

Reactions of silicon-, germanium- and tin-containing carbene complexes of tungsten $\text{Ph}_3\text{E}-\text{C}\equiv\text{W}(\text{OBu}^t)_3$ (E = Si, Ge, Sn) with hydrogen chloride: crystal structures of carbene complexes $\text{Ph}_3\text{E}-\text{CH}=\text{WCl}_2(\text{OBu}^t)_2$ (E = Si, Ge)

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Abstract

The novel organosilicon, -germanium and -tin-containing carbene complexes of tungsten of the type $\text{Ph}_3\text{E}-\text{CH}=\text{WCl}_2(\text{OBu}^t)_2$ (E = Si, Ge, Sn) have been prepared by the reaction of heteroelement-containing carbene complexes of tungsten $\text{Ph}_3\text{E}-\text{C}\equiv\text{W}(\text{OBu}^t)_3$ (E = Si, Ge, Sn) with hydrogen chloride. The tin-containing carbene complex was identified in solution by ^1H NMR spectroscopy. Silicon- and germanium-containing carbene complexes were isolated in high yields as crystalline solids and characterized by elemental analysis, IR, ^1H NMR, ^{13}C NMR and ^{29}Si NMR spectroscopy and X-ray diffraction studies. The geometry of the W atoms in the compounds can be described as a distorted square pyramid.

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Keywords: Carbene complexes; Tungsten; Silicon; Germanium; Tin; X-ray diffraction; Synthesis

1. Introduction

Alkylidene complexes of tungsten are known to be effective catalysts for the olefin metathesis reaction [1]. In the majority of such tungsten compounds, the carbene fragments contain alkyl groups; whereas there are only a very few similar complexes with group 14 element-containing organic substituents bonded to the carbene carbon atom [2]. To the best of our knowledge, systematic investigations aimed at finding effect of composition and structure of the carbene fragments upon the catalytic activity of these complexes in olefin metathesis reactions have not been carried out.

Herein, we describe the synthesis and structural characterization of tungsten carbene complexes con-

taining organosilicon, -germanium and -tin groups bound to the carbene carbon atom.

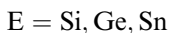
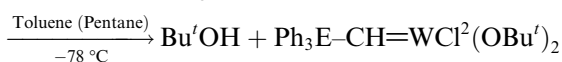
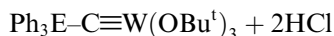
2. Results and discussion

One of the known synthetic routes to carbene complexes is the protonation of the metal-carbon triple bond in carbene compounds of the type $\text{R}-\text{C}\equiv\text{W}(\text{OBu}^t)_3$ (R = Bu^t, CH₂Bu^t) by hydrogen chloride [3]. Therefore, we used this reaction for the preparation of organosilicon, -germanium and -tin-containing carbene complexes of tungsten from carbene complexes of the type $\text{Ph}_3\text{E}-\text{C}\equiv\text{W}(\text{OBu}^t)_3$ (E = Si, Ge, Sn) synthesized by us recently [4].

We found that the reaction of $\text{Ph}_3\text{E}-\text{C}\equiv\text{W}(\text{OBu}^t)_3$ with two equivalents of HCl lead to the formation of one equivalent of $\text{Ph}_3\text{E}-\text{CH}=\text{WCl}_2(\text{OBu}^t)_2$ and one equivalent of Bu^tOH. So the reaction may be presented by the following equation:

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The tin-containing carbene complex $\text{Ph}_3\text{Sn}-\text{CH}=\text{WCl}_2(\text{OBu}^t)_2$ was identified in solution by ^1H NMR. The compound appeared to be thermally unstable and decomposed at room temperature over the period of 3 h. The silicon- and germanium-containing carbene complexes were isolated as air-sensitive pale-yellow crystalline solids. They were fully characterized by elemental analysis, IR, ^1H NMR, ^{13}C NMR, ^{29}Si NMR spectroscopy and X-ray diffraction studies.

