

Synthesis, structures and catalytic properties of germanium-containing tungsten alkylidene complex $\text{Me}_3\text{Ge}-\text{CH}=\text{W}(\text{NAr})(\text{OR})_2$ and metallacycle $[\text{CH}(\text{GeMe}_3)\text{CH}(\text{GeMe}_3)\text{CH}_2]\text{W}(\text{NAr})(\text{OR})_2$

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Abstract

Alkylidene complex of tungsten $\text{Me}_3\text{Ge}-\text{CH}=\text{W}(\text{NAr})(\text{OCMe}_2\text{CF}_3)_2$ (**1**) ($\text{Ar} = 2,6\text{-Pr}_2\text{C}_6\text{H}_3$) has been prepared by the reaction of $\text{Me}_3\text{GeCH}=\text{CH}_2$ with known alkylidene compound $\text{Bu}'-\text{CH}=\text{Mo}(\text{NAr})(\text{OCMe}_2\text{CF}_3)_2$ at a molar ratio 1:1. Metallacycle $[\text{CH}(\text{GeMe}_3)\text{CH}(\text{GeMe}_3)\text{CH}_2]\text{W}(\text{NAr})(\text{OCMe}_2\text{CF}_3)_2$ (**2**) was isolated from the same reaction when twofold excess of $\text{Me}_3\text{GeCH}=\text{CH}_2$ was used. The both compounds **1** and **2** were structurally characterized. They were found to have low activity in metathesis of 1-hexene and high activity in ROMP of cyclooctene and norbornene.

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Keywords: Alkylidene complexes; Metallacycle; Tungsten; Germanium; Synthesis; Structure elucidation; Olefin metathesis; Catalytic activity

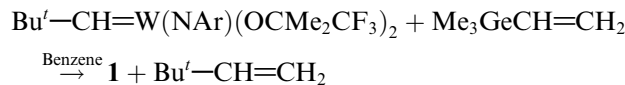
1. Introduction

Synthesis and catalytic properties of molybdenum and tungsten alkylidene complexes of the type $\text{Alkyl}-\text{CH}=\text{M}(\text{NAr})(\text{OR}')_2$ ($\text{M} = \text{Mo}, \text{W}$; $\text{Alkyl} = \text{Bu}'$, PhMe_2C ; $\text{Ar} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$; $\text{R}' = \text{Bu}'$, CMe_2CF_3 , $\text{CMe}(\text{CF}_3)_2$) in olefin metathesis reactions are well documented [1]. Much less known about similar molybdenum and tungsten compounds with heteroelement-containing substituents attached to carbene carbon [2]. We have recently found that catalytic activity of silicon- and germanium-containing alkylidene complexes of molybdenum $\text{R}_3\text{E}-\text{CH}=\text{Mo}(\text{NAr})(\text{OCMe}_2\text{CF}_3)_2$ ($\text{E} = \text{Si}, \text{Ge}$; $\text{R} = \text{Me}, \text{Ph}$) in metathesis of 1-hexene depended essentially on the nature of substituent bonded to carbene carbon atom [3].

Herein, we report the synthesis of the trimethylgermyl-containing tungsten alkylidene complex **1** and also metallacycle **2** and their catalytic properties in metathesis of 1-hexene and ROMP of cyclooctene and norbornene.

2. Results and discussion

For preparation of alkylidene complex **1** we used the known synthetic route, developed originally for preparation of silicon-containing alkylidene complexes of molybdenum [2a] and tungsten [2b]:



The course of the reactions was monitored by ^1H NMR. After completion of the reaction (5 h, at room temperature) the complex **1** was isolated as unstable in air bright-yellow

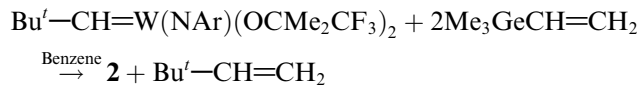
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crystals. Characteristic H_α and C_α signals were found in NMR spectra at 9.57 ppm and 231.8 ppm respectively. It should be noted that in benzene- d_6 complex **1** decomposed completely at room temperature within 5 days. According to X-ray data the complex **1** have a *syn*-conformation. The W and Ge atoms have a typical tetrahedral coordination environment (Fig. 1) the same as in early published $Me_3E-CH=Mo(NAr)(OCMe_2CF_3)_2$ (E = Si, Ge) complexes [2a–4].

