Synthesis and structures of bimetallic silicon-containing imido alkylidene complexes of tungsten (R′O)₂(ArN)W=CH–SiR₂–CH=W(NAr)(OR′)₂ (R = Me, Ph) and (R′O)₂(ArN)W=CH–SiMe₂SiMe₂–CH=W(NAr)(OR′)₂

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ABSTRACT

Bimetallic alkylidene complexes of tungsten $(R'O)_2(ArN)W=CH–SiR_2–CH=W(NAr)(OR')_2$ (R = Me (**1**), Ph (**2**)) and $(R'O)_2(ArN)W=CH–SiMe_2SiMe_2–CH=W(NAr)(OR')_2$ (**3**) (Ar = 2,6-$Pr^i_2C_6H_3$; R′ = CMe_2CF_3) have been prepared by the reactions of divinyl silicon reagents $R_2Si(CH=CH_2)_2$ with known alkylidene compounds $R''–CH=Mo(NAr)(OR')_2$. (R″ = Bu^t, $PhMe_2C$) Complexes **1–3** were structurally characterized. Ring opening metathesis polymerization (ROMP) of cyclooctene using compounds **1–3** as initiators led to the formation of high molecular weight polyoctenamers with predominant *trans*-units content in the case of **1** and **3** and predominant *cis*-units content in the case of **2**.

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1. Introduction

Monometallic Schrock type imido alkylidene compounds of molybdenum and tungsten and Grubbs type ruthenium alkylidene complexes are well known and widely used as catalysts in a variety of olefin metathesis reactions [1]. Bimetallic alkylidene complexes of molybdenum and ruthenium have been developed as well [2] and successfully employed as catalysts in ROMP of functionalized cycloolefins and cyclopolymerization of 1,6-heptadiynes for preparation of triblock copolymers [2b,c,3]. Very few similar bimetallic alkylidene complexes of tungsten are known [4] and their catalytic properties have not been investigated.

Herein we report the synthesis, X-ray diffraction studies of the bimetallic silicon-containing imido alkylidene complexes of tungsten **1–3** and their catalytic properties in ROMP of cyclooctene.
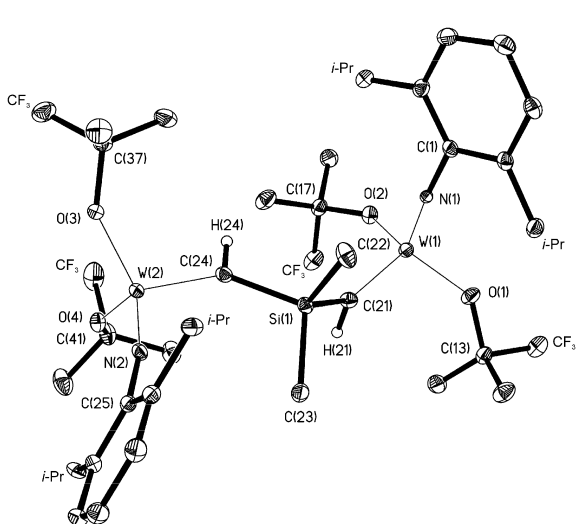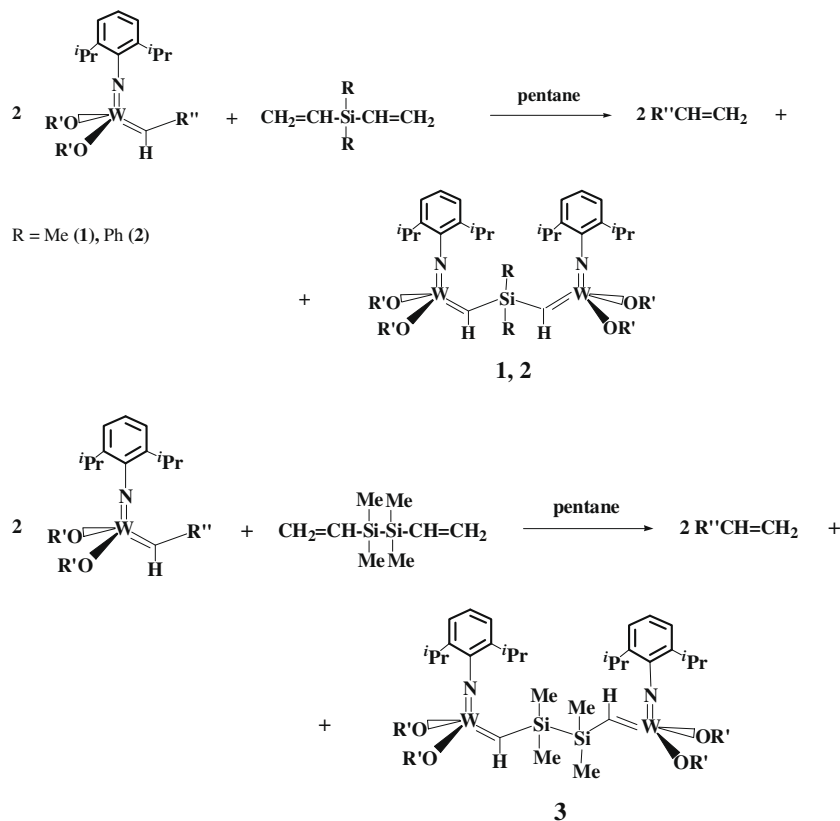
2. Results and discussion

