Synthesis and structures of germanium-containing tungsten carbyne complexes $Ph_3GeC{\equiv}W(CH_2Bu^t)_3$ and $Ph_3GeC{\equiv}W(CH_2SiMe_3)_3$

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New germanium-containing tungsten carbyne complexes $Ph_3GeC{\equiv}W(CH_2R)_3$ (R = Bu^t or $SiMe_3$) were synthesized by the reaction of the alkoxy derivative $Ph_3GeC{\equiv}W(OBu^t)_3$ with alkyllithium reagents RCH_2Li. The new compounds were isolated in individual form as crystals in 95 and 90% yields, respectively, and were characterized by elemental analysis, ^1H and ^{13}C NMR spectroscopy, and X-ray diffraction. X-ray diffraction study showed that the coordination environment of the W and Ge atoms in the $Ph_3GeC{\equiv}W(CH_2Bu^t)_3$ and $Ph_3GeC{\equiv}W(CH_2SiMe_3)_3$ complexes can be described as a distorted tetrahedron.

Key words: carbyne complexes, tungsten, germanium, synthesis, X-ray diffraction study.

Nowadays, olefin metathesis catalyzed by transition metal carbene complexes is widely used in organic synthesis.[1—6] Metathesis of acetylenic hydrocarbons mediated by transition metal carbyne complexes is much less well studied and is used to a lesser extent.[4—6] The tungsten carbyne complexes $RC{\equiv}W(OR')_3$ (R and R′ = Alkyl or Aryl) are most efficient catalysts for metathesis of acetylenic hydrocarbons.[4] The catalytic activity of complexes was found[4] to be to a large extent determined by the nature of alkoxy groups. The influence of the nature of the substituent R bound to the carbyne carbon atom is much less well known. Recently,[7,8] we have synthesized the tungsten carbyne complexes $Ph_3EC{\equiv}W(OBu^t)_3$ and $Ph_2E[C{\equiv}W(OBu^t)_3]_2$ (E = Si, Ge, or Sn) containing organosilicon, -germanium, and -tin substituents at the carbyne carbon atom. The resulting carbyne complexes exhibit high catalytic activity in metathesis of hept-3-yne (as a test substrate). The catalytic activity of tin-containing derivatives is substantially higher than that of silicon-containing complexes, and the trinuclear complexes $Ph_2E[C{\equiv}W(OBu^t)_3]_2$ are more efficient catalysts than the dinuclear complexes $Ph_3EC{\equiv}W(OBu^t)_3$.[9] In this connection, it was of interest to elucidate how the catalytic activity of silicon-, germanium-, and tin-containing tungsten carbyne complexes changes when the alkoxy groups are replaced by other ligands, in particular, by alkyl groups.

It is known that the *tert*-butoxy groups in the tungsten carbyne complexes $RC{\equiv}W(OBu^t)_3$ (R = Alk or Ar) are readily replaced by alkyl groups in the reactions with alkyllithium compounds or Grignard reagents.[10] In the present study, we used this method for the replacement of the *tert*-butoxy group in the germanium-containing tungsten carbyne complex by the neopentyl and trimethylsilylmethyl substituents.

Results and Discussion

It was demonstrated that the tungsten triphenylgermyl carbyne complex $Ph_3GeC{\equiv}W(OBu^t)_3$ (see Ref. 7) readily reacts with neopentyllithium and trimethylsilylmethyllithium to give new alkyl-containing carbyne complexes $Ph_3GeC{\equiv}W(CH_2Bu^t)_3$ and $Ph_3GeC{\equiv}W(CH_2SiMe_3)_3$, respectively (Scheme 1).

Scheme 1

$$Ph_3GeC{\equiv}W(OBu^t)_3 + 3\,RCH_2Li \longrightarrow Ph_3GeC{\equiv}W(CH_2R)_3 + 3Bu^tOLi$$

R = CMe_3 (**1**), $SiMe_3$ (**2**)

Reaction conditions: diethyl ether, 0 °C.

Both complexes were isolated in individual form as crystals in 95 and 90% yields, respectively. The ^1H and ^{13}C NMR spectra are consistent with the formulas of these compounds. The signals for the carbyne α-carbon atoms are observed at δ 321.7 and 325.1 and are shifted downfield by 49 and 52.6 ppm, respectively, compared to the corresponding signal of the tris(alkoxy)carbyne complex $Ph_3GeC{\equiv}W(OBu^t)_3$.[7] The spin-spin coupling constants $^1J_{C_\alpha\text{-}^{183}W}$ for complexes **1** and **2** are 210.1 and 192.9 Hz, respectively.