All distances at W atom are practically equal to the analogous ones in $Me_3E-CH=Mo(NAr)(OCMe_2CF_3)_2$ (E = Si, Ge) complexes. The W(1)C(1)Ge(1) angle of $137.7(2)^\circ$ is also very close to those angles in alkylidene complexes of molybdenum [E = Si ($138.5(1)^\circ$), Ge($137.6(1)^\circ$)]. Thus, there are no significant differences in the geometric parameters of **1** and $Me_3E-CH=Mo(NAr)(OCMe_2CF_3)_2$ (E = Si, Ge) complexes. However, some difference between the complexes $Me_3E-CH=M(NAr)(OCMe_2CF_3)_2$ (M = Mo, W; E = Si, Ge) and $Ph_3E-CH=Mo(NAr)(OCMe_2CF_3)_2$ (E = Si, Ge) [3,4] should be noted. The bond angles M–C–E (M = Mo, W; E = Si, Ge) in the methyl alkylidene complexes (Mo–C–Si – $138.5(1)^\circ$, Mo–C–Ge – $137.57(10)^\circ$, W–C–Ge – $137.7(2)^\circ$) are noticeably smaller than in the analogous

phenyl alkylidene complexes (Mo–C–Si – $144.8(2)^\circ$, Mo–C–Ge – $144.1(1)^\circ$). Apparently it is due to the different size of the Ph_3E and Me_3E ligands.

The reaction of $Bu^t-CH=W(NAr)(OR^t)_2$ with two equivalents of trimethylvinylgermane afforded the metallacycle **2**:



Compound **2** was isolated as unstable in air light-brown crystals. In C_6D_6 it dissociates with the formation of equilibrium mixture containing **1**, $Me_3GeCH=CH_2$ and **2** in approximately equal amount. According to the X-ray data the W(1) atom has a distorted trigonal bipyramidal coordination (Fig. 2). The C(1), C(9) atoms of tungstacyclobutane ring and $OCMe_2CF_3$ ligand occupy equatorial positions whereas other alkoxide ligand and imido function are placed in apical sites. The spatial configuration of **2** is quite similar to that of the $[CH(SiMe_3)CH(SiMe_3)CH_2]W(NAr)(OCMe(CF_3)_2)_2$ compound (**2a**) [2b] and differs somewhat from spatial configuration of $[CH_2CH_2CH_2]W(NAr)(OC(CF_2CF_2CF_3)(CF_3)_2)_2$ complex (**2b**) [2b].