Complexes **1–3** were prepared by the reactions of alkylidene compounds R″–CH=W(NAr)(OR′)₂ (R″ = Bu^t, $PhMe_2C$) [5] with divinyl silicon reagents:

The course of the reactions was tracked by ¹H NMR. The formation of complexes **1–3** was completed at room temperature in 2 days. Compounds **1–3** were isolated as air-sensitive crystalline solids. Characteristic H_α signals (9.40 ppm (**1**), 9.47 ppm (**2**), 9.42 ppm (**3**)) were found in NMR spectra at room temperature as broad singlets and no ^{183}W satellites were observed. A similar feature of ¹H NMR spectrum was found earlier for trimethylsilyl substituted alkylidene compound $Me_3SiCH=W(NAr)(OR')_2$ [5]. The C_α signals (230.4, 221.0, 226.8 ppm) in ¹³C NMR spectra of complexes **1–3** were shifted upfield in comparison with C_α signal (244.9 ppm) of neopentylidene complex $Bu^tCH=W(NAr)(OR')_2$ [5a] which is in accordance with more electrondonating character of organosilicon substituents compare to that of Bu^t– group [6].

Complexes **1–3** were characterized by X-ray diffraction studies. The tungsten alkylidene fragments CH=W(NAr)(OR′)₂ in trinuclear compounds **1** and **2** are linked *via* the R_2Si group (Figs. 1 and 2, Table 1). Complex **2** is isostructural with the earlier described bimetallic molybdenum complex $(R'O)_2(ArN)Mo=CH–SiPh_2–CH=Mo(NAr)(OR')_2$ (**2a**) [7]. In complexes **1** and **2** the silicon and tungsten atoms have a distorted tetrahedral coordination environment. The bond angles around W(1) and W(2) atoms fall in the range of 101.96(11)–113.96(9)° (**1**) and 103.20(10)–118.2(3)° (**2**) respectively. Tetrahedral angles around Si(1) in **1** and **2** are in the range of 106.7(4)–113.1(4)°. In both compounds **1** and **2** the arrangement of carbene fragments and NAr groups

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R = Me (**1**), Ph (**2**)

1, 2

3

Fig. 1. Molecular structure of complex **1** with 30% ellipsoid probability; F and H atoms (except H(21), H(24)) and methyl groups of *i*-Pr substituents are omitted for clarity.
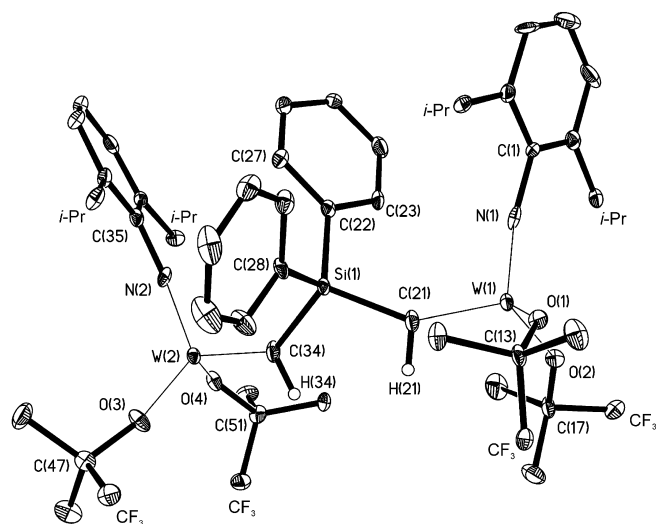
Fig. 2. Molecular structure of complex **2** with 30% ellipsoid probability; F and H atoms (except H(21), H(34)) and methyl groups of *i*-Pr substituents are omitted for clarity.