3. Crystal structures of $\text{Ph}_3\text{E}-\text{CH}=\text{WCl}_2(\text{OBu}^t)_2$ (E = Si, Ge)

X-ray diffraction studies show that the complexes $\text{Ph}_3\text{E}-\text{CH}=\text{WCl}_2(\text{OBu}^t)_2$ (E = Si (**1**), Ge (**2**)) contain planar $\text{E}(1)\text{C}(9)\text{W}(1)\text{O}(1)\text{O}(2)$ fragments (Fig. 1). The deviations from planarity for the $\text{E}(1)\text{C}(9)\text{W}(1)\text{O}(1)\text{O}(2)$ fragments are 0.018 Å for **1** and 0.007 Å for **2**. The geometry of the E(1) atom in both **1** and **2** is a distorted tetrahedron. The C–E(1)–C angles vary in the range of 106.1(2)–112.0(2)° for **1** and 106.1(1)–112.9(1)° for **2**.

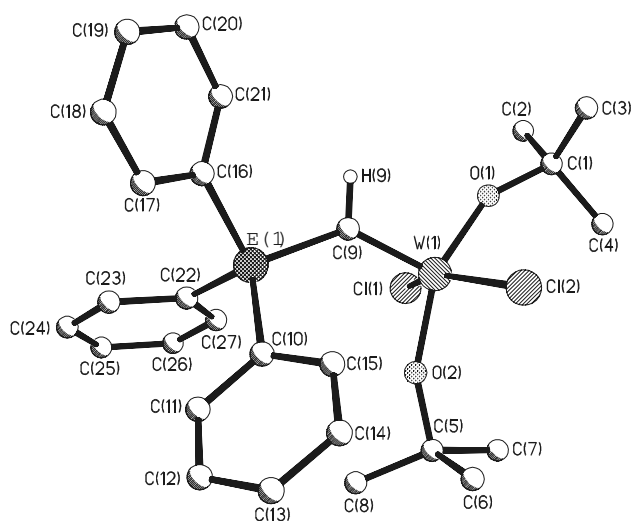


Fig. 1. The molecular structure of the complex **1** (E(1) = Si) and **2** (E(1) = Ge). The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): **1**: W(1)–O(1) 1.830(3), W(1)–O(2) 1.820(3), W(1)–Cl(1) 2.374(1), W(1)–Cl(2) 2.373(1), W(1)–C(9) 1.868(5), Si(1)–C(9) 1.861(5); O(1)W(1)Cl(1) 86.8(1), Cl(1)W(1)O(2) 87.7(1), O(2)W(1)Cl(2) 87.2(1), O(1)W(1)Cl(2) 86.5(1), O(1)W(1)C(9) 103.1(2), O(2)W(1)C(9) 102.3(2), Cl(1)W(1)C(9) 103.7(1), Cl(2)W(1)C(9) 103.6(1). **2**: W(1)–O(1) 1.807(1), W(1)–O(2) 1.809(1), W(1)–Cl(1) 2.385(1), W(1)–Cl(2) 2.378(1), W(1)–C(9) 1.870(2), Ge(1)–C(9) 1.949(2); O(1)W(1)Cl(1) 87.0(1), Cl(1)W(1)O(2) 87.0(1), O(2)W(1)Cl(2) 86.7(1), O(1)W(1)Cl(2) 87.5(1), O(1)W(1)C(9) 102.4(1), O(2)W(1)C(9) 102.4(1), Cl(1)W(1)C(9) 103.4(1), Cl(2)W(1)C(9) 104.5(1).

The geometry of the W(1) atoms in **1** and **2** can be described as a distorted square pyramid. The deviations of the W(1) atoms from the plane of the O(1)O(2)–Cl(1)Cl(2) fragment are 0.48 Å for **1** and **2**. The C(9)–W(1)–Cl and C(9)–W(1)–O angles vary in the range of 102.3(2)–103.7(1)° for **1** and 102.4(1)–104.5(1)° for **2**. The E(1)–C(9)–W(1) angles in **1** and **2** are similar (136.1(3)° for **1** and 135.6(1)° for **2**). Note that bond angles E(1)–C(9)–H(9) for **1** and **2** (112.6(3.8)° and 113.6(1.4)°, respectively) and bond angles W(1)–C(9)–H(9) for **1** and **2** (110.7(3.8)° and 110.8(1.4)°, respectively) are practically equal.