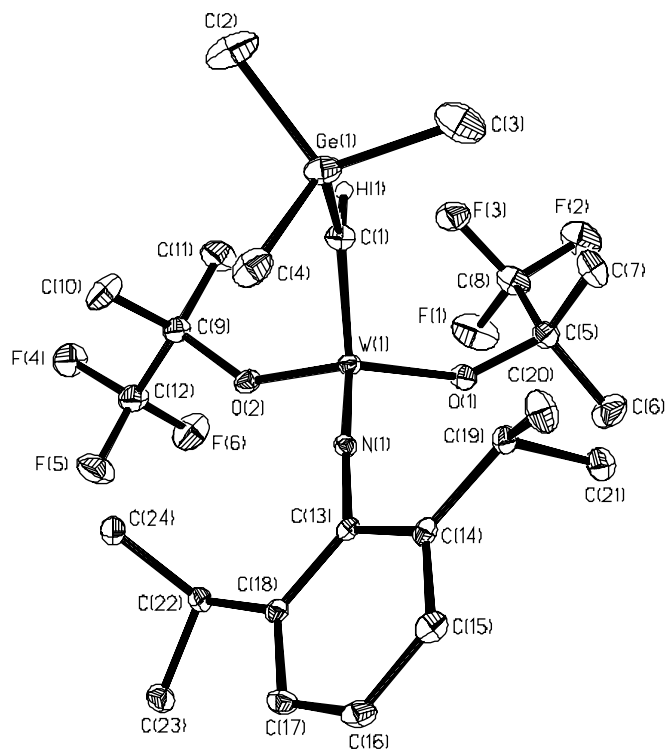


Fig. 1. Molecular structure of complex **1** (30% probability thermal ellipsoids). Selected bond lengths (Å) and angles ($^\circ$): W(1)–N(1) 1.739(3), W(1)–C(1) 1.882(3), W(1)–O(2) 1.893(2), W(1)–O(1) 1.895(2), Ge(1)–C(1) 1.927(4), Ge(1)–C(2) 1.934(4), Ge(1)–C(3) 1.924(5), Ge(1)–C(4) 1.924(4), N(1)–C(13) 1.394(4); N(1)–W(1)–C(1) 103.7(1), N(1)–W(1)–O(2) 112.8(1), C(1)–W(1)–O(2) 108.7(1), N(1)–W(1)–O(1) 111.7(1), C(1)–W(1)–O(1) 110.5(1), O(2)–W(1)–O(1) 109.2(1), C(4)–Ge(1)–C(3) 111.9(2), C(4)–Ge(1)–C(1) 109.4(2), C(3)–Ge(1)–C(1) 109.1(2), C(4)–Ge(1)–C(2) 107.4(2), C(3)–Ge(1)–C(2) 109.5(2), C(1)–Ge(1)–C(2) 109.5(2), C(13)–N(1)–W(1) 169.2(2), W(1)–C(1)–Ge(1) 137.7(2).

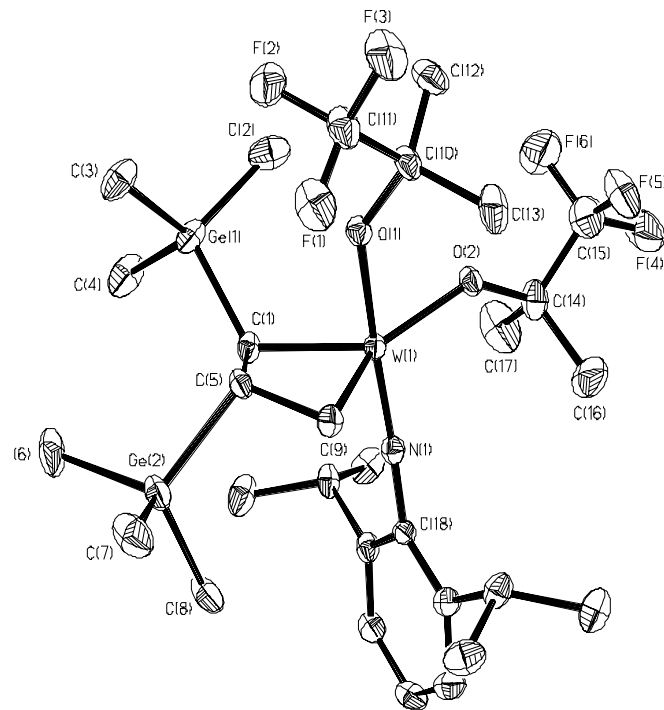


Fig. 2. Molecular structure of complex **2** (30% probability thermal ellipsoids). Selected bond lengths (Å) and angles ($^\circ$): W(1)–N(1) 1.769(3), W(1)–O(1) 1.983(2), W(1)–O(2) 1.924(3), W(1)–C(1) 2.058(4), W(1)–C(9) 2.079(4), W(1)–C(5) 2.354(4), Ge(1)–C(2) 1.930(6), Ge(1)–C(3) 1.931(5), Ge(1)–C(4) 1.954(5), Ge(1)–C(1) 1.971(4), Ge(2)–C(6) 1.931(6), Ge(2)–C(8) 1.942(5), Ge(2)–C(7) 1.954(6), Ge(2)–C(5) 1.980(4), O(1)–C(10) 1.406(5), O(2)–C(14) 1.420(5), N(1)–C(18) 1.390(3); N(1)–W(1)–O(2) 97.94(13), N(1)–W(1)–O(1) 173.66(14), O(2)–W(1)–O(1) 83.27(11), N(1)–W(1)–C(1) 92.80(15), O(2)–W(1)–C(1) 134.70(14), O(1)–W(1)–C(1) 90.71(13), N(1)–W(1)–C(9) 90.99(15), O(2)–W(1)–C(9) 141.04(15), O(1)–W(1)–C(9) 84.26(14), C(1)–W(1)–C(9) 82.12(16), N(1)–W(1)–C(5) 99.44(14), O(2)–W(1)–C(5) 162.39(12), O(1)–W(1)–C(5) 79.76(12), C(1)–W(1)–C(5) 41.57(16), C(9)–W(1)–C(5) 41.51(15).

