Synthesis of trinuclear silicon-, germanium-, and tin-containing tungsten carbene complexes $[(Bu^tO)_2(Cl)_2W{=}CH]_2EPh_2$ (E = Si, Ge, or Sn). Crystal structure of $[(Bu^tO)_2(Cl)_2W{=}CH]_2SiPh_2$ complex

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New trinuclear organosilicon, organogermanium, and organotin-containing tungsten carbene complexes $Ph_2E[CH{=}WCl_2(OBu^t)_2]_2$ (E = Si, Ge, or Sn) were synthesized by the reaction of the trinuclear carbyne complexes $Ph_2E[C{\equiv}W(OBu^t)_3]_2$ with HCl. The tin-containing carbene complex is thermally unstable and was identified in solution by ^1H and ^{13}C NMR spectroscopy. The silicon- and germanium-tungsten carbene complexes were isolated in high yields as individual crystals and were characterized by elemental analysis, IR spectroscopy, and ^1H and ^{13}C NMR spectroscopy. The structure of the silicon-containing complex $Ph_2Si[CH{=}WCl_2(OBu^t)_2]_2$ was established by X-ray diffraction.

Key words: carbene complexes, tungsten, silicon, germanium, tin, synthesis, X-ray diffraction study.

Certain types of tungsten carbene complexes serve as catalysts for metathesis of olefinic hydrocarbons.[1—5] One of potential procedures for the synthesis of carbene complexes is based on protonation of the carbyne complexes $W(\equiv CR)(OBu^t)_3$, including those containing various functional groups at the carbyne carbon atom.[6] The resulting carbene complexes $W(=CHR)(OBu^t)_2X_2$ are inactive in olefin metathesis. However, these complexes exhibit high catalytic activity in these reactions in the presence of Lewis acids AlX_3 or GaX_3 (X = Cl or Br).[7,8] The starting carbyne complexes can easily be synthesized by stoichiometric metathesis of acetylenic derivatives with dimeric tungsten alkoxide $W_2(OBu^t)_6$.[9—11]

Earlier,[12] we have found that the reactions of the organosilicon, organogermanium, and organotin-containing carbyne complexes $Ph_3E{-}C{\equiv}W(OBu^t)_3$ (E = Si, Ge, or Sn) with two equivalents of HCl in toluene or pentane at −78 °C afforded one equivalent of new tungsten carbene complexes $Ph_3E{-}CH{=}WCl_2(OBu^t)_2$ and one equivalent of *tert*-butyl alcohol.

Subsequent studies demonstrated that the reaction of the trinuclear tungsten carbyne complexes $Ph_2E[C{\equiv}W(OBu^t)_3]_2$ with four equivalents of gaseous hydrogen chloride performed under analogous conditions produced new carbene complexes $Ph_2E[CH{=}WCl_2(OBu^t)_2]_2$ (E = Si (**1**), Ge (**2**), and Sn(**3**)) in high yields:

$$Ph_2E[C{\equiv}W(OBu^t)_3]_2 + 4\ HCl \rightarrow$$
$$\rightarrow Ph_2E[CH{=}WCl_2(OBu^t)_2]_2 + 2\ Bu^tOH$$

E = Si (**1**), Ge (**2**), Sn (**3**)

Reaction conditions: toluene (pentane), −78—20 °C.

Tin-containing trinuclear carbene complex **3** was not isolated in individual form. This compound is thermally unstable and decomposes at room temperature after ~1 h. Complex **3** was identified in solution by ^1H and ^{13}C NMR spectroscopy.

After recrystallization from pentane, trinuclear silicon- and germanium-containing tungsten carbene complexes **1** and **2** were isolated as individual crystals in 80 and 90% yields, respectively. The compounds were characterized by elemental analysis, IR spectroscopy, and ^1H and ^{13}C NMR spectroscopy.

In due course, the trinuclear carbene complexes in solution apparently undergo isomerization. This is evidenced by the fact that the ^1H and ^{13}C NMR spectra of the complexes have the main signal along with several signals with lower intensities in the regions of carbene protons and carbene carbon atoms, the latter being presumably assigned to isomeric forms of the complexes (Table 1). We failed to isolate these isomeric compounds in individual form.

