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# Synthesis and structures of bimetallic silicon-containing imido alkylidene complexes of tungsten $(R'O)_2(ArN)W{=}CH{-}SiR_2{-}CH{=}W(NAr)(OR')_2$ (R = Me, Ph) and $(R'O)_2(ArN)W{=}CH{-}SiMe_2SiMe_2{-}CH{=}W(NAr)(OR')_2$

Andrey L. Bochkarev, Galina V. Basova, Irina K. Grigorieva, Natalia E. Stolyarova, Irina P. Malysheva, Georgii K. Fukin, Evgenii V. Baranov, Yurii A. Kurskii, Leonid N. Bochkarev *, Gleb A. Abakumov

*G.A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Tropinina 49, Nizhny Novgorod 603950, Russia*

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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**.



## 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 $^1$H 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 $H_\alpha$ 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 $^1$H NMR spectrum was found earlier for trimethylsilyl substituted alkylidene compound $Me_3SiCH{=}W(NAr)(OR')_2$ [5]. The $C_\alpha$ signals (230.4, 221.0, 226.8 ppm) in $^{13}$C NMR spectra of complexes **1**–**3** were shifted upfield in comparison with $C_\alpha$ 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

* Corresponding author. Tel.: +7 (831) 4627010; fax: +7 (831) 4627497.
*E-mail address:* lnb@iomc.ras.ru (L.N. Bochkarev).

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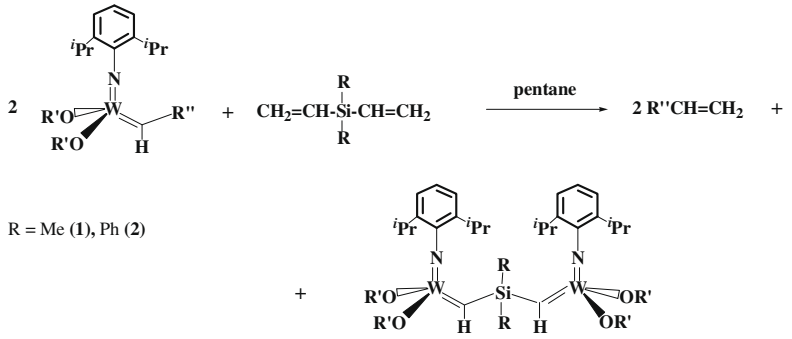


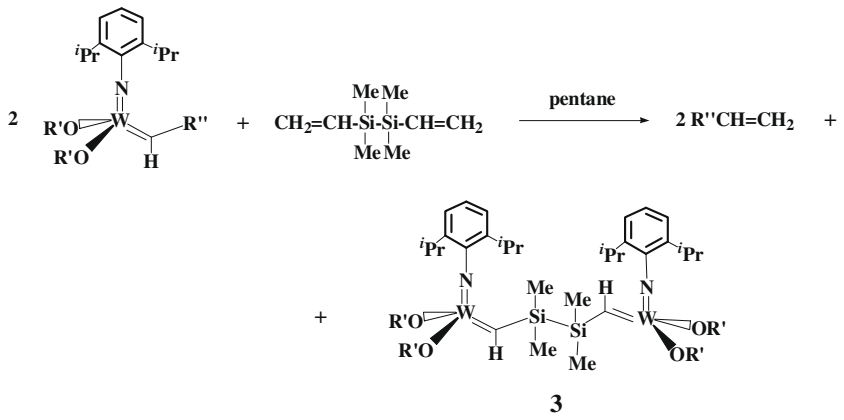


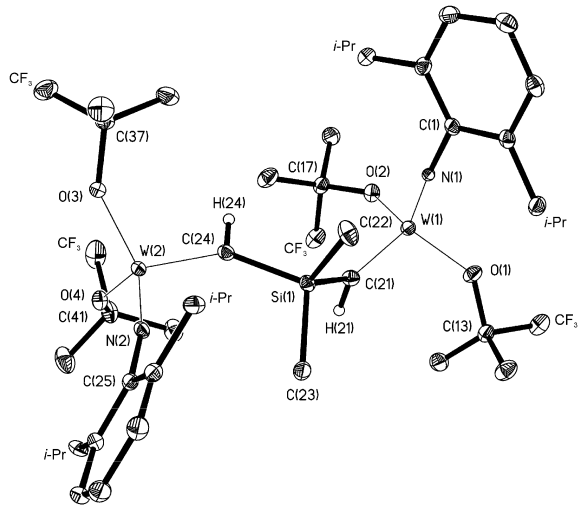


**Fig. 1.** Molecular structure of complex **1** with 30% ellipsoid probability; F and H atoms (except H(21), H(24)) and methyl groups of *i*-Pr substituents are omitted for clarity.

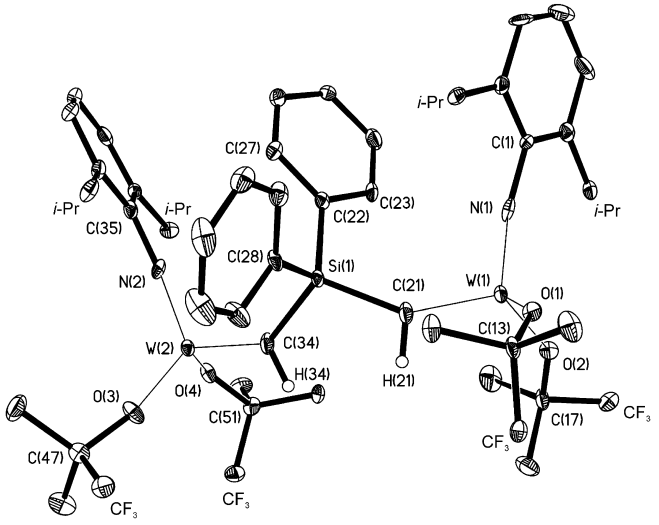


**Fig. 2.** Molecular structure of complex **2** with 30% ellipsoid probability; F and H atoms (except H(21), H(34)) and methyl groups of *i*-Pr substituents are omitted for clarity.

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 $Me_3SiCH{=}W(NAr)(OR')_2$ (1.877(4) Å) [5,8], $PhMe_2SiCH{=}W(NAr)(OR')_2$ (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 $-Me_2SiSiMe_2-$ group (Fig. 3,