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X-ray diffraction study demonstrated that complexes **1** and **2** (Figs 1 and 2, respectively) are structurally similar to the *tert*-butoxy-containing carbyne complexes $Ph_3EC{\equiv}W(OBu^t)_3$ (E = Ge or Sn) studied earlier.[8] The tungsten and germanium atoms in complexes **1** and **2** have a distorted tetrahedral coordination. The Ph and CH_2Bu^t substituents in molecule **1** are in a staggered conformation with respect to each other, which minimizes their mutual repulsion. Both eclipsed and staggered conformations are observed in molecule **2** due to disorder of the Ph and $SiMe_3$ groups.

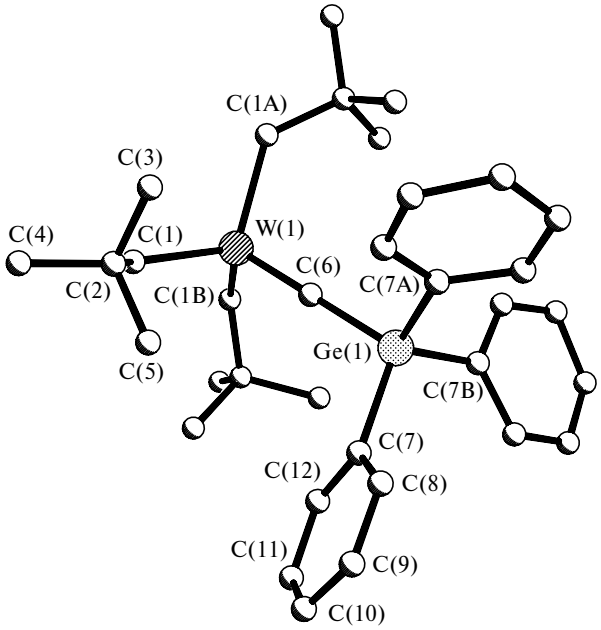

Fig. 1. Molecular structure of molecule **1**.

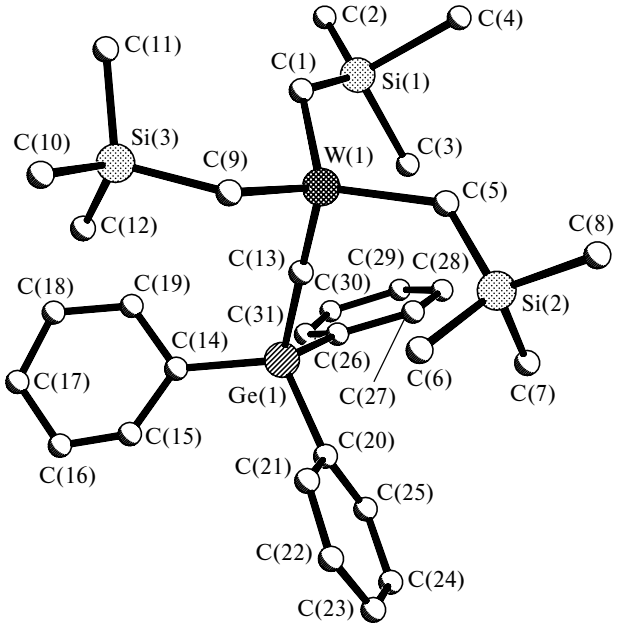

Fig. 2. Molecular structure of molecule **2**.

The $W{-}C_\alpha$ and $Ge{-}C_\alpha$ distances are 1.763(4) and 1.923(4) Å, respectively, in **1** and 1.749(2) and 1.921(2) Å in **2**. In the $Ph_3GeC{\equiv}W(OBu^t)_3$ complex,[8] the corresponding $W{-}C_\alpha$ distances are 1.758(7) and 1.757(6) Å and the $Ge{-}C_\alpha$ bond lengths are 1.898(7) and 1.927(6) Å. However, it is impossible to correctly compare the bond lengths in molecules **1**, **2**, and $Ph_3GeC{\equiv}W(OBu^t)_3$ due to large experimental errors in the determination of the distances in the tris(alkoxy)carbyne complex.

