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Synthesis and structures of silicon-, germanium-, and tin-containing tungsten carbyne complexes $(\mathrm{Bu^tO})_3\mathrm{W{\equiv}C{-}EPh_3}$ and $[(\mathrm{Bu^tO})_3\mathrm{W{\equiv}C}]_2\mathrm{EPh_2}$ (E = Si, Ge, Sn)

A. V. Safronova, L. N. Bochkarev, N. E. Stolyarova, I. K. Grigor′eva, I. P. Malysheva,
G. V. Basova, G. K. Fukin, Yu. A. Kurskii, S. Ya. Khorshev, and G. A. Abakumov*

*G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,
49 ul. Tropinina, Nizhny Novgorod 603950, Russian Federation.
Fax: +7 (831 2) 66 1497. E-mail:lnb@imoc.sinn.ru*

New tungsten carbyne complexes $(\mathrm{Bu^tO})_3\mathrm{W{\equiv}C{-}SiPh_3}$, $[(\mathrm{Bu^tO})_3\mathrm{W{\equiv}C}]_2\mathrm{SiPh_2}$, $[(\mathrm{Bu^tO})_3\mathrm{W{\equiv}C}]_2\mathrm{GePh_2}$, and $[(\mathrm{Bu^tO})_3\mathrm{W{\equiv}C}]_2\mathrm{SnPh_2}$ were prepared by the reactions of $(\mathrm{Bu^tO})_6\mathrm{W_2}$ with $\mathrm{Ph_3SiC{\equiv}C{-}Pr}$ or $\mathrm{Ph_2E(C{\equiv}C{-}Pr)_2}$ (E = Si, Ge, Sn) in individual crystalline form in 48—80% yields. The structures of both the $(\mathrm{Bu^tO})_3\mathrm{W{\equiv}C{-}GePh_3}$ and $(\mathrm{Bu^tO})_3\mathrm{W{\equiv}C{-}SnPh_3}$ compounds synthesized earlier and the new complexes were established by X-ray diffraction analysis.

Key words: carbyne complexes, synthesis, X-ray diffraction analysis.

It is known[1—3] that the tungsten carbyne complexes $(\mathrm{Bu^tO})_3\mathrm{W{\equiv}C{-}R}$ (R = Me, Et, Pr, $\mathrm{Bu^t}$, Ph) serve as catalysts for metathesis of acetylenic hydrocarbons. Data on analogous tungsten complexes containing organosilicon, -germanium, or -tin substituents at the carbyne carbon atom and their catalytic properties are scarce.[3]

Earlier,[4] we have reported that the reactions of element-substituted acetylenes $\mathrm{Ph_3GeC{\equiv}C{-}Pr}$ and $\mathrm{Ph_3SnC{\equiv}C{-}Et}$ with tungsten alkoxide $(\mathrm{Bu^tO})_6\mathrm{W_2}$ afforded the germanium- and tin-containing carbyne complexes $(\mathrm{Bu^tO})_3\mathrm{W{\equiv}C{-}GePh_3}$ (**1**) and $(\mathrm{Bu^tO})_3\mathrm{W{\equiv}C{-}SnPh_3}$ (**2**), respectively. In the present study, we used this procedure for the preparation of a new silicon-containing tungsten complex $(\mathrm{Bu^tO})_3\mathrm{W{\equiv}C{-}SiPh_3}$ (**3**).

$$\mathrm{W_2(OBu^t)_6 + Ph_3SiC{\equiv}CPr} \xrightarrow{i} \underset{\mathbf{3}}{\mathrm{Ph_3SiC{\equiv}W(OBu^t)_3}} + \underset{\mathbf{4}}{\mathrm{PrC{\equiv}W(OBu^t)_3}}$$

i. 20 °C, 1 h, pentane.

According to the ^{1}H NMR spectroscopic data, the reaction afforded new complex **3** and known compound **4** in virtually 100% yields. After separation of compound **4** by vacuum sublimation, complex **3** was obtained in the crystalline state in 80% yield as air-unstable colorless crystals readily soluble in organic solvents.

We found that diphenyldi(pent-1-yn-1-yl)silane, -germane, and -stannane $\mathrm{Ph_2E(C{\equiv}CPr)_2}$ (E = Si, Ge, Sn) also readily reacted with ditungsten hexa-*tert*-butoxide under analogous conditions to form the previously unknown trinuclear silicon-, germanium-, and tin-containing tungsten carbyne complexes $[(\mathrm{Bu^tO})_3\mathrm{W{\equiv}C}]_2\mathrm{EPh_2}$ (E = Si (**5**), Ge (**6**), Sn (**7**)).

$$\mathrm{2\,W_2(OBu^t)_6 + Ph_2E(C{\equiv}CPr)_2} \xrightarrow{i} \underset{\mathbf{5-7}}{[\mathrm{(Bu^tO)_3W{\equiv}C}]_2\mathrm{EPh_2}} + \mathrm{2}\,\underset{\mathbf{4}}{\mathrm{(Bu^tO)_3W{\equiv}C{-}Pr}}$$

E = Si (**5**), Ge (**6**), Sn (**7**)

i. 20 °C, 10—30 min, pentane.

