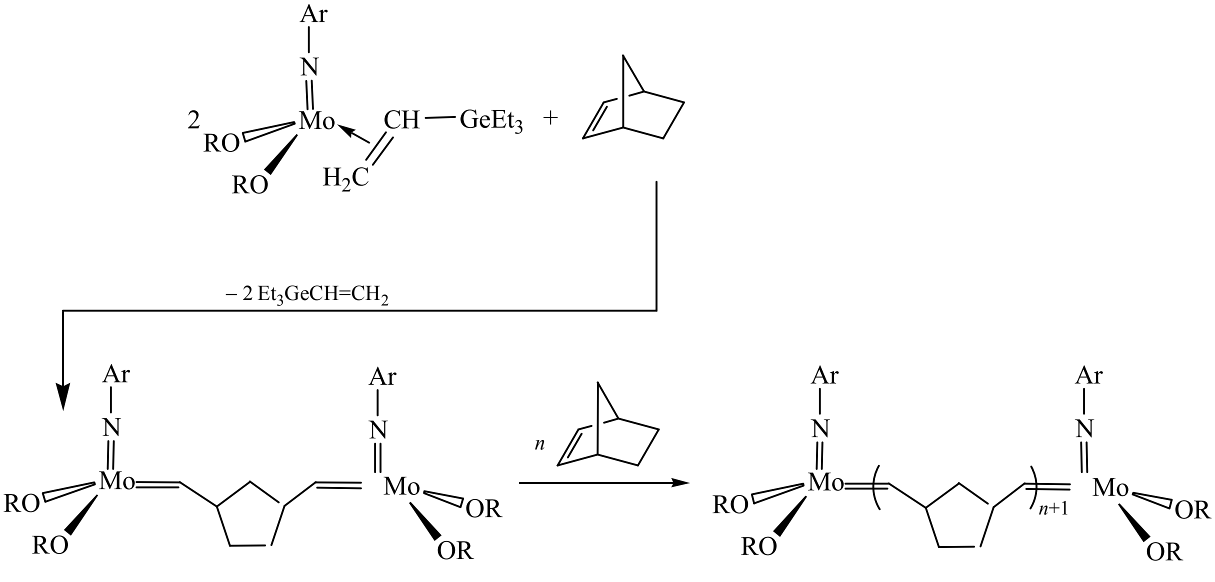


Table 3. The main crystallographic data and refinement parameters for the complexes **I–III**

Parameters	**I**	**II**	**III**
Empirical formula	$C_{27}H_{45}F_6MoNO_2Si$	$C_{27}H_{45}F_6NO_2SiW$	$C_{27}H_{45}F_6GeNO_2W$
Molecular weight	653.67	741.58	786.08
Crystal size, mm	0.45×0.26×0.06	0.93×0.74×0.58	0.39×0.30×0.20
Space group	$P2(1)/c$	$P2(1)/c$	$Pna2(1)$
a, Å	10.8531(5)	10.8339(5)	18.3618(15)
b, Å	31.2414(16)	31.2873(15)	13.1897(11)
c, Å	10.5572(5)	10.5856(5)	13.0592(10)
α, deg	90	90	90
β, deg	118.1360(10)	118.2790(10)	90
γ, deg	90	90	90
Volume, Å^3	3156.6(3)	3159.9(3)	3162.8(4)
Z	4	4	4
d_{calc}, mg m^{-3}	1.375	1.559	1.651
μ, mm^{-1}	0.512	3.752	4.643
T_{min}/T_{max}	0.8022/0.9699	0.1281/0.2195	0.2646/0.4570
$F(000)$	1360	1488	1560
2θ, deg	55	52	55
Number of independent reflections (R_{int})	29696 (0.0286)	26564 (0.0398)	28483 (0.0298)
R_1 [$I > 2\sigma(I)$]	0.0366	0.0316	0.0291
wR_2 (all data)	0.0863	0.0685	0.0625
Number of refined parameters	515	358	343
GOOF	1.051	1.110	1.073
The residual peaks of electron density, e Å^{-3}	–0.386/0.939	–1.022/1.440	–1.046/2.086

of two Phenomenex columns with the Phenogel sorbent with pore size 10^4 and 10^5 Å (eluent THF, 2 ml min^{-1}, 40°C). The calibration of the columns was carried out with 13 polystyrene standards. The ratio of *trans*- and *cis*-units in polyoctenamers and polynorbornene was determined by ^{13}C NMR spectroscopy according to known methods [20, 21].