The Si(1)–C(Ph) distances in **1** are 1.854(4)–1.869(5) Å, which are shorter than Ge(1)–C(Ph) distances in **2** (1.943(2)–1.956(2) Å). The difference between the E(1)–C(Ph) distances in **1** and **2** is somewhat bigger than the difference of the covalent radii of Si and Ge atoms (~0.06 Å [5]). The same tendency is observed for the Si(1)–C(9) (1.861(5) Å) and the Ge(1)–C(9) (1.949(2) Å) distances. The W(1)–Cl and W(1)–O distances vary in the narrow range of 2.373(1)–2.385(1) and 1.807(1)–1.830(3) Å, respectively. The W(1)–C(9) distances also are close to each other (1.868(5) Å for **1** and 1.870(2) Å for **2**). In the previously studied organosilicon-containing tungsten carbenes [6], the $\text{W}=\text{C}(\text{H})\text{SiMe}_3$ fragments have the important structural parameters (W=C: 1.876 and 1.872 Å; Si–C: 1.852 and 1.832 Å; WCSi: 136.4 and 138.5°) similar to those of complexes **1** and **2**. Note that the W(IV) complex [7] (but not W(VI) as in our case) containing the analogous $\text{W}=\text{C}(\text{H})\text{CMe}_3$ fragment has the neopentylidene ligand in a highly distorted geometry where the W=C(H)–C angle is 168.7(3)° and the W=C–H angle is 72.2(20)°.

4. Conclusion

The novel organosilicon, -germanium and -tin-containing carbene complexes of tungsten of the type $\text{Ph}_3\text{E}-\text{CH}=\text{WCl}_2(\text{OBu}^t)_2$ (E = Si, Ge, Sn) have been prepared by the reaction of heteroelement-containing carbene complexes of tungsten with hydrogen chloride. The tin-containing complex was identified in solution by ^1H NMR spectroscopy. The silicon- and germanium-containing complexes were characterized by elemental analysis, IR, ^1H NMR, ^{13}C NMR and ^{29}Si NMR spectroscopy and X-ray diffraction studies.

5. Experimental

5.1. General

All manipulations were carried out in evacuated sealed ampoules using standard Schlenk techniques. The solvents were thoroughly dried and degassed.

Table 1

Crystal data and structure refinement details for **1** and **2**

	Ph ₃ Si–CH=WCl ₂ (OBu ^t) ₂ (1)	Ph ₃ Ge–CH=WCl ₂ (OBu ^t) ₂ (2)
Empirical formula	C ₂₇ H ₃₄ Cl ₂ O ₂ SiW	C ₂₇ H ₃₄ Cl ₂ O ₂ GeW
Formula weight	673.38	717.88
Temperature (K)	110(2)	183(2)
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	P2 ₁ /c
Unit cell dimensions	<i>a</i> = 34.791(12), <i>b</i> = 8.881(3), <i>c</i> = 19.671(7) Å; β = 110.100(7)°	<i>a</i> = 16.9320(13), <i>b</i> = 10.2807(8), <i>c</i> = 18.4200(13) Å; β = 115.424(1)°
Volume (Å ³)	5708(3)	2895.9(4)
Z	8	4
Density (calculated) (g/cm ³)	1.567	1.647
Absorption coefficient (mm ⁻¹)	4.297	5.212
<i>F</i> (000)	2672	1408
Crystal size (mm ³)	0.1 × 0.2 × 0.8	0.45 × 0.35 × 0.25
θ range for data collection (°)	2.13 to 30.10	2.23 to 29.01
Index ranges	−48 ≤ <i>h</i> ≤ 48, −12 ≤ <i>k</i> ≤ 12, −27 ≤ <i>l</i> ≤ 27	−23 ≤ <i>h</i> ≤ 15, −13 ≤ <i>k</i> ≤ 13, −24 ≤ <i>l</i> ≤ 24
Reflections collected	33,327	20,818
Independent reflections	8355 [<i>R</i> _{int} = 0.0591]	7579 [<i>R</i> _{int} = 0.0286]
Completeness to θ = 25.00° (%)	99.3	98.4
Absorption correction	SADABS	SADABS
Maximum/minimum transmission	0.3577/0.0675	0.3557/0.2026
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	8355/0/302	7579/16/417
Goodness-of-fit on <i>F</i> ²	0.968	1.038
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0430, <i>wR</i> ₂ = 0.1040	<i>R</i> ₁ = 0.0238, <i>wR</i> ₂ = 0.0547
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0697, <i>wR</i> ₂ = 0.1178	<i>R</i> ₁ = 0.0300, <i>wR</i> ₂ = 0.0568
Largest difference peak and hole (eÅ ⁻³)	3.787 and −1.597	0.948 and −1.506