After separation of compound **4** by vacuum sublimation, complexes **5**, **6**, and **7** were isolated in individual form in 48, 74, and 70% yields, respectively, as air-unstable colorless crystals readily soluble in organic solvents.

The structures of compounds **1** and **2**, which we have synthesized earlier, as well as of complexes **5**—**7** prepared in the present study were established by X-ray diffraction analysis.

X-ray diffraction study of the crystalline carbyne complexes $(\mathrm{Bu^tO})_3\mathrm{W{\equiv}C{-}GePh_3}$ (**1**) and $(\mathrm{Bu^tO})_3\mathrm{W{\equiv}C{-}SnPh_3}$ (**2**) demonstrated that they are isostructural (Fig. 1). The W and Ge (Sn) atoms in compounds **1** and **2** have a distorted tetrahedral coordination (Table 1). The W(1)—C(13) distances in complex **1** (1.785(7) and 1.757(6) Å*) are close to the analogous

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* Hereinafter, the second values of the geometric characteristics for complexes **1** and **2** correspond to another independent molecule.

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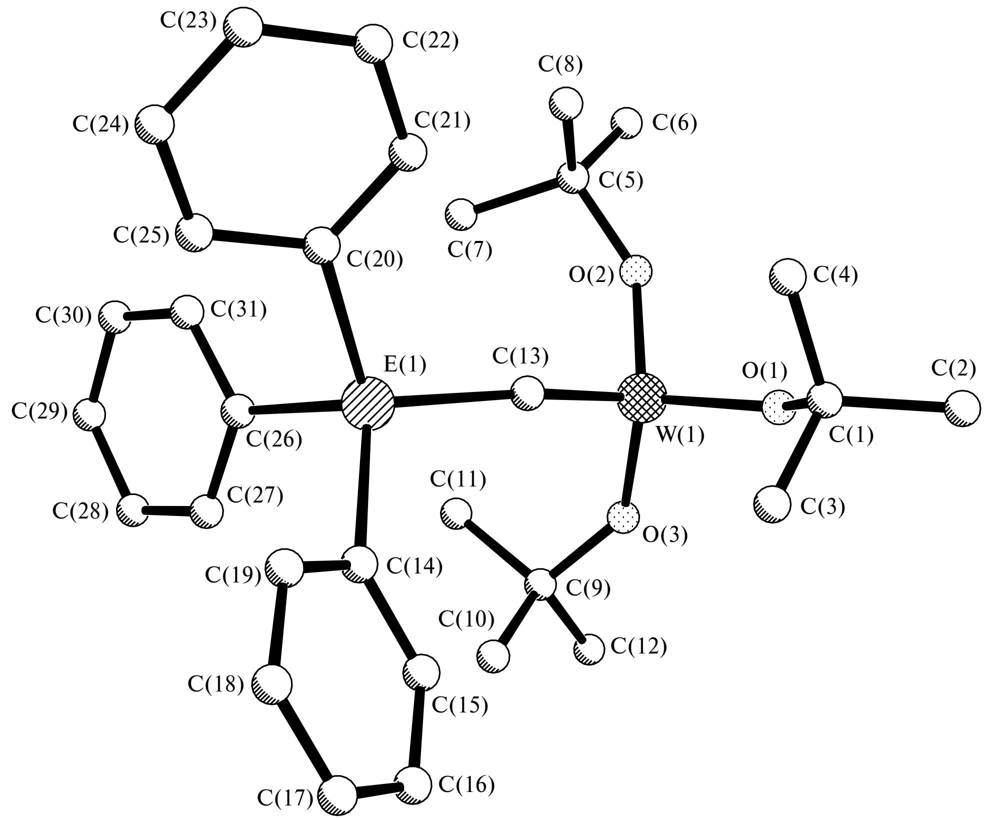

Fig. 1. Molecular structures of complexes **1** and **2**: E(1) = Ge(1) (**1**), Sn(1) (**2**).

distances in complex **2** (1.757(7) and 1.749(6) Å). The Ge(1)—C(13) distances in complex **1** are 1.898(7) and 1.927(6) Å. The Sn(1)—C(13) distances in complex **2** are 2.110(7) and 2.116(6) Å. The Ge—C(Ph) and Sn—C(Ph) distances in complexes **1** and **2** are in the ranges of 1.939(7)—1.971(7) and 2.130(6)—2.151(6) Å, respec-