Single crystals of complexes **I–III** were obtained by crystallization from pentane. X-ray diffraction studies of complexes **I–III** were carried out on a SMART APEX diffractometer (φ–ω-scan, Mo-K_α-radiation, $\lambda = 0.71073$ Å, graphite monochromator) at 100(2) K. Structures were solved by the direct method and refined by least-squares method on F^2_{hkl} in the anisotropic approximation for all nonhydrogen atoms. H atoms at C^6 in **I** and all the hydrogen atoms in **II** (except for H^1) and **III** were placed into the geometrically calculated positions and refined with the "*rider*" model, the remaining H atoms were found from difference synthesis of electron density and refined isotropically. All calculations were performed using the program package SHELXTL v. 6.10 [22]. The program SADABS [23] was used to introduce corrections on extinction. The key bond lengths and bond angles, the main crystallographic characteristics, and parameters of X-ray experiment are given in Tables 1 and 3.

(2,6-Diisopropylphenylimido)-bis(1,1-dimethyl-2,2,2-trifluoroethanolato)(triethylsilylmethylidene)-molybdenum Et$_3$SiCH=Mo(NAr)(OR)$_2$ (I). To a solution of PhMe$_2$C–CH=Mo(NAr)(OR)$_2$ (1.1 g, 1.67 mmol) in 5 ml of pentane was added Et$_3$SiCH=CH$_2$ (0.36 g, 2.53 mmol) in 2 ml of pentane. The reaction mixture was stirred for 20 h at room temperature. The solvent and volatile products were removed by evaporation in a vacuum. After recrystallization of the residue from a minimum amount of pentane at –50°C 0.50 g (46%) of compound **I** was obtained as unstable in air orange crystals. ^{1}H NMR spectrum (C$_6$D$_6$), δ, ppm (*J*, Hz): 0.64 q [6H, MoCHSi(C*H*$_2$Me$_3$)$_3$], 0.91 t [9H, MoCHSi(CH$_2$*Me*$_3$)$_3$], 1.21 d (12H, CH*Me*$_2$), 1.37 and 1.28 s (each 6H, OC*Me*$_2$CF$_3$), 3.71 sept (2H, C*H*Me$_2$), 7.01 s (3H, H$_{\text{arom}}$), 13.22 s (1H, MoC*H*SiEt$_3$). ^{13}C NMR spectrum (C$_6$D$_6$), δ, ppm (*J,* Hz): 5.7 (Si*C*H$_2$CH$_3$), 7.7 (SiCH$_2$*C*H$_3$), 23.9 (CH*Me*$_2$), 24.3 and 24.4 (OC*Me*$_2$CF$_3$), 28.6 (*C*HMe$_2$), 78.9 q ($^2J_{\text{CF}}$ 28.6, O*C*Me$_2$CF$_3$), 123.2 (C-*m*), 127.2 q (OCMe$_2$*C*F$_3$, J_{CF} 285.5), 128.3 (C-*p*), 145.8 (C-*o*) , 154.1 (C-*ipso*), 270.9 (Mo*C*HSiEt$_3$). Found, %: C 49.50, H 7.60. C$_{27}$H$_{45}$F$_6$ MoNO$_2$Si. Calculated, %: C 49.39, H 7.47.