around tungsten atoms corresponds to *syn* conformation. The distances W=C in **1** (1.891(2), 1.896(2) Å) and in **2** (1.880(8), 1.906(8) Å) are comparable with that of monometallic silicon-containing alkylidene complexes Me₃SiCH=W(NAr)(OR′)₂ (1.877(4) Å) [5,8], PhMe₂SiCH=W(NAr)(OR′)₂ (1.888(3) Å) [8]. The values of W–C–Si angles in **1** (138.52(18)° and 138.82(14)°) are almost equal whereas these angles in **2** are essentially different (147.4(5)°, 137.7(5)°). A similar feature was observed in molybdenum analog **2a** (Mo–C–Si angles are 146.0(1) and 137.4(1)°) [7]. Apparently, the nonequivalence of the Mo–C–Si angles in **2** and **2a** is caused by different conformation of these

molecules in comparison with **1**. The NAr and OR′ substituents at tungsten atoms arrange the staggered conformation relatively to each other along W–W line in **1** (dihedral angle between N(1)W(1)W(2) and N(2)W(2)W(1) planes is 85.7°) and the eclipsed conformation in **2** and **2a** (dihedral angle between the same planes are 20.1° and 17.6°, respectively). Obviously, this leads to steric stress in WCSiCW framework of **2** (and in MoCSiCMo framework of **2a**) and as a result one of the WCSi (MoCSi) angles increases essentially in comparison with another.

The tungsten alkylidene fragments CH=W(NAr)(OR′)₂ in tetranuclear complex **3** are linked *via* the –Me₂SiSiMe₂– group (Fig. 3,

Table 1
Selected bond lengths (Å) and angles (°) in **1**–**3**.

Bond	d/Å		
	1	**2**	**3**
W(1)–N(1)	1.733(2)	1.714(6)	1.7270(8)
W(1)–O(1)	1.8882(17)	1.862(5)	1.895(2)
W(1)–O(2)	1.8821(19)	1.894(5)	1.892(2)
W(1)–C(21)	1.891(2)	1.880(8)	1.901(3)
N(1)–C(1)	1.403(4)	1.426(9)	1.4003(9)
O(1)–C(13)	1.427(3)	1.439(10)	1.410(4)
O(2)–C(17)	1.418(3)	1.416(9)	1.414(4)
W(2)–N(2)	1.740(2)	1.736(6)	–
W(2)–O(3)	1.882(2)	1.838(5)	–
W(2)–O(4)	1.891(2)	1.884(5)	–
W(2)–C(24)	1.896(2)	–	–
W(2)–C(34)	–	1.906(8)	–
N(2)–C(25)	1.401(3)	–	–
N(2)–C(35)	–	1.395(10)	–
O(3)–C(37)	1.417(4)	–	–
O(3)–C(47)	–	1.421(10)	–
O(4)–C(41)	1.413(3)	–	–
O(4)–C(51)	–	1.438(9)	–
Si(1)–C(21)	1.865(2)	1.870(8)	1.851(3)
Si(1)–C(22)	1.860(3)	1.854(8)	1.876(3)
Si(1)–C(23)	1.869(3)	–	1.884(3)
Si(1)–C(28)	–	1.885(9)	–
Si(1)–C(24)	1.854(3)	–	–
Si(1)–C(34)	–	1.843(8)	–
Si(1)–Si(1A)	–	–	2.3469(17)