Table 1. Selected bond lengths (*d*) and bond angles (ω) in complexes **1** and **2***

Bond	*d*/Å
Complex **1**	
W(1)—C(13)	1.785(7)/1.757(6)
W(1)—O(1)	1.867(5)/1.854(5)
W(1)—O(2)	1.871(5)/1.863(5)
W(1)—O(3)	1.860(5)/1.870(5)
Ge(1)—C(13)	1.898(7)/1.927(6)
Ge(1)—C(14)	1.959(7)/1.946(8)
Ge(1)—C(20)	1.967(8)/1.971(7)
Ge(1)—C(26)	1.939(7)/1.952(7)
Complex **2**	
W(1)—C(13)	1.757(7)/1.749(6)
W(1)—O(1)	1.869(4)/1.860(4)
W(1)—O(2)	1.867(5)/1.863(4)
W(1)—O(3)	1.870(4)/1.870(5)
Sn(1)—C(13)	2.110(7)/2.116(6)
Sn(1)—C(14)	2.140(6)/2.130(6)
Sn(1)—C(20)	2.150(6)/2.139(6)
Sn(1)—C(26)	2.145(6)/2.151(6)

Angle	ω/deg
Complex **1**	
C(13)—W(1)—O(3)	110.0(3)/108.3(3)
C(13)—W(1)—O(1)	106.1(3)/108.4(3)
O(3)—W(1)—O(1)	111.6(2)/110.4(2)
C(13)—W(1)—O(2)	107.8(3)/108.6(3)
O(3)—W(1)—O(2)	111.2(2)/111.5(2)
O(1)—W(1)—O(2)	109.9(2)/109.4(2)
C(13)—Ge(1)—C(26)	110.5(3)/111.8(3)
C(13)—Ge(1)—C(14)	111.3(3)/111.9(3)
C(26)—Ge(1)—C(14)	108.7(3)/108.3(3)
C(13)—Ge(1)—C(20)	107.0(3)/108.7(3)
C(26)—Ge(1)—C(20)	111.7(3)/110.1(3)
C(14)—Ge(1)—C(20)	107.5(3)/105.9(3)
W(1)—C(13)—Ge(1)	176.7(4)/179.2(4)

Angle	ω/deg
Complex **2**	
C(13)—W(1)—O(3)	108.5(3)/108.0(3)
C(13)—W(1)—O(1)	107.9(3)/107.5(3)
O(1)—W(1)—O(3)	111.5(2)/111.1(2)
C(13)—W(1)—O(2)	107.2(2)/108.2(2)
O(2)—W(1)—O(3)	110.2(2)/111.4(2)
O(2)—W(1)—O(1)	111.4(2)/110.5(2)
C(13)—Sn(1)—C(26)	107.2(2)/111.6(2)
C(13)—Sn(1)—C(14)	111.6(2)/112.7(3)
C(14)—Sn(1)—C(26)	110.5(2)/108.2(2)
C(13)—Sn(1)—C(20)	115.4(2)/107.3(2)
C(26)—Sn(1)—C(20)	105.4(2)/110.3(2)
C(14)—Sn(1)—C(20)	106.7(3)/106.6(3)
W(1)—C(13)—Sn(1)	171.9(4)/172.2(4)

* The geometric characteristics of another independent molecule are given after a slash.