(2,6-Diisopropylphenylimido)-bis(1,1-dimethyl-2,2,2-trifluoroethanolato)(triethylsilylmethyliden)-tungsten Et$_3$Si–CH=W(ArN)(OR)$_2$ (II). To a solution of *t*-Bu–CH=W(NAr)(OR)$_2$ (0.47 g, 0.69 mmol) in 5 ml of pentane was added 0.10 g (0.71 mmol) of Et$_3$SiCH=CH$_2$ in 2 ml of pentane. The reaction mixture was stirred for 5 h at room temperature. The solvent and volatile products were removed by evaporation in a vacuum. The residual light brown oily substance was recrystallized from the minimum amount of pentane at –50°C. Compound **II** was isolated as unstable in air yellow crystals. Yield 0.13 g (25%). ^{1}H NMR spectrum (C$_6$D$_6$), δ, ppm (*J*, Hz): 0.66 m [6H, WCHSi (C*H*$_2$Me$_3$)$_3$], 0.96 d [9H, WCHSi(CH$_2$*Me*$_3$)$_3$], 1.24 d (12H, CH*Me*$_2$), 1.28 and 1.37 s (each 6H, OC*Me*$_2$CF$_3$), 3.71 sept (2H, C*H*Me$_2$), 7.20–6.90 m (3H, H$_{\text{arom}}$), 9.30 s (1H, WC*H*SiEt$_3$). ^{13}C NMR spectrum (C$_6$D$_6$), δ, ppm (*J,* Hz): 6.8 (Si*C*H$_2$CH$_3$), 7.9 (SiCH$_2$*C*H$_3$), 23.9 (CH*Me*$_2$), 24.0 (OCMe*Me*CF$_3$), 24.6 (*C*HMe$_2$), 28.3 (OC*Me*MeCF$_3$), 80.0 q (O*C*Me$_2$CF$_3$, $^2J_{\text{CF}}$ 29.1), 122.9 (C-*m*), 126.7 (C-*p*), 127.1 q (CF$_3$, J_{CF} 285.2), 144.9 (C-*o*), 152.0 (C-*ipso*), 225.9 (W*C*HSiSH$_2$Me$_3$). Found, %: C 43.84; H 6.18. C$_{27}$H$_{45}$F$_6$NO$_2$SiW. Calculated, %: C 43.73; H 6.12.

(2,6-Diisopropylphenylimido)-bis-(1,1-dimethyl-2,2,2-trifluoroethanolato)(triethylgermylmethyliden)-tungsten Et$_3$Ge–CH=W(ArN)(OR)$_2$ (III). To a solution of *t*-Bu–CH=W(NAr)(OR)$_2$ (0.56 g, 0.82 mmol) in 5 ml of pentane was added 0.15 g (0.81 mmol) of Et$_3$GeCH=CH$_2$ in 2 ml of pentane. The reaction mixture was stirred for 3 days at room temperature. The solvent and all volatile products were removed by evaporation in a vacuum. The residual light brown oily substance was recrystallized from pentane at –50°C. Compound **III** was isolated as unstable in the air yellow crystals. Yield 0.21 g (30%). ^{1}H NMR spectrum (C$_6$D$_6$), δ, ppm (*J*, Hz): 0.87 m (6H, WCHGeC*H$_2$*Me$_3$), 1.04 t (9H, WCHGeCH$_2$*Me*$_3$), 1.26 d (12H, CH*Me*$_2$), 1.27 and 1.37 s (each 6H, OC*Me*$_2$CF$_3$), 3.73 sept (2H, C*H*Me$_2$), 7.20–6.90 m (3H, H$_{\text{arom}}$), 9.49 s (1H, WC*H*GeEt$_3$). ^{13}C NMR spectrum (C$_6$D$_6$), δ, ppm (*J*, Hz): 7.4 (Ge–*C*H$_2$–CH$_3$), 8.3 (Ge–CH$_2$–*C*H$_3$), 23.8 (CH*Me*$_2$), 24.0 (OCMe*Me*CF$_3$), 24.6 (*C*HMe$_2$), 28.3 (OC*Me*MeCF$_3$), q 79.7 (O*C*Me$_2$CF$_3$, $^2J_{\text{CF}}$ 28.4,), 122.8 (C-*m*), 126.6 (C-*p*), 127.4 q (CF$_3$, J_{CF} 285.0), 144.7 (C-*o*), 152.4 (C-*ipso*), 227.3 (W*C*HGeCH2Me$_3$). Found, %: C 41.33; H 5.85. C$_{27}$H$_{45}$F$_6$GeNO$_2$W. Calculated, %: C 41.25; H 5.77.