Silicon-containing complex **1** was structurally characterized by X-ray diffraction (Fig. 1). The silicon atom

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Table 1. ^{1}H and ^{13}C NMR spectroscopic data for isomeric forms of complexes **1**, **2**, and **3**

E	δ		$^{2}J_{H,M}$/Hz (M)
	H_α (CH=)	C_α (CH=)	
Si	10.15	238.6	9.6 (^{183}W)
	12.29	269.0	10.5 (^{183}W)
	12.51	218.6	11.8 (^{183}W)
Ge	10.17	242.9	—
	10.53	245.8	—
	12.22	271.1	—
Sn	9.38	—	72.0 ($^{117/119}Sn$)
	9.90	—	74.3 ($^{117/119}Sn$)
	10.10	—	16.3 (^{183}W)
			62.7 ($^{117/119}Sn$)
	12.01	—	—

has a distorted tetrahedral coordination, and the tungsten atoms are in a distorted tetragonal-pyramidal coordination environment.

The W—C and Si—C distances are 1.876(2), 1.883(2) Å and 1.887(3), 1.863(2) Å, respectively. The Si(1)—C(9)—W(1) and Si(1)—C(10)—W(2) angles are 126.5(1)° and 133.1(2)°. The W—C (1.868(5) and 1.870(2) Å) and Si—C (1.861(5) Å) distances in the $Ph_3E—CH=WCl_2(OBu^t)_2$ complexes (E = Si or Ge), which we have studied earlier,[12] have similar values. The Si—C—W angles in the latter complexes (136.1(3)° and 135.6(1)°) are slightly larger than those in complex **1**. In addition, there is a very weak intramolecular Si...O interaction in complex **1**. The Si(1)...O(1) and Si(1)...O(4) distances in **1** and the Si...O distance in $Ph_3Si—CH=WCl_2(OBu^t)_2$ [12] are 3.367(1), 3.513(1), and 3.658(3) Å, respectively (the sums of the van der Waals radii of silicon and oxygen is 3.45 Å[13]).

The dihedral angle between the W(1)C(9)H(9)Si(1) and W(1)C(10)H(10)Si(1) fragments is 107.6°.

Experimental

All operations were carried out in evacuated sealed tubes with the use of the standard Schlenk technique. The solvents were thoroughly dried and degassed. The starting reagents, *viz.*, the trinuclear organosilicon, organogermanium, and organotin-containing carbyne complexes $Ph_2E[C{\equiv}W(OBu^t)_3]_2$ (E = Si, Ge, or Sn), were synthesized according to a procedure described earlier.[11] The IR spectra were measured on a Perkin—Elmer-577 spectrometer. Samples were prepared under argon as Nujol mulls. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-200 spectrometer (200 MHz for ^{1}H and 50 MHz for ^{13}C). The chemical shifts are given on the δ scale relative to Me_4Si as the internal standard.

The decomposition temperatures of the compounds synthesized were measured in evacuated sealed capillary tubes and are uncorrected.

Chromatographic analysis of volatile products was carried out on a Tsvet-500 chromatograph (0.3×200 cm steel column filled with SE-30 (5%) on Inerton AW) equipped with a katharometer as the detector with the use of helium as the carrier gas.

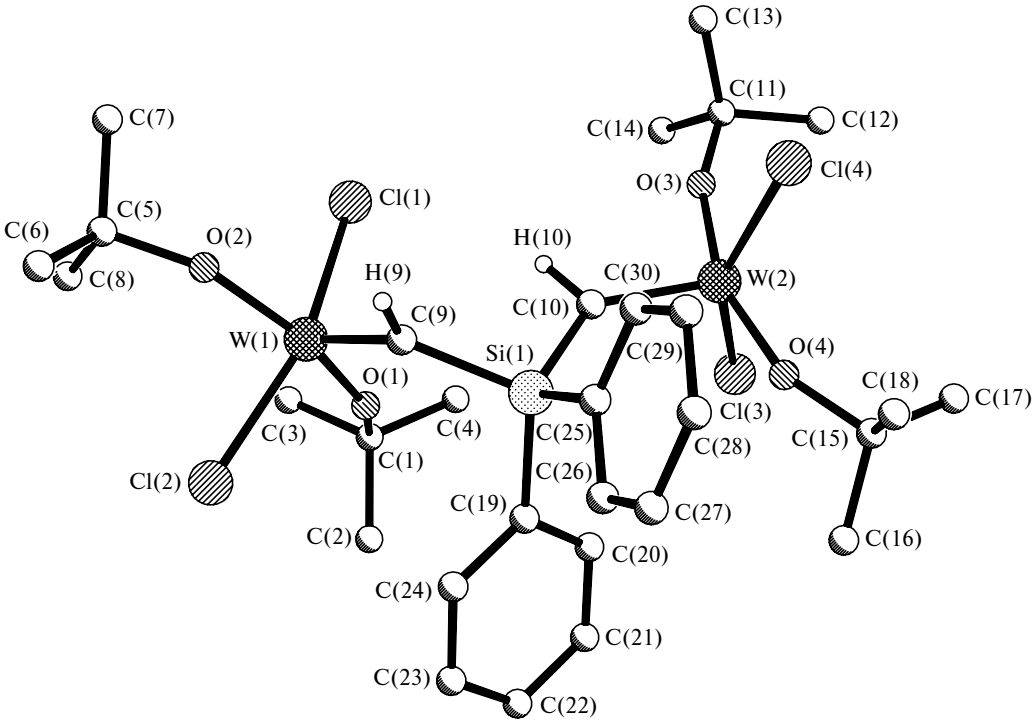

Fig. 1. Molecular structure of complex **1**.