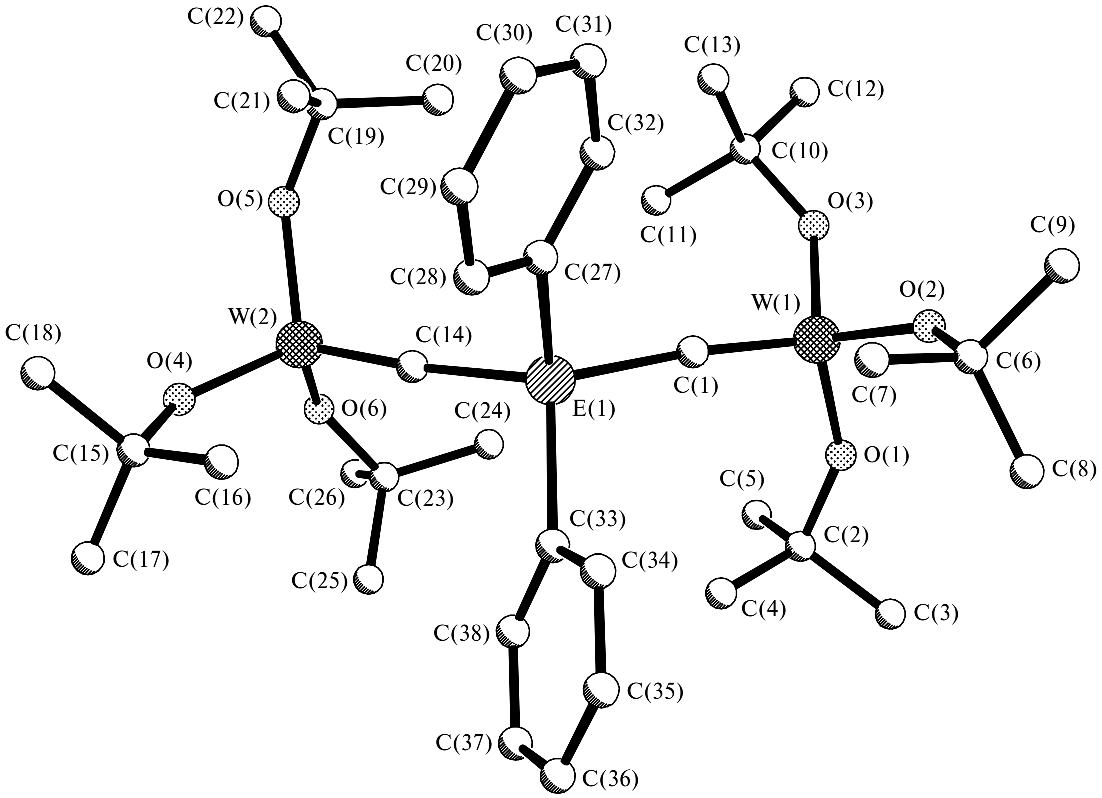

Fig. 2. Molecular structure of complex **7** (E(1) = Sn(1)). The E(1) atoms in complexes **5** (E(1) = Si(1)) and **6** (E(1) = Ge(1)), unlike that in complex **7**, lie on a twofold axis.

tively, and are somewhat longer than the Ge(1)—C(13) and Sn(1)—C(13) distances. The difference in the Ge—C and Sn—C bond lengths in complexes **1** and **2** corresponds, in fact, to the difference between the covalent radii of the Sn (1.36 Å [5]) and Ge (1.19 Å [5]) atoms.

The W(1)—C(13)—Ge(1) and W(1)—C(13)—Sn(1) angles are correspondingly 176.7(4)° and 179.2(4)° in complex **1** and 171.9(4)° and 172.2 (4)° in complex **2**.

X-ray diffraction study of the crystalline dicarbyne complexes $[(Bu^tO)_3W{\equiv}C]_2EPh_2$ (E = Si (**5**), Ge (**6**), Sn (**7**)) also demonstrated that these compounds are structurally similar (Fig. 2). The W and Si (Ge, Sn) atoms in compounds **5**—**7**, like those in complexes **1** and **2**, have a distorted tetrahedral coordination (Tables 2 and 3).

The W(1)—C(1) distances are 1.777(3), 1.761(2), and 1.759(3) (1.762(3)) Å*, respectively, for complexes **5**—**7**. The Si(1)—C(1), Ge(1)—C(1), and Sn(1)—C(1) distances in **5**—**7** are 1.842(3), 1.923(2), and 2.107(3) (2.111(3)) Å, respectively. The Si—C(Ph), Ge—C(Ph), and Sn—C(Ph) distances are 1.885(3), 1.957(2), and 2.140(3) (2.140(3)) Å, respectively, which, like those in complexes **1** and **2**, are somewhat longer than the Si(Ge, Sn)≡C distances. The differences in the Si—C, Ge—C, and Sn—C bond lengths in complexes **5**—**7** correspond to the differences between the covalent radii

Table 2. Selected bond lengths (*d*) and bond angles (ω) in complexes **5** and **6**

Parameter	Complex **5**	Complex **6**
Bond	*d*/Å	
W(1)—C(1)	1.777(3)	1.761(2)
W(1)—O(1)	1.859(2)	1.871(2)
W(1)—O(2)	1.871(2)	1.853(2)
W(1)—O(3)	1.868(2)	1.865(2)
E(1)—C(1)	1.842(3)	1.923(2)
E(1)—C(14)	1.885(3)	1.957(2)
Angle	ω/deg	
C(1)—W(1)—O(1)	108.3(1)	108.9(1)
C(1)—W(1)—O(2)	108.9(1)	107.9(1)
C(1)—W(1)—O(3)	110.9(1)	110.4(1)
O(1)—W(1)—O(2)	110.0(1)	110.1(1)
O(1)—W(1)—O(3)	108.6(1)	110.7(1)
O(3)—W(1)—O(2)	110.2(1)	108.8(1)
C(1)—E(1)—C(1A)	115.3(2)	115.5(1)
C(1)—E(1)—C(14)	109.1(1)	106.8(1)
C(1)—E(1)—C(14A)	107.2(1)	109.2(1)
C(14)—E(1)—C(14A)	108.9(2)	109.1(1)
W(1)—C(1)—E(1)	172.3(2)	172.8(1)

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* Hereinafter, the geometric characteristics for another symmetrically independent molecule of complex **7** are given in parentheses.