Reaction of PhCMe$_2$CH=Mo(NAr)(OR)$_2$ with Et$_3$GeCH=CH$_2$. To a solution of PhCMe$_2$CH= Mo(NAr)(OR)$_2$ (0.17 g, 0.26 mmol) in 1.5 ml of C$_6$D$_6$ was added Et$_3$GeCH=CH$_2$ (0.48 g, 2.60 mmol) in 1 ml of C$_6$D$_6$. According to the ^{1}H NMR spectroscopy the reaction completed within 5 min at room temperature, and the color of the reaction mixture changed from dark yellow to dark red. The solvent and excess Et$_3$GeCH=CH$_2$ were removed by evaporation in a vacuum at room temperature. Dark red oily residue is a mixture of **(2,6-diisopropylphenylimido)-bis-(1,1-dimethyl-2,2,2-trifluoroethanolato)(triethylvinyl-germanium)molybdenum (IV)** and **2-methyl-2-phenyl-5-triethylgermylpent-3-ene**. The total yield of compounds was 0.24 g (94%). NMR studies showed that the π-complex **IV** in a solution in C$_6$D$_6$ is in the form of two isomers in 82:18 ratio. **Isomer 1** (82%). ^{1}H NMR spectrum (C$_6$D$_6$), δ, ppm (*J,* Hz): 0.76 q (6H, GeC*H$_2$*CH$_3$), 1.03 m (9H, GeCH$_2$C*H$_3$*), 1.35 and 1.31 s (each 6H, OC*Me*$_2$CF$_3$), 1.22 d (12H, CH*Me*$_2$), 1.98 t (1H, CH$_2$=C*H*GeEt$_3$, $^3J_{\text{HH}}$ 14.6), 2.59 m (2H, C*H$_2$*=CHGeEt$_3$, $^3J_{\text{HH}}$ 14.8), 3.85 sept (2H, C*H*Me$_2$ $^3J_{\text{HH}}$ 6.8), 6.96 br.s (3H, H$_{\text{arom}}$). ^{13}C NMR spectrum (C$_6$D$_6$), δ, ppm (*J,* Hz): 6.0 (*C*H$_2$CH$_3$), 9.3 (GeCH$_2$*C*H$_3$), 23.5 and 24.16 (OC*Me*$_2$CF$_3$), 28.6 (*C*HMe$_2$), 28.9 and 29.4