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

Bond	*d*/Å	Angle	ω/deg
W(1)—O(1)	1.809(2)	O(1)—W(1)—O(2)	154.59(8)
W(1)—O(2)	1.813(2)	O(1)—W(1)—Cl(1)	86.61(6)
W(1)—C(9)	1.876(2)	O(1)—W(1)—Cl(2)	87.45(6)
W(1)—Cl(2)	2.3845(6)	O(2)—W(1)—Cl(2)	87.57(5)
W(1)—Cl(1)	2.3998(6)	O(2)—W(1)—Cl(1)	87.46(6)
W(2)—O(4)	1.806(2)	Cl(1)—W(1)—Cl(2)	154.99(2)
W(2)—O(3)	1.806(2)	O(3)—W(2)—Cl(3)	87.51(6)
W(2)—C(10)	1.883(2)	O(3)—W(2)—Cl(4)	86.83(6)
W(2)—Cl(3)	2.3738(6)	O(4)—W(2)—O(3)	159.05(8)
W(2)—Cl(4)	2.3908(6)	O(4)—W(2)—Cl(3)	87.94(6)
Si(1)—C(10)	1.863(2)	O(4)—W(2)—Cl(4)	86.93(6)
Si(1)—C(19)	1.868(2)	Cl(3)—W(2)—Cl(4)	149.97(2)
Si(1)—C(25)	1.871(2)	C(10)—Si(1)—C(9)	104.1(1)
Si(1)—C(9)	1.877(3)	C(10)—Si(1)—C(19)	112.8(1)
		C(10)—Si(1)—C(25)	112.5(1)
		C(19)—Si(1)—C(25)	108.9(1)
		C(19)—Si(1)—C(9)	110.7(1)
		C(25)—Si(1)—C(9)	107.6(1)
		W(1)—C(9)—Si(1)	126.5(1)
		W(2)—C(10)—Si(1)	133.1(1)

Single crystals of the $Ph_2Si[CH{=}WCl_2(OBu^t)_2]_2$ complex were grown by crystallization from pentane. The intensities of reflections were measured on an automated Smart APEX diffractometer (graphite monochromator, Mo-Kα radiation, φ—ω scanning technique, λ = 0.71073 Å) at 100(2) K. The structure was solved by direct methods using the SHELXTL program package[14] and refined by the least-squares method against $F^2{}_{hkl}$ with anisotropic displacement parameters for all nonhydrogen atoms. All H atoms were located from difference Fourier maps and refined isotropically. Absorption corrections were applied using the SADABS program.[15] The main bond lengths and bond angles are given in Table 2. The crystallographic data and characteristics of X-ray diffraction study are listed in Table 3.

Diphenyldi[dichloro-bis(*tert*-butoxy)tungstenmethylideno]silane (1). Four equivalents of gaseous HCl (28.6 mL, 1.28 mmol) were condensed into a solution of the $Ph_2Si[C{\equiv}W(OBu^t)_3]_2$ complex (0.32 g, 0.32 mmol) in toluene (5 mL) at −78 °C. The solution immediately turned orange-red. Then the reaction mixture was warmed to room temperature, after which the solution turned yellow-green. The solvent and volatile products were removed *in vacuo*. *tert*-Butyl alcohol was detected (0.020 g, 85%) by GLC analysis of the volatile products. The solid residue was crystallized from pentane, and pale-yellow crystals of the $Ph_2Si[CH{=}WCl_2(OBu^t)_2]_2$ complex were obtained in a yield of 0.25 g (80%). The crystals decompose in the temperature range of 95—97 °C. Found (%): C, 35.70; H, 5.11. $C_{30}H_{48}Cl_4O_4SiW_2$. Calculated (%): C, 35.72; H, 5.14. IR, ν/cm^{-1}: 1410, 1090, 730, 690, 490 (Ph_2Si); 1140, 930 (W—O—C); 1345, 1230 (Bu^t); 1005 (HC=). ^{1}H NMR (C_6D_6), δ: 1.14 and 1.45 (both s, 18 H each, Me); 7.12—7.34 (m, 6 H, H(3), H(4)); 8.01—8.15 (m, 4 H, H(2)); 12.05 (s, 2 H, HC=, $^1J_{H_\alpha,C}$ = 130.4 Hz, $^2J_{H_\alpha,^{183}W}$ = 9.4 Hz). ^{13}C NMR (C_6D_6), δ: 29.4 and 29.7 (both Me); 91.5 (WO$\underline{C}$Me$_3$, $^2J_{C,^{183}W}$ = 9.8 Hz); 92.1 (WO$\underline{C}$Me$_3$, $^2J_{C,^{183}W}$ = 8.5 Hz); 128.3 (CH(3)); 130.4 (CH(4)); 136.5 (C(1)); 137.1 (CH(2));, 264.6 (W=C, $^1J_{C,^{183}W}$ = 143.0 Hz).