Table 3. Selected bond lengths (d) and bond angles (ω) in complex **7**

Bond	d/Å
W(1)—C(1)	1.759(3)
W(1)—O(1)	1.845(2)
W(1)—O(2)	1.862(2)
W(1)—O(3)	1.867(2)
Sn(1)—C(1)	2.107(3)
Sn(1)—C(27)	2.140(3)
W(2)—C(14)	1.762(3)
W(2)—O(4)	1.868(3)
W(2)—O(5)	1.869(2)
W(2)—O(6)	1.864(2)
Sn(1)—C(14)	2.111(3)
Sn(1)—C(33)	2.140(3)

Angle	ω/deg
C(1)—W(1)—O(1)	109.5(1)
C(1)—W(1)—O(2)	109.8(1)
C(1)—W(1)—O(3)	109.1(1)
O(1)—W(1)—O(2)	108.2(1)
O(1)—W(1)—O(3)	110.0(1)
O(2)—W(1)—O(3)	110.3(1)
C(1)—Sn(1)—C(14)	113.5(1)
C(1)—Sn(1)—C(33)	110.3(1)
C(14)—Sn(1)—C(33)	108.0(1)
W(1)—C(1)—Sn(1)	170.6(2)
C(14)—W(2)—O(4)	108.6(1)
C(14)—W(2)—O(5)	107.7(1)
C(14)—W(2)—O(6)	108.2(1)
O(4)—W(2)—O(5)	109.5(1)
O(4)—W(2)—O(6)	110.7(1)
O(5)—W(2)—O(6)	112.1(1)
C(1)—Sn(1)—C(27)	108.2(1)
C(14)—Sn(1)—C(27)	108.8(1)
C(33)—Sn(1)—C(27)	107.9(1)
W(2)—C(14)—Sn(1)	173.8(2)

of the Si (1.13 Å [5]), Ge (1.19 Å [5]), and Sn (1.36 Å [5]) atoms.

The W(1)—C(1)—Si(1), W(1)—C(1)—Ge(1), and W(1)—C(1)—Sn(1) angles are 172.3(2)°, 172.8(1)°, and 170.6(2)° (173.7(2)°), respectively.

The sum of the covalent radii for the W atom (1.33 Å [5]) and the "triply bound" C atom (0.6 Å [6,7]) is larger than the experimental W≡C bond lengths (1.749(6)—1.785(7) Å). We do not discuss the substantial, at first glance, difference in the W—C bond lengths in two independent molecules of complex **1** because of a poor accuracy of determination of these distances (1.785(7) and 1.757(6) Å). For the above-mentioned bond lengths, the confidence intervals overlap with each other: 1.764—1.806 for 1.785(7) Å and 1.739—1.775 for 1.757(6) Å. Besides, the crystal packing of complex **1** has no intermolecular contacts, which could be responsible for such a large difference in the distances of the same type in the independent molecules. In a few other compounds containing the W≡C—Si fragments,[8—11] the W—C and Si—C(Me) distances are in the ranges of 1.739—1.769 and 1.835—1.875 Å, respectively.

Experimental

All operations were carried out in evacuated sealed tubes and using the standard Schlenk techniques with the use of thoroughly dried and degassed solvents. The starting reagents $W_2(OBu^t)_6$,[12] $Ph_3SiC{\equiv}CPr$,[13] $Ph_2Si(C{\equiv}CPr)_2$,[13] $Ph_2Ge(C{\equiv}CPr)_2$,[13] and $Ph_2Sn(C{\equiv}CPr)_2$ [13] were prepared according to known procedures.

The IR spectra were recorded on a Perkin-Elmer-577 spectrometer. Samples were prepared as Nujol mulls under argon. The ^{1}H, ^{13}C, ^{29}Si, and ^{119}Sn NMR spectra were measured on a Bruker DPX-200 spectrometer with $SiMe_4$ as the internal standard.

The decomposition temperatures of the compounds synthesized were determined in evacuated sealed tubes and were not corrected.