($CH\mathit{Me}_2$), 57.3 ($\mathit{C}H_2=CHGeEt_3$), 59.7 ($CH_2=\mathit{C}HGeEt_3$) 78.6 q ($O\mathit{C}Me_2CF_3$, ${}^2J_{CF}$ 28.5) 80.81 q ($O\mathit{C}Me_2CF_3$, ${}^2J_{CF}$ 28.9), 123.1 (C-*m*), 127.5 q ($OCMe_2\mathit{C}F_3$, ${}^1J_{CF}$ 285.5), 128.0 (C-*p*), 146.9 (C-*o*), 153.98 (C-*ipso*). **Isomer 2** (18%). ^{1}H NMR spectrum (C_6D_6), δ, ppm (*J*, Hz): 0.76 q (6H, $Ge–C\mathit{H}_2–CH_3$), 1.03 m (9H, $GeCH_2C\mathit{H}_3$), 1.35 and 1.31 s (each 6H, $OC\mathit{Me}_2CF_3$), 1.22 d (12H, $CH\mathit{Me}_2$), 2.19 d.d (1H, $C\mathit{H}_2=CHGeEt_3$, ${}^2J_{HH}$ 3.8, ${}^3J_{HH}$ 14.0), 2.85 t (1H, $CH_2=C\mathit{H}GeEt_3$, ${}^3J_{HH}$ 13.8), 3.16 d.d (1H, $C\mathit{H}_2=CHGeEt_3$, ${}^2J_{HH}$ 3.6, ${}^3J_{HH}$ 14.0), 3.85 sept (2H, $C\mathit{H}Me_2$ ${}^3J_{HH}$ 6.8), 6.96 br.s (3H, H_{arom}). ^{13}C NMR spectrum (C_6D_6), δ, ppm (*J*, Hz): 6.09 ($\mathit{C}H_2–CH_3$), 9.5 ($GeCH_2\mathit{C}H_3$), 23.5 and 24.16 ($OC\mathit{Me}_2CF_3$), 28.6 ($\mathit{C}HMe_2$), 28.9 and 29.4 ($CH\mathit{Me}_2$), 55.9 ($\mathit{C}H_2=CHGeEt_3$), 61.9 ($CH_2=\mathit{C}HGeEt_3$), 78.6 q ($O\mathit{C}Me_2CF_3$, ${}^2J_{CF}$ 28.5), 80.81 q ($O\mathit{C}Me_2CF_3$, ${}^2J_{CF}$ 28.9), 123.1 (C-*m*), 127.5 q ($OCMe_2\mathit{C}F_3$, ${}^1J_{CF}$ 285.5), 128.0 (C-*p*), 146.9 (C-*o*) , 153.98 (C-*ipso*).

2-Methyl-2-phenyl-5-triethylgermylpent-3-ene. After fractionation of the reaction mixture in a vacuum at 100–110°C unsaturated derivative $PhMe_2C–CH=CH–CH_2–GeEt_3$ was isolated as stable in air colorless oily substance. Yield 0.07 g (94%). IR spectrum ν, cm^{-1}: 3082 w, 3060 w, (C_{arom}–H), 3023 w (H–C=CH), 2959 s, 2906 s, 2872 s. (CH_3, CH_2), 1650 w (C=C, trans), 1601 w, 1492 w ($C_{arom}–C_{arom}$), 1462 m, 1380 m (CH_3, CH_2), 1430 w ($C_{arom}–C_{arom}$), 1260 w, 1138 w (C_{arom}–H), 969 m (HC=CH), 765 m (C_{arom}–H), 574 m ($GeEt_3$), 547 w ($GeEt_3$). The signals in ^{1}H and ^{13}C NMR spectra of the isolated compound correspond to the signals of $PhMe_2C–CH=CH–CH_2–GeEt_3$ in the reaction mixture prior to fractionation. ^{1}H NMR spectrum (C_6D_6), δ, ppm (*J*, Hz): 0.74 q (6H, $GeC\mathit{H}_2CH_3$), 1.01 t (9H, $GeCH_2C\mathit{H}_3$), 1.37 s (6H, $C\mathit{Me}_2Ph$), 1.64 d (2H, $C\mathit{H}_2GeEt_3$), 5.47 m (2H, $C\mathit{H}=C\mathit{H}$), 7.16 t (1, H_{arom}), 7.28 t (2H, H_{arom}), 7.36 d (2H, H_{arom}). ^{13}C NMR NMR spectrum (C_6D_6), δ, ppm: 4.1 ($Ge\mathit{C}H_2CH_3$), 9.1 ($GeCH_2\mathit{C}H_3$), 17.1 ($\mathit{C}H_2GeEt_3$), 29.3 ($C\mathit{Me}_2Ph$), 40.5 ($\mathit{C}Me_2Ph$), 123.9 ($CH=\mathit{C}H$), 125.6 (C-*p*), 126.3 (C-*o*), 128.0 (C-*m*), 137.8 ($\mathit{C}H=CH$), 149.9 (C-*ipso*). Found,%: C 68.21, H 9.71. $C_{18}H_{30}Ge$. Calculated, %: C 67.80, H 9.44.