The four-membered –W(1)–C(1)–C(5)–C(9)– metallacycle in **2** is bent. The dihedral angle between W(1)C(1)C(9) and C(1)C(5)C(9) planes is 20.1° that is a significantly smaller than in **2a** (29.9°) whereas the same metallacycle in **2b** is absolutely flat. The GeMe₃ groups in **2** (the same as SiMe₃ groups in **2a**) occupy a *trans*-positions relatively to each other, thus minimizing a non-bonding repulsion between them. Apparently steric factors in tungstacyclobutane ring in **2** lead to the distortion of metallacycle from the planarity. It should be noted that in complexes [CH₂CHBu'CH₂]–W(NAr)(OCMe₂(CF₃)₂)₂ [5] and [CHBu'CH₂CH₂(CO₂Me)]W(NAr)(OCMe₂(CF₃)₂)₂ [6], which also contain substituents in tungstacyclobutane rings, the metallacycles are also bent.

A low quality of the X-ray data obtained for **2a** and **2b** prevent a proper comparison of WC₃ geometry in **2a** and **2b** with that in **2** (Fig. 3). However, it can be noted that the bond length W(1)–N(1) in **2** (1.769(3) Å) is noticeably longer than analogous distance in **2a** (1.738(9) Å).

The W...C distances in complexes [CH₂CHBu'CH₂]W(NAr)(OCMe₂(CF₃)₂)₂ (2.79(1) Å), [CHBu'CH₂CH₂(CO₂Me)]W(NAr)(OCMe₂(CF₃)₂)₂ (2.772(8) Å) are significantly longer than those in **2–2b**.

The equatorial (1.983(2) Å) and axial (1.924(3) Å) W–O(1,2) distances in **2** are distinctly different. The equatorial alkoxide ligand in **2** is bent away from the imido ligand. The N(1)W(1)O(2) angle in **2** is 97.9(1)°. The same situation is observed in **2a** (97.3(4)°). The analogous angle in **2b** is significantly bigger (102.1(6)°). It is interesting to note that the axial W–O–C angle increase from **2** (141.0(3)°) to

2a (149.3(8)°) and to **2b** (172.4(13)°). The same tendency is also observed for equatorial W–O–C angles (136.5(2)° in **2**, 140.4(9)° in **2a** and 146.6(11)° in **2b**). In fact this tendency reflects both the increase of electronegativity of alkoxide ligands in **2–2b** and the change of their steric sizes.

The alkylidene complex **1** and metallacycle **2** were found to reveal low catalytic activity in metathesis of neat 1-hexene. The rate constants (0.5 × 10⁻⁵ L mol⁻¹ s⁻¹ and 1.8 × 10⁻⁵ L mol⁻¹ s⁻¹ for **1** and **2**, respectively) are one order of magnitude lesser than rate constant (1.73 × 10⁻⁴ L mol⁻¹ s⁻¹) of the same reaction with similar germanium-containing molybdenum alkylidene complex Me₃Ge–CH=Mo(NAr)(OCMe₂CF₃)₂ as catalyst [3].