To summarize, alkyl-containing tungsten carbyne complexes with organogermanium substituents at the carbyne carbon atom were synthesized in high yields and structurally characterized. Studies of the catalytic properties of the compounds in metathesis of acetylenic hydrocarbons are presently underway.

Experimental

All operations were carried out in evacuated sealed ampoules with the use of the standard Schlenk technique. The solvents were thoroughly dried and degassed. The starting complex $Ph_3GeC{\equiv}W(OBu^t)_3$ (see Ref. 7) and alkyllithium derivatives were synthesized according to known procedures.[11] The ^1H and ^{13}C NMR spectra of all compounds were recorded on a Bruker DPX-200 spectrometer (200 MHz for ^1H and 50 MHz for ^{13}C). The chemical shifts are given on the δ scale relative to Me_4Si as the internal standard.

The X-ray diffraction data sets were collected on an automated Smart APEX diffractometer (graphite monochromator, Mo-Kα radiation, φ—ω scanning technique, λ = 0.71073 Å). All structures were solved by direct methods using the SHELXTL program package[12] and refined by the least-squares method against F^2_{hkl} with anisotropic displacement parameters for all nonhydrogen atoms. All hydrogen atoms were placed in geometrically calculated positions and refined using a riding model. Absorption corrections were applied using the SADABS program.[13] Selected bond lengths and bond angles are given in Table 1. Principal crystallographic data and details of X-ray diffraction study are listed in Table 2. In complexes **1** and **2**, all Ph and $SiMe_3$ groups are disordered over two positions. It should be noted that the triclinic unit cell of complex **2** can be transformed into the trigonal unit cell with the parameters $a = b =$ 10.3071(4) Å, c = 57.021(3) Å, α = β = 90°, γ = 120°, which are similar to the unit cell parameters of complex **1**. However, we failed to solve and refine the structure of **2** in the trigonal system. Apparently, disorder in the crystals of **2** reduces the symmetry system to triclinic.

Triphenylgermylmethylidyne-tris(neopentyl)tungsten (1). A solution of $LiCH_2Bu^t$ (0.29 g, 3.72 mmol) in diethyl ether (5 mL) was added to a colorless solution of $Ph_3GeC{\equiv}W(OBu^t)_3$ (0.88 g, 1.22 mmol) in diethyl ether (10 mL) at 0 °C. Slow heating of the reaction mixture to room temperature was accompanied by the appearance of a yellow-brown color of the solution. The diethyl ether was removed by evaporation *in vacuo*. The residue was extracted with pentane (2×10 mL). The pentane extracts were combined and the solvent was removed. The

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

Bond	d/Å	Angle	ω/deg	Angle	ω/deg
1		**1**		**2**	
W(1)—C(6)	1.763(4)	C(6)—W(1)—C(1A)	106.93(7)	C(13)—W(1)—C(5)	104.2(1)
W(1)—C(1A)	2.086(2)	C(6)—W(1)—C(1)	106.93(7)	C(13)—W(1)—C(1)	104.5(1)
W(1)—C(1)	2.086(2)	C(1A)—W(1)—C(1)	111.89(6)	C(5)—W(1)—C(1)	115.49(8)
W(1)—C(1B)	2.086(2)	C(6)—W(1)—C(1B)	106.93(7)	C(13)—W(1)—C(9)	104.1(1)
Ge(1)—C(6)	1.923(4)	C(1A)—W(1)—C(1B)	111.89(6)	C(5)—W(1)—C(9)	115.18(7)
Ge(1)—C(7)	1.948(3)	C(1)—W(1)—C(1B)	111.89(6)	C(1)—W(1)—C(9)	111.78(9)
Ge(1)—C(7A)	1.948(3)	C(6)—Ge(1)—C(7)	109.5(1)	C(14)—Ge(1)—C(20)	111.63(9)
Ge(1)—C(7B)	1.948(3)	C(6)—Ge(1)—C(7A)	109.5(1)	C(14)—Ge(1)—C(13)	110.7(1)
2		C(7)—Ge(1)—C(7A)	109.5(1)	C(20)—Ge(1)—C(13)	110.41(8)
W(1)—C(13)	1.749(2)	C(6)—Ge(1)—C(7B)	109.5(1)	C(14)—Ge(1)—C(26)	110.26(8)
W(1)—C(5)	2.082(2)	C(7)—Ge(1)—C(7B)	109.5(1)	C(13)—Ge(1)—C(26)	105.9(1)
W(1)—C(1)	2.087(2)	C(7A)—Ge(1)—C(7B)	109.5(1)	W(1)—C(13)—Ge(1)	179.1(2)
W(1)—C(9)	2.099(2)	W(1)—C(6)—Ge(1)	180.0		
Ge(1)—C(14)	1.948(1)				
Ge(1)—C(20)	1.947(1)				
Ge(1)—C(13)	1.921(2)				
Ge(1)—C(26)	1.957(1)				