Metathesis polymerization of cyclooctene using initiators I–III. In an ampule containing 0.0173 g (0.026 mmol) of initiator **I** was added 0.30 g (2.68 mmol) of cyclooctene. The mixture was stirred at room temperature. During 50 min formed a solid transparent block. The reaction mixture was additionally kept at room temperature for 1 h. The resulting polymer was dissolved in 50 ml of THF with the addition of benzaldehyde (0.5 g) and precipitated with methyl alcohol. The formed polymer was additionally purified by reprecipitation with methanol from THF and dried in a vacuum at room temperature to constant weight. Yield of the polymer was 0.23 g (77%).

Experiments on the polymerization of cyclooctene with the initiators **II** and **III** were carried out similarly.

Metathesis polymerization of norbornene using π-complex IV. In an ampule containing 0.03 g (0.04 mmol) of π-complex **IV** (as an equimolar mixture with $PhMe_2C–CH=CH–CH_2–GeEt_3$) in 1 ml of benzene at room temperature was added 0.60 g (6.38 mmol) of norbornene in 1 ml of benzene. After 3 min the reaction mixture became a viscous mass. The resulting polymer was dissolved in THF with the addition of benzaldehyde to decompose the catalyst, and precipitated with methanol. The polymer obtained was additionally purified by reprecipitation with methanol from THF and dried in a vacuum at room temperature to a constant weight. Yield of the polymer 0.57 g (96%).

Metathesis polymerization of NBE–$(CH_2)_5$–Carb using π-complex IV. In an ampule containing 0.03 g (0.04 mmol) of π-complex **IV** (equimolar mixture with $PhMe_2C–CH=CH–CH_2–GeEt_3$) in 1 ml of benzene at room temperature was added 0.10 g (0.30 mmol) of NBE–$(CH_2)_5$–Carb in 1 ml of benzene. The mixture was stirred at room temperature. After 1 h the reaction mixture became a viscous mass. The resulting polymer was isolated as described above. We obtained 0.07 g (70%) of carbazole-contaning functionalized polynorbornene, a light-brown powdery substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.01–2.23 m (10H), 2.35–2.81 m (2H), 4.88–5.65 m (3H), 7.20–7.39 m (6H), 8.07 br.s (2H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 27.60, 29.09, 31.80, 43.20, 108.88, 118.84, 120.50, 122.94, 125.70, 140.543.

ACKNOWLEDGMENTS

This work was supported by Russian Foundation for Basic Research (project no. 08-03-00436, 09-03-97034-r_Povolzhye_a).

REFERENCES

1. Schrock, R.R., *Chem. Rev*., 2002, vol. 102, p. 145.
2. Schrock, R.R., *Angew. Chem. Int. Ed*., 2006, vol. 45, p. 3748.