Angle	ω/°		
	1	**2**	**3**
C(21)–W(1)–N(1)	101.96(11)	105.0(3)	102.22(10)
O(1)–W(1)–N(1)	113.96(9)	111.5(3)	109.73(9)
O(2)–W(1)–N(1)	112.24(10)	111.9(3)	114.82(8)
O(1)–W(1)–O(2)	108.70(8)	109.4(2)	109.77(10)
O(2)–W(1)–C(21)	109.53(10)	109.4(3)	110.96(11)
C(21)–W(1)–O(1)	110.26(10)	109.4(3)	109.03(11)
W(1)–N(1)–C(1)	172.46(15)	170.0(5)	177.58(14)
W(1)–O(1)–C(13)	139.87(15)	143.7(5)	142.21(17)
W(1)–C(21)–Si(1)	138.52(18)	147.4(5)	140.96(18)
W(1)–O(2)–C(17)	147.04(14)	145.2(5)	148.43(18)
C(24)–W(2)–N(2)	103.20(10)	–	–
C(34)–W(2)–N(2)	–	105.7(3)	–
O(3)–W(2)–N(2)	115.46(9)	118.2(3)	–
O(4)–W(2)–N(2)	110.01(10)	108.1(3)	–
O(3)–W(2)–O(4)	109.81(9)	107.3(2)	–
O(4)–W(2)–C(24)	109.10(10)	–	–
O(4)–W(2)–C(34)	–	109.2(3)	–
C(24)–W(2)–O(3)	108.94(10)	–	–
C(34)–W(2)–O(3)	–	108.1(3)	–
W(2)–N(2)–C(25)	168.70(18)	–	–
W(2)–N(2)–C(35)	–	170.8(6)	–
W(2)–O(3)–C(37)	147.59(16)	–	–
W(2)–O(3)–C(47)	–	167.4(6)	–
W(2)–C(24)–Si(1)	138.82(14)	–	–
W(2)–C(34)–Si(1)	–	137.7(5)	–
W(2)–O(4)–C(41)	144.45(16)	–	–
W(2)–O(4)–C(51)	–	143.0(5)	–
C(21)–Si(1)–C(22)	111.05(13)	109.8(4)	112.64(14)
C(21)–Si(1)–C(23)	109.25(14)	–	107.16(15)
C(21)–Si(1)–C(28)	–	108.9(4)	–
C(21)–Si(1)–C(24)	107.09(12)	–	–
C(21)–Si(1)–Si(1A)	–	–	108.68(11)
C(21)–Si(1)–C(34)	–	108.4(4)	–
C(22)–Si(1)–C(23)	110.19(15)	–	108.48(16)
C(22)–Si(1)–C(28)	–	109.9(4)	–
C(22)–Si(1)–C(24)	109.77(14)	–	–
C(22)–Si(1)–Si(1A)	–	–	109.61(12)
C(22)–Si(1)–C(34)	–	113.1(4)	–
C(23)–Si(1)–C(24)	109.43(12)	–	–
C(23)–Si(1)–Si(1A)	–	–	110.24(11)
C(28)–Si(1)–C(34)	–	106.7(4)	–
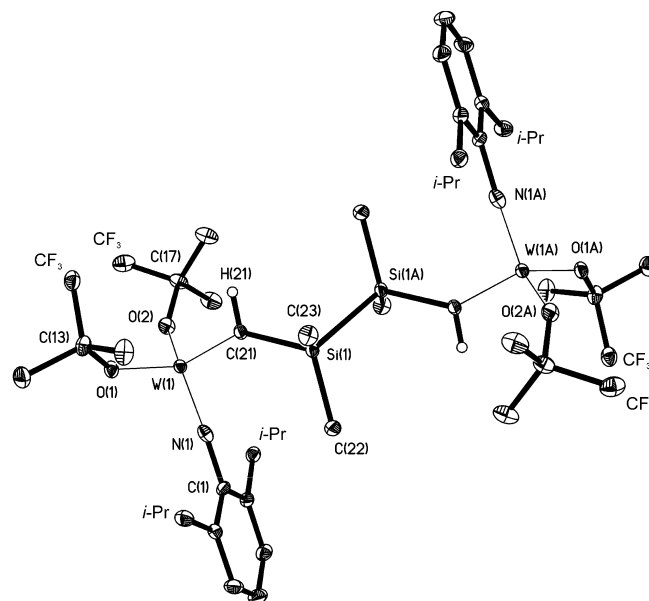
Fig. 3. Molecular structure of complex **3** with 30% ellipsoid probability; F and H atoms (except H(21)) and methyl groups of *i*-Pr substituents are omitted for clarity.

Table 2
Some characteristics of polyoctenamers obtained using tungsten bimetallic initiators.