The X-ray diffraction data sets were collected on an automated Smart APEX diffractometer (λ Mo-Kα, φ—ω scan technique). The principal crystallographic characteristics and details of X-ray data collection and structure refinement are given in Table 4. All structures were solved by direct methods and refined by the least-squares methods based on F^2_{hkl} with anisotropic thermal parameters for all nonhydrogen atoms. The H atoms in complexes **1**, **2**, and **7** were placed in geometrically calculated positions and refined using the riding model. The H atoms in complexes **5** and **6** were revealed from difference Fourier syntheses and refined isotropically, except for the hydrogen atoms at C(8) in molecule **5**, which were placed in geometrically calculated positions and refined using the riding model. In all the structures under study, high residual density peaks (2.363—4.062 e $\cdot$ Å^{-3}) were observed in the vicinity of the W atoms due to high absorption, which was difficult to take into account properly. All calculations were carried out using the SHELXTL program package.[14]

Tris(*tert*-butoxy)triphenylsilylmethylidinetungsten (3). A colorless solution of $Ph_3SiC{\equiv}CPr$ (0.336 g, 1.029 mmol) in pentane (5 mL) was added to a dark-red solution of $W_2(OBu^t)_6$ (0.829 g, 1.028 mmol) in pentane (10 mL). After storage at ~20 °C for 1 h, the reaction mixture turned pale-brown. According to the ^{1}H NMR spectroscopic data, the mixture contained only equivalent amounts of the $Ph_3SiC{\equiv}W(OBu^t)_3$ (**3**) and $PrC{\equiv}W(OBu^t)_3$ (**4**) complexes. The pentane was removed by evaporation *in vacuo*. Compound **4** was isolated from the solid residue by vacuum sublimation (85—90 °C, 10^{-2}—10^{-3} Torr, 1 h) as colorless crystals in a yield of 0.394 g (83.65%). The results of ^{1}H and ^{13}C NMR spectroscopy are consistent with the data published in the literature.[15] After sublimation, the solid residue was recrystallized from pentane to prepare complex **3** in a yield of 0.528 g (80.00%) as colorless crystals, t.decomp. 113—115°C. Found (%): C, 55.21; H, 6.56. $C_{31}H_{42}O_3SiW$. Calculated (%): C, 55.19; H, 6.28. IR, ν/cm^{-1}: 3050, 1420, 1090, 730, 690, 470 (Ph_3Si), 1150, 940 (W—O—C), 1350, 1235 (Bu^t). ^{1}H NMR (C_6D_6), δ: 1.08 (s, 27 H, Bu^t); 6.87—7.03 (m, 9 H, H(3), H(4)); 7.62—7.67 (m, 6 H, H(2)). ^{13}C NMR (C_6D_6), δ: 31.9 (CH_3), 80.8 ($WOCMe_3$, $^2J_{C,^{183}W}$ = 4.9 Hz); 127.9 (C(2)H); 129.4 (C(4)H); 136.7 (C(3)H); 138.9 (C(1)); 283.4 (W≡C, $^1J_{C,^{183}W}$ = 254.5 Hz).

Diphenyldi[tris(*tert*-butoxy)tungstenmethylidino]silane (5). A colorless solution of $Ph_2Si(C{\equiv}CPr)_2$ (0.257 g, 0.812 mmol) in pentane (5 mL) was added to a dark-red solution of $W_2(OBu^t)_6$ (1.308 g, 1.622 mmol) in pentane (10 mL). After storage at ~20 °C for 30 min, the reaction mixture turned pale-brown. According to the ^{1}H NMR spectroscopic data, the mixture contained only the $Ph_2Si[C{\equiv}W(OBu^t)_3]_2$ (**5**) and $PrC{\equiv}W(OBu^t)_3$ (**4**) complexes. The pentane was removed by evaporation *in vacuo*. Compound **4** was isolated from the solid residue by vacuum sublimation (85—90 °C, 10^{-2}—10^{-3} Torr, 1 h) in a yield of 0.424 g (57.07%) as colorless crystals. The results of ^{1}H and ^{13}C NMR spectroscopy are consistent with the data pub-

Table 4. Crystallographic data and details of structure refinement of complexes **1**, **2**, and **5**—**7**