Ring opening polymerization of cyclooctene and norbornene initiated by complex **1** and metallacycle **2** proceeds readily at room temperature. The polyoctenylenes formed were found to have predominantly *trans* configuration while polynorbornenes – predominantly *cis* configuration. Some characteristics of polymeric materials are presented in Table 1. Unfortunately we so far could not determine the molecular weights of the polyoctenylenes because of their insufficient solubility in THF, CHCl₃ and other common organic solvents necessary for GPC experiments.

3. Experimental

3.1. General

All manipulations were carried out in evacuated sealed ampoules using standard Schlenk techniques. The solvents

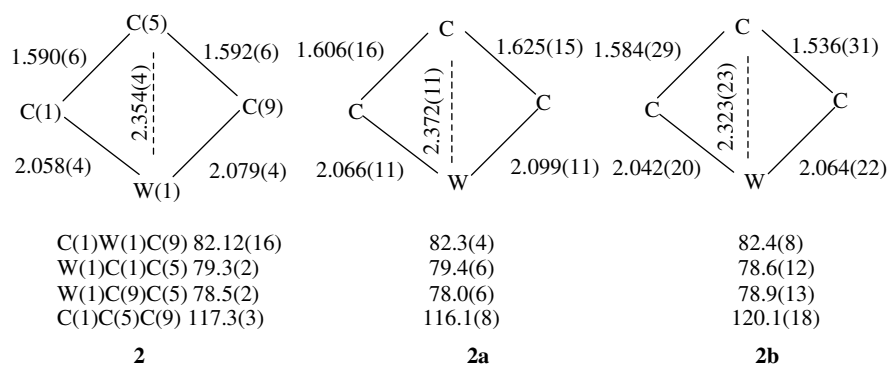


Fig. 3. The geometry of WC₃ fragments in **2–2b**.

Table 1
Some characteristics of obtained polymers

Catalyst	Monomer	Conversion (%)	<i>Cis:trans</i> ratio	<i>M_w</i>	<i>M_n</i>	<i>PDI</i>	<i>T_m</i> (°C)
1	Cyclooctene ^a	88	11:89	368 600	175 300	2.10	63.0 ± 0.3
	Norbornene ^b	75	86:14				57.6 ± 0.4
2	Cyclooctene ^c	92	17:83	81 300	42 300	1.92	49.6 ± 0.1
	Norbornene ^d	78	84:16				60.0 ± 0.1

^a [Monomer]:[Catalyst] = 100.

^b [Monomer]:[Catalyst] = 250.

^c [Monomer]:[Catalyst] = 43.

^d [Monomer]:[Catalyst] = 182.

were thoroughly dried and degassed. Compound $\text{Bu}^t\text{-CH}=\text{W}(\text{NAr})(\text{OCMe}_2\text{CF}_3)_2$ [2c] and $\text{Me}_3\text{GeCH}=\text{CH}_2$ [7] were prepared according to a literature procedure. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-200 NMR spectrometer. The chemical shifts are reported in parts per million with tetramethylsilane (0.00 ppm) as the internal standard. The molecular-weight distribution (MWD) of polynorbornenes was determined by gel-permeation chromatography (GPC) using a set of five styrogel columns with a pore diameter of 1×10^5 , 3×10^4 , 1×10^4 , 1×10^3 and, 250 Å (Waters, USA). The detector was an R-403 differential refractometer (Waters), and the eluent was tetrahydrofuran. Narrow-MWD polystyrene references were used for calibration. The contents of *cis* and *trans* units in the polymers were determined by ^1H and ^{13}C NMR spectroscopy according to a literature procedure [8–10]. Melting temperatures of the polymers were determined using differential scanning calorimeter (NETZSCH DSC 204 F1) using a first heating rate of $10^\circ\text{C}/\text{min}$ from 10 to 80°C .