Table 2. Crystallographic data and characteristics of the structure refinement for complexes **1** and **2**

Parameter	**1**	**2**
Molecular formula	$C_{34}H_{48}GeW$	$C_{31}H_{48}GeSi_3W$
Molecular weight	713.16	761.40
Crystal dimensions/mm	0.13×0.08×0.08	0.48×0.36×0.34
T/K	293(2)	100(2)
Space group	$R\bar{3}$	$P\bar{1}$
a/Å	10.1800(3)	10.2841(5)
b/Å	10.1800(3)	10.3301(5)
c/Å	56.871(2)	19.0070(9)
α/deg	90	79.358(1)
β/deg	90	82.230(1)
γ/deg	120	62.773(1)
V/Å^3	5104.0(3)	1761.6(2)
Z	6	2
d_{calc}/g cm^{-3}	1.392	1.435
μ/cm^{-1}	42.79	42.34
Absorption correction	SADABS	SADABS
T_{min}/T_{max}	0.6062/0.7259	0.2357/0.3270
F(000)	2148	764
$2\theta_{max}$/deg	58	58
Number of measured/independent reflections (R_{int})	18108/3020 (0.0202)	12802/8994 (0.0196)
R_1 (based on F for reflections with $I > 2\sigma(I)$)	0.0278	0.0345
wR_2 (based on F^2 for all reflections)	0.0703	0.0875
Number of parameters in refinement	146	520
GOOF	1.115	1.035
Residual electron density peaks (min/max), e Å^{-3}	−0.252/1.983	−1.320/2.772

$Ph_3GeC{\equiv}W(CH_2Bu^t)_3$ compound was obtained as bright-yellow crystals (0.83 g, 95%). Found (%): C, 57.19; H, 6.73. $C_{34}H_{48}GeW$. Calculated (%): C, 57.26; H, 6.78. ^{1}H NMR (toluene-d_8), δ: 1.03 (s, 27 H, CMe_3); 1.15 (s, 6 H, CH_2); 7.17—7.15 (m, 9 H, H(3), H(4)); 7.84—7.87 (m, 6 H, H(2)). ^{13}C NMR (toluene-d_8), δ: 33.8 (CH_3), 34.6 ($\underline{C}Me_3$), 105.8 ($\underline{C}H_2Bu^t$, $^1J_{C\text{-}^{183}W}$ = 92.4 Hz), 128.2 (CH(3)), 128.9 (CH(4)), 135.6 (CH(2)), 139.6 (C(1)), 321.7 (W≡C, $J_{C\text{-}^{183}W}$ = 210.1 Hz).

Triphenylgermylmethylidyne-tris(trimethylsilylmethyl)tungsten (2). The synthesis and isolation of the $Ph_3GeC{\equiv}W(CH_2SiMe_3)_3$ complex were performed as described above. The $Ph_3GeC{\equiv}W(CH_2SiMe_3)_3$ compound was prepared from $Ph_3GeC{\equiv}W(OBu^t)_3$ (1.01 g, 1.40 mmol) and $LiCH_2SiMe_3$ (0.40 g, 4.25 mmol) as bright-yellow crystals (0.96 g, 90%). Found (%): C, 48.83; H, 6.31. $C_{31}H_{48}GeSi_3W$. Calculated (%): C, 48.90; H, 6.35. ^{1}H NMR (C_6D_6), δ: 0.3 (s, 27 H, $SiMe_3$), 1.4 (s, 6 H, CH_2), 7.30—7.38 (m, 9 H, H(3), H(4)); 8.04—8.07 (m, 6 H, H(2)). ^{13}C NMR (C_6D_6), δ: 2.5 (CH_3), 78.1 ($\underline{C}H_2SiMe_3$, $^1J_{C\text{-}^{183}W}$ = 79.9 Hz), 128.4 (CH(3)), 129.2 (CH(4)), 135.7 (CH(2)), 140.3 (C(1)), 325.1 (W≡C, $^1J_{C\text{-}^{183}W}$ = 192.9 Hz).

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