Initiator	Yield (%)	*cis*:*trans* ratio (%)	$\overline{M}_w$	$\overline{M}_n$	PDI
1[a]	85	18:82	1544700	971700	1.59
2[a]	50	91:9	370140	229950	1.61
3[a]	88	20:80	1343300	726000	1.80

[a] [Monomer]:[catalyst] = 100.

center in the middle of the Si–Si bond. The tungsten and silicon atoms have a typical distorted tetrahedral coordination environment. Bond angles around the tungsten atom W(1) are in the range of 102.22(10)–114.82(8)° and bond angles around the silicon atom Si(1) are in the range of 107.16(5)–112.64(14)°. The W(1)–C(21) distance (1.901(3) Å) is close to W–C distances in **1**, **2** as well as to Mo–C distances in **2a** and in tetranuclear molybdenum complex (Bu^{t}O)$_2$(ArN)Mo=C(R)–Me$_2$SiSiMe$_2$–C(R)=Mo(NAr)(OBu^t)$_2$ (R = –CH=CH–CMe$_2$Ph) (**3a**) [9] (1.876(2)–1.906(9) Å). The W(1)–C(21)–Si(1) angle (140.96(18)°) in **3** is somewhat greater than W–C–Si angles (138.52(18)° and 138.82(14)°) in **1**. The Si(1)–Si(1A) distance in the disilane bridge is 2.3469(17) Å, that is comparable with the analogous distance in **3a** (2.351(5) Å).

Complexes **1**–**3** were found to initiate ROMP of cyclooctene and led to the formation of high molecular weight polyoctenamers (Table 2). In the case of initiators **1** and **3** polymerization in bulk completed at room temperature in 20–30 min. The polyoctenamers formed contained predominantly *trans*-units. In the case of complex **2** the polymerization proceeded more slowly. The yield of polyoctenamer in 10 h was 50%. According NMR data the polymer contained predominantly *cis*-units.

3. Experimental

3.1. General

All manipulations were carried out in evacuated sealed ampoules using standard Schlenk techniques. The solvents were thoroughly dried and degassed. Compound R″–CH=W(NAr)(OR)$_2$ (R″ = Bu^t, PhMe$_2$C) [5], R$_2$Si(CH=CH$_2$)$_2$ (R = Me, Ph) [10] and CH$_2$=CH–SiMe$_2$-

Table 1). The crystal cell of **3** contains the molecule of hexane which is not shown. The molecule of **3** has a crystallographic inversion

SiMe$_2$–CH=CH$_2$ [10] were prepared according to a literature procedure. ^{1}H 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 polyoctenamers was determined by gel-permeation chromatography (GPC) on chromatograph Knauer with Smartline RID 2300 differential refractometer as detector. A set of two columns Phenomenex with Phenogel sorbent (pore diameter of 10^4 and 10^5 Å) was used. The eluent was tetrahydrofuran (40 °C, 2 ml/min). Narrow-MWD polystyrene references were used for calibration. The contents of *cis*- and *trans*-units in the polymers were determined by ^{13}C NMR spectroscopy according to a literature procedure [11].

3.2. Preparation of (R′O)$_2$(ArN)W=CH–SiMe$_2$–CH=W(NAr)(OR′)$_2$ (1)

Me$_2$Si(CH=CH$_2$)$_2$ (0.053 g, 0.47 mmol) in 2 ml of pentane was added to a solution of Bu^t–CH=W(NAr)(OR′)$_2$ (0.61 g, 0.94 mmol) in 5 mL of pentane. The reaction mixture was kept at room temperature for 2 days. Evaporation of the solvent and volatiles *in vacuo* and crystallization of the solid residue from minimal amount of pentane at −20 °C afforded 0.33 g (55%) of **1** as bright-yellow crystals. *Anal.* Calc. for C$_{44}$H$_{66}$F$_{12}$N$_2$O$_4$SiW$_2$: C, 40.32; H, 5.08. Found: C, 40.28; H, 5.15%. ^{1}H NMR (200 MHz, C$_6$D$_6$) δ 9.40 (s, 2H, WCHSi, 7.30–6.90 (m, 6H, H$_{arom}$), 3.64 (sept, 4H, CHMe$_2$), 1.36 and 1.28 (s, 12H each, OCMe$_2$CF$_3$), 1.23 (d, 24H, CHMe$_2$), 0.38 (s, 6H, (WCH)$_2$SiMe$_2$). ^{13}C NMR (50 MHz, C$_6$D$_6$) δ 228.2 (WCHSiMe$_2$), 152.0 (C$_{ipso}$), 144.8 (C$_o$), 127.1 (q, J_{CF} = 285.3 Hz, CF$_3$), 126.8 (C$_p$), 122.9 (C$_m$), 80.3 (q, $^2J_{CF}$ = 29.0 Hz, OCMe$_2$CF$_3$), 28.2 (OCMeMeCF$_3$), 24.6 (CHMe$_2$), 24.2 (OCMeMeCF$_3$), 23.8 (CHMe$_2$), 4.0 and 3.5 (SiMe$_2$).