3.2. Preparation of (2,6-diisopropylphenylimido)-bis(1,1-dimethyl-2,2,2-trifluoroethanolato)-trimethylgermylmethylidene)-tungsten (1)

A solution of $\text{Me}_3\text{GeCH}=\text{CH}_2$ (0.20 g, 1.38 mmol) in 2 mL of benzene was added to a solution of $\text{Bu}^t\text{-CH}=\text{W}(\text{NAr})(\text{OCMe}_2\text{CF}_3)_2$ (1.0 g, 1.46 mmol) in 3 mL of benzene. The reaction mixture was kept at room temperature for 5 h. Evaporation of the solvent and volatiles in vacuo and crystallization of the solid residue from pentane afforded 0.49 g (45.0%) of **1** as bright-yellow crystals. Anal. Calc. for $\text{C}_{24}\text{H}_{39}\text{F}_6\text{GeNO}_2\text{W}$: C, 38.75; H, 5.28. Found: C, 38.87; H, 5.21%. ^1H NMR (200 MHz, C_6D_6) δ 9.57 (s, 1H, WCHGeMe_3), 7.20–6.90 (m, 3H, H_{arom}), 3.67 (sept, 2H, CHMe_2), 1.34 and 1.26 (s, 6H each, OCMe_2CF_3), 1.24 (d, 12H, CHMe_2), 0.23 (s, 9H, WCHGeMe_3). ^{13}C NMR (50 MHz, C_6D_6) δ 231.8 (WCHGeMe_3), 152.5 (C_{ipso}), 144.7 (C_o), 127.1 (q, $J_{\text{CF}} = 285$ Hz, CF_3), 126.6 (C_p), 122.8 (C_m), 79.9 (q, $^2J_{\text{CF}} = 28.8$ Hz, OCMe_2CF_3), 28.2 (OCMe MeCF_3), 24.6 (CHMe_2), 24.1 (OCMe MeCF_3), 23.7 (CHMe_2), 1.4 (MoCHGeMe_3).

3.3. Preparation of 1-(2,6-diisopropylphenylimido)-1,1-bis(1,1-dimethyl-2,2,2-trifluoroethanolato)-2,3-bis(trimethylgermyl)-1-tungstacyclobutane (2)

A solution of $\text{Me}_3\text{GeCH}=\text{CH}_2$ (0.65 g, 4.46 mmol) in 2 mL of benzene was added to a solution of $\text{Bu}^t\text{-CH}=\text{W}(\text{NAr})(\text{OCMe}_2\text{CF}_3)_2$ (1.5 g, 2.19 mmol) in 5 mL of benzene. The reaction mixture was kept at room temperature for 5 h. Slow evaporation of the solvent and volatiles in vacuo at room temperature led to the formation of light-brown crystals of **2**. The isolated yield was 1.17 g (60.0%). Anal. Calc. for $\text{C}_{29}\text{H}_{51}\text{F}_6\text{Ge}_2\text{NO}_2\text{W}$: C, 39.19; H, 5.74. Found: C, 39.17; H, 5.77%. ^1H NMR (200 MHz, C_6D_6) 7.00–6.65 (m, 3H, H_{arom}), 5.43 (m, 1H, $J_{\text{HH}} = 4.8$

and 10.0 Hz, $\alpha\text{CHH}'$), 4.12–4.00 (m 4H, $\alpha\text{CHH}'$, $\alpha\text{CH-GeMe}_3$, CHMe_2), 1.61 (d, 6H, OCMe_2CF_3), 1.51 (d, 6H, OCMe_2CF_3), 1.26 (m, 12H, CHMe_2), 0.47 (s, 9H, GeMe_3), 0.06 (s, 9H, GeMe_3), -0.74 (q, 1H, $J \approx 9.9$ Hz, βCHGeMe_3).

3.4. Metathesis of 1-hexene

The kinetic experiments and determinations of rate constants were performed as described in the literature [3,11,12]. In a typical experiment to an ampoule containing 35.8 mg of catalyst and connected with gas burette 1.234 g (1.46 mL) of neat 1-hexene was added in argon atmosphere. The mixture was stirred magnetically. Amount of ethylene was determined volumetrically.