Parameter	**1**	**2**	**5**	**6**	**7**
Molecular formula	$C_{31}H_{42}O_3GeW$	$C_{31}H_{42}O_3SnW$	$C_{38}H_{64}O_6GeW_2$	$C_{38}H_{64}O_6SnW_2$	$C_{38}H_{64}O_6SnW_2$
Molecular weight	719.09	765.19	1012.68	1057.18	1103.28
Crystal dimensions/mm	0.5×0.3×0.2	0.5×0.2×0.04	0.4×0.3×0.1	0.16×0.16×0.08	0.2×0.15×0.1
T/K	110(2)	110(2)	100(2)	100(2)	100(2)
Space group	$P2_1/n$	$P2_1/n$	$C2/c$	$C2/c$	$P2_1/n$
a/Å	10.054(4)	10.391(2)	19.6827(12)	19.6760(16)	14.2480(13)
b/Å	31.930(12)	16.155(4)	10.2214(6)	10.2164(8)	19.1022(17)
c/Å	19.134(7)	37.429(9)	22.2890(14)	22.3362(18)	16.1153(15)
β/deg	92.707(8)	92.499(5)	107.658(1)	107.429(2)	94.269(2)
V/Å^3	6135(4)	6277(2)	4272.9(5)	4283.8(6)	4373.9(7)
Z	8	8	4	4	4
d_{calc}/g cm^{-3}	1.557	1.619	1.574	1.639	1.675
μ/cm^{-1}	47.54	44.85	54.47	60.93	58.51
Absorption correction			SADABS program		
T_{min}/T_{max}	0.194/0.493	0.1505/0.3577	0.2193/0.6119	0.4423/0.9522	0.3874/0.5923
F(000)	2864	3008	2008	2080	2152
$2\theta_{max}$/deg	54	60	58	58	58
Number of independent reflections (R_{int})	13367 (0.1628)	18288 (0.0702)	5518 (0.029)	5604 (0.0308)	11607 (0.0482)
R_1 (based on F for reflections with $I > 2\sigma(I)$)	0.0574 (8665)	0.0570 (11188)	0.033 (5216)	0.0289 (5401)	0.0272 (10091)
wR_2 (based on F^2 for all reflections)	0.1299	0.1455	0.0944	0.0714	0.0687
Number of parameters in the refinement	649	649	338	341	424
Weighting scheme			$w^{-1}=\sigma^2(F_o^2)+(\alpha P)^2+\beta P$, where $P = 1/3(F_o^2 + 2F_c^2)$		
α	0.0511	0.0724	0.0583P	0.0366	0.0315
β	0	0	15.8020	7.0235	6.8071
GOOF	0.922	0.996	1.094	1.099	1.061
Residual electron density peaks/Å^{-3}, e_{min}/e_{max}	−2.144/3.038	−1.659/3.441	−3.216/4.062	−2.902/2.363	−1.237/2.426

lished in the literature.[15] After sublimation, the solid residue was recrystallized from pentane to prepare complex **5** in a yield of 0.394 g (47.99%) as colorless crystals, t.decomp. 112—115 °C. Found (%): C, 45.03; H, 6.34. $C_{38}H_{64}O_6SiW_2$. Calculated (%): C, 45.07; H, 6.37. IR, ν/cm^{-1}: 1440, 1070, 730, 695, 455 (Ph_2Si), 1150, 940 (W—O—C), 1350, 1230 (Bu^t). ^1H NMR (toluene-d_8), δ: 1.40 (s, 54 H, Bu^t); 7.23—7.36 (m, 6 H, H(3), H(4)); 8.12—8.16 (m, 4 H, H(2)). ^{13}C NMR (toluene-d_8), δ: 32.3 (CH_3), 80.3 ($WOCMe_3$, $^2J_{C,^{183}W}$ = 4.9 Hz); 127.3 (C(2)H); 137.1 (C(3)H); 128.8 (C(4)H); 143.2 (C(1)); 290.1 (W≡C, $^1J_{C,^{183}W}$ = 251.2 Hz). ^{29}Si NMR (toluene-d_8), δ: −53.2

Diphenyldi[tris(*tert*-butoxy)tungstenmethylidino]germane (6). Complex **6** was synthesized and isolated as described above. Compound **4** was prepared from $(Bu^tO)_6W_2$ (1.700 g, 2.108 mmol) and $Ph_2Ge(C{\equiv}CPr)_2$ (0.381 g, 1.055 mmol) in a yield of 0.798 g (82.61%) as colorless crystals (the results of ^1H and ^{13}C NMR spectroscopy are identical with the data published in the literature[15]). Complex **6** was isolated in a yield of 0.829 g (74.39%) as colorless crystals, t.decomp. 102—104 °C. Found (%): C, 43.21; H, 6.12. $C_{38}H_{64}O_6GeW_2$. Calculated (%): C, 43.17; H, 6.10. IR, ν/cm^{-1}: 1440, 1070, 730, 695, 455 (Ph_2Ge), 1150, 940 (W—O—C), 1350, 1230 (Bu^t). ^1H NMR (toluene-d_8), δ: 1.39 (s, 54 H, Bu^t); 7.22—7.36 (m, 6 H, H(3), H(4)); 8.02—8.07 (m, 4 H, H(2)). ^{13}C NMR (toluene-d_8), δ: 32.2 (CH_3); 79.9 ($WOCMe_3$, $^2J_{C,^{183}W}$ = 4.9 Hz); 127.3 (C(3)H); 128.6 (C(4)H); 136.0 (C(2)H); 145.3 (C(1)); 279.9 (W≡C, $^1J_{C,^{183}W}$ = 271.6 Hz).