The preparation of **1** using neophylidene complex PhMe$_2$C–CH=W(NAr)(OR′)$_2$ as a starting reagent was carried out in a similar manner. The yield of compound **1** was 47%.

3.3. Preparation of (R′O)$_2$(ArN)W=CH–SiPh$_2$–CH=W(NAr)(OR′)$_2$ (2)

Ph$_2$Si(CH=CH$_2$)$_2$ (0.082 g, 0.35 mmol) in 2 ml of pentane was added to a solution of Bu^t–CH=W(NAr)(OR′)$_2$ (0.45 g, 0.69 mmol) in 5 mL of pentane. The reaction mixture was kept at room temperature for 2 days. Evaporation of the solvent and volatiles *in vacuo* and crystallization of the solid residue from minimal amount of pentane at −20 °C afforded 0.14 g (30%) of **1** as dark-yellow crystals. *Anal.* Calc. for C$_{54}$H$_{70}$F$_{12}$SiN$_2$O$_4$W$_2$: C, 45.2; H, 4.92. Found: C, 45.14; H, 4.85%. ^{1}H NMR (200 MHz, C$_6$D$_6$) δ 9.47 (s, 2H, WCHSi), 7.90–6.80 (m, 16H, H$_{arom}$), 4.95 (sept, 4H, CHMe$_2$), 1.33 and 1.29 (s, 12H each, OCMe$_2$CF$_3$), 1.23 (d, 24H, CHMe$_2$). ^{13}C NMR (50 MHz, C$_6$D$_6$) δ 221.0 (WCHSiMe$_2$), 152.1, 146.0, 136.1, 135.7, 129.5, 129.3 (Ar), 127.0 (q, J_{CF} = 285.0 Hz, CF$_3$), 123.0, 122.8 (Ar), 80.8 (q, $^2J_{CF}$ = 30.0 Hz, OCMe$_2$CF$_3$), 28.3 (CHMe$_2$), 24.2, 24.0 (OCMe$_2$CF$_3$), 23.7 (CHMe$_2$).

3.4. Preparation of (R′O)$_2$(ArN)W=CH–SiMe$_2$SiMe$_2$–CH=W(NAr)(OR′)$_2$ (3)

CH$_2$=CH–SiMe$_2$SiMe$_2$–CH=CH$_2$ (0.092 g, 0.54 mmol) in 2 ml of pentane was added to a solution of Bu^t–CH=W(NAr)(OR′)$_2$ (0.70 г, 1.07 ммоля) in 5 mL of pentane. The reaction mixture was kept at room temperature for 2 days. Evaporation of the solvent and volatiles *in vacuo* and crystallization of the solid residue from minimal amount of pentane at −20 °C afforded 0.48 g (65%) of **1** as bright-yellow crystals. *Anal.* Calc. for C$_{46}$H$_{72}$F$_{12}$Si$_2$N$_2$O$_4$W$_2$: C, 40.36; H,

Table 3
The details of crystallographic, collection and refinement data for **1**–**3**.