3.5. Polymerization of cyclooctene

To an ampoule containing 0.045 g (0.061 mmol) of catalyst **1** 0.68 g (6.1 mmol) of cyclooctene was added at room temperature. The mixture was magnetically stirred and in a less than a minute became light-orange transparent solid. The polyoctenylene formed was purified three times by precipitation by methanol from CHCl_3 and dried in vacuum at room temperature until the weight was not changed. The yield was 0.59 g (88%). Polymerization of cyclooctene using compound **2** as catalyst was carried out in similar manner. The polymerization time was 2 h. From 0.42 g (3.8 mmol) of cyclooctene and 0.08 g (0.090 mmol) of catalyst **2** 0.40 g (92%) of polyoctenylene was obtained.

3.6. Polymerization of norbornene

To an ampoule containing 0.0297 g (0.040 mmol) of catalyst **1** in 2 mL of benzene 0.94 g (10.0 mmol) of norbornene in 3 mL of benzene was added at room temperature. The mixture was magnetically stirred and in less than a minute became light-orange transparent viscous and after that the polynorbornene formed was purified three times by precipitation by methanol from CHCl_3 and dried in vacuum at room temperature until the weight was not changed. The yield was 0.71 g (75%). Polymerization of norbornene using compound **2** as catalyst was carried out in similar manner. The polymerization time was 2 min. From 0.65 g (6.9 mmol) of norbornene and 0.0344 g (0.039 mmol) of catalyst **2** 0.51 g (78%) of polynorbornene was obtained.

3.7. Crystallographic data for **1** and **2**

The data were collected on a Bruker AXS “SMART APEX” diffractometer (graphite-monochromator, Mo $K\alpha$ -radiation, $\varphi - \omega$ -scan technique, $\lambda = 0.71073$ Å). The intensity data were integrated in the SAINT program [13]. SADABS [14] was used to perform area-detector scaling and absorption corrections. The structures were solved by

Table 2
The details of crystallographic, collection and refinement data for **1** and **2**

	1	2
Empirical formula	C ₂₄ H ₃₉ F ₆ GeNO ₂ W	C ₂₉ H ₅₁ F ₆ Ge ₂ NO ₂ W
Formula weight	744.00	888.74
Temperature (K)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>n</i>
<i>a</i> (Å)	10.2484(6)	17.8086(9)
<i>b</i> (Å)	30.7012(19)	11.9442(6)
<i>c</i> (Å)	10.6441(7)	18.3515(10)
β (°)	118.570(1)	112.711(1)
Volume (Å ³)	2941.2(3)	3600.9(3)
<i>Z</i>	4	4
Density (calculated) (g/cm ³)	1.680	1.639
Absorption coefficient (mm ⁻¹)	4.988	4.901
<i>F</i> (000)	1464	1760
Crystal size (mm)	0.22 × 0.06 × 0.03	0.34 × 0.15 × 0.14
θ_{\max} Range for data collection °	29.12	26.00
Index ranges	-14 ≤ <i>h</i> ≤ 13, -41 ≤ <i>k</i> ≤ 42, -14 ≤ <i>l</i> ≤ 14	-14 ≤ <i>h</i> ≤ 21, -14 ≤ <i>k</i> ≤ 14, -22 ≤ <i>l</i> ≤ 22
Reflections collected	30808	21043
Independent reflections [<i>R</i> _{int}]	7830 [0.0327]	7067 [0.0286]
Absorption correction	SADABS	
Maximum/minimum transmission	0.8648/0.4067	0.5470/0.2866
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data/restraints/parameters	7830/0/320	7067/20/358
Goodness-of-fit on <i>F</i> ²	1.102	1.038
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0341, <i>wR</i> ₂ = 0.0792	<i>R</i> ₁ = 0.0408, <i>wR</i> ₂ = 0.0983
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0417, <i>wR</i> ₂ = 0.0819	<i>R</i> ₁ = 0.0477, <i>wR</i> ₂ = 0.1010
Largest difference in peak and hole (e Å ⁻³)	2.343 and -1.301	2.422 and -1.044

direct methods and were refined on *F*² using all reflections with SHELXTL package [15]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms in **1** and **2** were placed in calculated positions and refined in the “riding-model”. The details of crystallographic, collection and refinement data are shown in the Table 2. CCDC-611758 **1** and 611759 **2** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/const/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223/336 033; e-mail: deposit@ccdc.cam.ac.uk].

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