3. Schrock, R.R. and Czekelius, C., *Adv. Synth. Catal.*, 2007, vol. 349, p. 55.
4. Schrock, R.R., *Chem. Rev.*, 2009, vol. 109, p. 3211.
5. Schrock, R.R., Murdzek, J.S., Bazan, G.C., Robbins, J., DiMare, M., and O'Regan, M.B., *J. Am. Chem. Soc.*, 1990, vol. 112, p. 3875.
6. Schrock, R.R., DePue, R.T., Feldman, J., Schaverien, C.J., Dewan, J.C., and Lui, A.H., *J. Am. Chem. Soc.*, 1988, vol. 110, p. 1423.
7. Bochkarev, L.N., Nikitinskii, A.V., Begantsova, Yu. E., Shcherbakov, V.I., Stolyarova, N.E., Grigorieva, I.K., Malysheva, I.P., Basova, G.V., Fukin, G.K., Baranov E.V., Kurskii, Yu.A., and Abakumov, G.A., *J. Organomet. Chem.*, 2005, vol. 690, p. 3212.
8. Bochkarev, L.N., Begantsova, Yu.E., Shcherbakov, V.I., Stolyarova, N.E., Grigorieva, I.K., Malysheva, I.P., Basova, G.V., Bochkarev, A.L., Barinova, Yu.P., Fukin, G.K., Baranov E.V., Kurskii, Yu.A., and Abakumov, G.A., *J. Organomet. Chem.*, 2005, vol. 690, p. 5720.
9. Bochkarev, L.N., Begantsova, Yu.E., Bochkarev, A.L., Stolyarova, N.E., Grigorieva, I.K., Malysheva, I.P., Basova, G.V., Platonova E.O., Fukin, G.K., Baranov E.V., Kurskii, Yu.A., and Abakumov, G.A., *J. Organomet. Chem.*, 2006, vol. 691, p. 5240.
10. Begantsova, Yu.E., Bochkarev, L.N., Barinova, Yu.P., Basova, G.V., Stolyarova, N.E., Grigor'eva, I.K., Malysheva, I.P., Fukin, G.K., Baranov E.V., Kurskii, Yu.A., and Abakumov, G.A., *Russ. Chem. Bull., Inter. Ed.*, 2007, vol. 56, p. 255.
11. Bochkarev, A.L., Begantsova, Yu.E., Platonova E.O., Basova, G.V., Grigorieva, I.K., Stolyarova, N.E., Malysheva, I.P., Fukin, G.K., Baranov E.V., Kurskii, Yu.A., Bochkarev, L.N., and Abakumov, G.A., *Izv. Akad. Nauk, Ser. Khim.*, 2008, no. 9, p. 1840.
12. Batsanov, S.S., *Zh. Neorg. Khim.*, 1991, vol. 36, no. 12, p. 3015.
13. Chauvin, Y., *Angew. Chem., Int. Ed.*, 2006, vol. 45, p. 3741.
14. Robbins, J., Bazan, G.C., Murdzek, J.S., O'Regan, M.B., and Schrock, R.R., *Organometallics*, 1991, vol. 10, p. 2902.
15. Tsang, W.C.P., Jamieson, J.Y., Aeilts, S.L., Hultzsch, K.C., Schrock, R.R., and Hoveyda, A.H., *Organometallics*, 2004, vol. 23, p. 1997.
16. Schrock, R.R., Duval-Lungulescu, M., Tsang, W.C.P., and Hoveyda, A.H., *J. Am. Chem. Soc.*, 2004, vol. 126, p. 1948.
17. Meyers, A., Kimyonok, A., and Weck, M., *Macromolecules,* 2005, vol. 38, p. 8671.
18. Grazulevicius, J.V., Strohriegl, P., Pielichowski, J., and Pielichowski, K*., Prog. Polym. Sci.,* 2003, vol. 28, p. 1297.
19. Rosenberg, S.D., Walburn, J.J., Stankovich, T.P., Balint, A.E., and Ramdsen, H.E., *J. Org. Chem.,* 1957, vol. 22, p. 8200.
20. Dounis, P., Feat, W.J., and Kenwright, A.M., *Polymer*, 1955, vol. 36, p 2787.
21. Hamilton, J.G., *Polymer,* 1998, vol. 39, p. 1669.
22. Sheldrick, G.M., *SHELXTL, v. 6.12, Structure Determination Software Suite*, Bruker AXS, Madison, Wisconsin (USA), 2000.
23. Sheldrick, G.M., *SADABS, v. 2.01, Bruker/Siemens Area Detector Absorption Correction Program*, Bruker AXS, Madison, Wisconsin (USA), 1998.