Complex	1	2	3 × C$_6$H$_{14}$
Empirical formula	C$_{44}$H$_{66}$F$_{12}$N$_2$O$_4$SiW$_2$	C$_{54}$H$_{70}$F$_{12}$N$_2$O$_4$SiW$_2$	C$_{52}$H$_{86}$F$_{12}$N$_2$O$_4$Si$_2$W$_2$
Formula weight	1310.78	1434.91	1455.11
T (K)	100(2)	100(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	C2/c	P-1	P2(1)/c
Unit cell dimensions			
a (Å)	39.3471(9)	10.8398(9)	16.0437(7)
b (Å)	10.9406(3)	13.6029(11)	13.3368(6)
c (Å)	29.8684(7)	20.6931(16)	15.5532(7)
α (°)	90	77.307(2)	90
β (°)	125.14	77.828(2)	113.0580(10)
γ (°)	90	76.638(2)	90
V (Å^3)	10513.9(4)	2854.6(4)	3062.1(2)
Z	8	2	2
ρ (calculated) (g cm^{-3})	1.656	1.669	1.578
Absorption coefficient (mm^{-1})	4.477	4.131	3.871
Crystal size (mm^3)	0.25 × 0.08 × 0.06	0.15 × 0.09 × 0.05	0.21 × 0.10 × 0.08
θ range for data collection (°)	2.33–27.50	1.56–26.00	2.63–27.50
Limiting indices	−50 ⩽ h ⩽ 50, −14 ⩽ k ⩽ 14, −38 ⩽ l ⩽ 38	−13 ⩽ h ⩽ 13, −16 ⩽ k ⩽ 16, −25 ⩽ l ⩽ 25	−20 ⩽ h ⩽ 20, −17 ⩽ k ⩽ 17, −20 ⩽ l ⩽ 20
Reflections collected/unique	49431/12058	22067/10946	28375/6984
R (int)	0.0300	0.0967	0.0417
Completeness (to θ)	99.7% (27.50)	97.5% (26.00)	99.2% (27.50)
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Maximum and minimum transmission	0.7750 and 0.4007	0.8201 and 0.5762	0.7471 and 0.4970
Refinement method	Full-matrix least-squares on F^2	Full-matrix-block least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	12058/47/566	10946/0/674	6984/11/328
Final R indices ($I > 2\sigma(I)$)	R_1 = 0.0313, wR_2 = 0.0712	R_1 = 0.0820, wR_2 = 0.0975	R_1 = 0.0364, wR_2 = 0.0853
R indices (all data)	R_1 = 0.0411, wR_2 = 0.0746	R_1 = 0.1433, wR_2 = 0.1066	R_1 = 0.0536, wR_2 = 0.0904
Goodness-of-fit (GOF) on F^2	1.042	1.015	1.055
Largest difference peak and hole (e Å^{-3})	1.625 and −1.581	2.380 and −2.529	5.721 and −1.226

5.30. Found: C, 40.29; H, 5.38%. ^{1}H NMR (200 MHz, C_6D_6) δ 9.42 (s, 2H, WC*H*Si), 7.20–6.90 (m, 6H, H_{arom}), 3.67 (sept, 4H, C*H*Me$_2$), 1.40 and 1.30 (s, 12H each, OC*Me*$_2$CF$_3$), 1.25 (d, 24H, CH*Me*$_2$), 0.29 (s, 12H, Si$_2$*Me*$_4$).

The preparation of **3** using neophylidene complex PhMe$_2$C–CH=W(NAr)(OR′)$_2$ as a starting reagent was carried out in a similar manner. The yield of compound **3** was 61%.

3.5. Polymerization of cyclooctene

Cyclooctene (0.42 g, 3.82 mmol) was added at room temperature to an ampoule containing 0.050 g (0.038 mmol) of catalyst **1**. The mixture was stirred and in 20 min became light-orange transparent solid. The polyoctenamer formed was dissolved in THF containing 0.3 ml of benzaldehyde (for decomposition of catalyst) and purified three times by precipitation by methanol from THF and dried in vacuum at room temperature until the weight was not changed. The yield was 0.36 g (85%). Polymerization of cyclooctene using compounds **2** and **3** as catalyst was carried out in similar manner.

3.6. Crystallographic data for **1, 2** and **3**

The single crystals of compounds **1** and **2** were obtained by crystallization from pentane at −20 °C. The single crystals of compound **3** were obtained by crystallization from hexane at −20 °C. Intensity data for **1**, **2** and **3** were collected on a Smart Apex diffractometer with graphite monochromated Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å) in the $\omega-\varphi$ scan mode ($\omega = 0.3°$, 10 s on each frame). The intensity data were integrated by SAINT program [12]. SADABS [13] was used to perform area-detector scaling and absorption corrections. The structures were solved by direct method and were refined on F^2 using all reflections with SHELXTL package [14]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined in the "riding-model" (U_{iso}(H) = 1.5U_{eq}(C) in CH$_3$-groups и U_{iso}(H) = 1.2U_{eq}(C) in other ligands). Complex **1** contains disordered in two positions C(Me)$_2$CF$_3$ group. Complex **3** contains one solvate molecule of hexane which is disposed in inversion center. Selected bond distances and angles for **1**, **2** and **3** are given in Table 2 and the details of crystallographic, collection and refinement data are given in Table 3.

Supplementary material

CCDC 746330 (**1**), 746331 (**2**) and 746332 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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