Diphenyldi[tris(*tert*-butoxy)tungstenmethylidino]stannane (7). Complex **7** was synthesized and isolated as described above. Compound **4** was prepared from $(Bu^tO)_6W_2$ (1.285 g, 1.594 mmol) and $Ph_2Sn(C{\equiv}CPr)_2$ (0.325 g, 0.798 mmol) in a yield of 0.397 g (54.38%) as colorless crystals (the results of ^1H and ^{13}C NMR spectroscopy are in agreement with the data published in the literature[15]). Complex **7** was isolated in a yield of 0.615 g (69.97%) as colorless crystals, t.decomp. 112—114 °C. Found (%): C, 41.34; H, 5.82. $C_{38}H_{64}O_6SnW_2$. Calculated (%): C, 41.37; H, 5.85. IR, ν/cm^{-1}: 1435, 1060, 720, 690, 445 (Ph_2Sn), 1150, 945 (W—O—C), 1350, 1230 (Bu^t). ^1H NMR (toluene-d_8), δ: 1.42 (s, 54 H, Bu^t); 7.20—7.35 (m, 6 H, H(3), H(4)); 7.95—7.98 (m, 4 H, H(2)). ^{13}C NMR (toluene-d_8), δ: 32.0 (CH_3); 79.3 ($WOCMe_3$, $^2J_{C,^{183}W}$ = 4.4 Hz); 128.4 (C(2)H, $^2J_{C,^{117}Sn}$ = 53.0 Hz, $^2J_{C,^{119}Sn}$ = 54.9 Hz); 128.7 (C(4)H, $^4J_{C,Sn}$ = 12.2 Hz); 137.6 (C(3)H, $^3J_{C,Sn}$ = 39.9 Hz), 146.7 (C(1), $^1J_{C,^{117}Sn}$ = 537.5 Hz, $^1J_{C,^{119}Sn}$ = 562.2 Hz); 277.0 (W≡CSn, $^1J_{C,^{183}W}$ = 270.7 Hz, $^1J_{C,^{117}Sn}$ = 247.8 Hz, $^1J_{C,^{117}Sn}$ = 259.5 Hz). ^{119}Sn NMR (toluene-d_8), δ: −258.7 ($^2J_{^{119}Sn,^{183}W}$ = 732.2 Hz).

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References

1. M. Schuster and S. Blechert, *Angew. Chem.*, 1997, **109**, 2125.
2. U. H. F. Bunz and L. Kloppenburg, *Angew. Chem., Int. Ed.*, 1999, **38**, 478.
3. R. R. Schrock, *Chem. Rev.*, 2002, **102**, 145.
4. L. N. Bochkarev, A. V. Safronova, V. I. Shcherbakov, N. E. Stolyarova, G. V. Basova, S. Ya. Khorshev, Yu. A. Kurskii, and G. A. Abakumov, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 510 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 552].
5. S. S. Batsanov, *Zh. Neorg. Khim.,* 1991, **36**, 3015 [*J. Inorg. Chem. USSR*, 1991, **36**, 1694 (Engl. Transl.)].
6. L.Pauling, *Acta Cryst.*, 1957, **10**, 374.
7. G. B. Bokii and L. O. Atovmyan, *Zh. Strukt. Khim.,* 1961, **2**, 308 [*J. Struct. Chem. USSR*, 1961, **2** (Engl. Transl.)].
8. L. Giannini, E. Solari, S. Dovesi, C. Floriani, N. Re, A. Chiesi-Villa, and C. Rizzoli, *J. Am. Chem. Soc.*, 1999, **121**, 2784.
9. S. W. Seidel, R. R. Schrock, and W. M. Davis, *Organometallics*, 1998, **17**, 1058.
10. K. G. Caulton, M. H. Chisholm, W. E. Streib, and Ziling Xue, *J. Am. Chem. Soc.*, 1991, **113**, 6082.
11. E. O. Fischer, H. Hollfelder, P. Friedrich, F. R. Kreissl, and G. Huttner, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 401.
12. R. R. Schrock, M. L. Listemann, and L. G. Sturgeoff, *J. Am. Chem. Soc.*, 1982, **104**, 4291.
13. A. M. Sladkov and L. K. Luneva, *Zh. Obshch. Khim.*, 1966, **36**, 553 [*J. Gen. Chem. USSR*, 1966, **36** (Engl. Transl.)].
14. G. M. Sheldrick, *SHELXTL*, V.6.10, Bruker AXS Inc., Madison, WI-53719, USA, 1997.
15. M. L. Listemann and R. R. Schrock, *Organometallics*, 1985, **4**, 74.

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