Table 3. Principal crystallographic data and characteristics of the structure refinement for complex **1**

Parameter	Characteristics
Molecular formula	$C_{30}H_{48}Cl_4O_4SiW_2$
Molecular weight	1010.27
Crystal dimensions/mm	0.20×0.10×0.06
Crystal system	Monoclinic
Space group	*P*2(1)/*n*
a/Å	16.0141(9)
b/Å	11.6059(6)
c/Å	21.7904(12)
β/deg	107.0810(10)
V/Å^3	3871.3(4)
Z	4
d_{calc}/g cm^{-3}	1.733
μ/cm^{-1}	62.75
T_{min}/T_{max}	0.3667/0.7046
F(000)	1960
$2\theta_{max}$/deg	29.03
Number of observed /independent reflections (R_{int})	39586/10225 (0.0295)
R_1 (based on *F* for reflections with $I > 2\sigma(I)$)	0.0209
wR_2 (based on F^2 for all reflections)	0.0470
Number of parameters in refinement	562
Number of restrictions	0
GOOF(F^2)	1.037
Residual electron density peaks, min/max/e Å^{-3}	−0.835/1.988

Diphenyldi[dichloro-bis(*tert*-butoxy)tungstenmethylideno]germane (2). The synthesis and isolation of the $Ph_2Ge[CH{=}WCl_2(OBu^t)_2]_2$ complex were carried out as described above. The reaction of $Ph_2Ge[C{\equiv}W(OBu^t)_3]_2$ (0.68 g, 0.64 mmol) with gaseous HCl (57.3 mL, 2.56 mmol) afforded Bu^tOH (0.041 g, 87%) (GLC) and $Ph_2Ge[CH{=}WCl_2(OBu^t)_2]_2$ as small pale-yellow crystals (0.61 g, 90%). The $Ph_2Ge[CH{=}WCl_2(OBu^t)_2]_2$ complex decomposes in the temperature range of 100—105 °C. Found (%): C, 34.19; H, 4.91. $C_{30}H_{48}Cl_4O_4GeW_2$. Calculated (%): C, 34.21; H, 4.92. IR, ν/cm^{-1}: 3030, 1460, 1080, 735, 690, 460 (Ph_2Ge); 1150, 930 (W—O—C); 1350, 1230 (Bu^t); 1000 (HC=). ^{1}H NMR (toluene-d_8), δ: 1.13 and 1.45 (both s, 18 H each, Me); 7.10—7.28 (m, 6 H, H(3), H(4)); 7.89—7.94 (m, 4 H, H(2)); 12.00 (s, 2 H, HC=, $^1J_{H_\alpha,C}$ = 143.3 Hz, $^2J_{H_\alpha,^{183}W}$ = 5.3 Hz). ^{13}C NMR (toluene-d_8), δ: 29.4 and 29.7 (both Me); 91.4 and 91.7 (both WO$\underline{C}$Me$_3$); 128.6 (CH(3)); 130.0 (CH(4)); 136.2 (C(1)); 139.0 (CH(2)); 267.7 (W=C).

Reaction of the $Ph_2Sn[C{\equiv}W(OBu^t)_3]_2$ complex with HCl. Gaseous HCl (21.5 mL, 0.96 mmol) was condensed into a solution of $Ph_2Sn[C{\equiv}W(OBu^t)_3]_2$ (0.26 g, 0.24 mmol) in toluene-d_8 (0.7 mL) at −78 °C in an NMR tube. ^{1}H NMR (toluene-d_8), δ: 11.4 (s, 2 H, HC=, $^1J_{H_\alpha,C}$ = 142.0 Hz, $^2J_{H_\alpha,^{183}W}$ = 13.8 Hz). ^{13}C NMR (toluene-d_8), δ: 264.3 (C≡W).

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