Complexes Ph₃SiC≡W(OBu^t)₃, Ph₃GeC≡W(OBu^t)₃, Ph₃SnC≡W(OBu^t)₃ were prepared according to [4]. Infrared spectra were recorded with a “Perkin–Elmer-577” spectrometer. The samples were prepared under argon as Nujol mulls. ¹H NMR, ¹³C NMR and ²⁹Si NMR spectra were obtained with a “Bruker DPX-200” spectrometer. The chemical shifts are reported in parts per million with tetramethylsilane (0.00 ppm) as the internal standard. GLC analysis was carried out using a Tsvet-500 gas chromatograph with a 0.3 × 200 cm stainless-steel column filled with SE-30 (5%) on Inerton AW (with katharometer as a detector and helium as the carrier gas).

5.2. Preparation of Ph₃Si–CH=WCl₂(OBu^t)₂ (**1**)

Two equivalents of gaseous HCl (33.2 mL, 1.48 mmol) were condensed into a solution of Ph₃SiC≡W(OBu^t)₃ (0.50 g, 0.74 mmol) in pentane or toluene (5 mL) at −78 °C. The solution turned orange-red immediately. Upon warming to room temperature the solution became yellow-green. The solvent and volatile products were removed in vacuo. Bu^tOH (45.5 mg, 0.61 mmol, 83%) was found in the volatile products by GLC analysis. The solid product was recrystallized from pentane to give pale-yellow crystals of Ph₃Si–CH=WCl₂(OBu^t)₂ (0.44 g, 0.65 mmol, 88%). Complex **1** decomposed at 97–100 °C without melting. Anal. Calc. for C₂₇H₃₄O₂Cl₂SiW: C, 48.16; H, 5.09. Found: C, 48.38; H, 5.10%. IR (KBr,

cm⁻¹): 1410, 1090, 730, 690, 490 (Ph₃Si), 1140, 930 (W–O–C), 1345, 1230 (Bu^t), 1005 (HC≡). ¹H NMR (200 MHz, toluene-d⁸) δ 11.83 (s, 1H, HC≡, ¹*J*_{HαC} = 130.5, ²*J*_{HαW} = 10.8), 7.66–7.71 (m, 6H, *H*(2)), 7.14–7.17 (m, 9H, *H*(3,4)), 1.45 (s, 9H, CH₃), 1.07 (s, 9H, CH₃). ¹³C NMR (50 MHz, toluene-d⁸) δ 264.19 (W=C, ¹*J*_{C-183W} = 143.3), 137.44 (C(1)), 136.84 (CH(2)), 130.10 (CH(4)), 128.22 (CH(3)), 92.25 (WOCMe₃), 91.20 (WOCMe₃), 29.66 (CH₃), 29.28 (CH₃). ²⁹Si NMR (39.7 MHz, toluene-d⁸) δ −14.5 (Ph₃Si, ²*J*_{29Si-183W} = 13.1).

5.3. Preparation of Ph₃Ge–CH=WCl₂(OBu^t)₂ (**2**)

The procedure was essentially the same as described above. From Ph₃Ge–C≡W(OBu^t)₃ (0.88 g, 1.22 mmol) and HCl gas (54.8 mL, 2.44 mmol) Ph₃Ge–CH=WCl₂(OBu^t)₂ was obtained as pale-yellow crystals (0.82 g, 1.14 mmol, 93%). Bu^tOH (76.97 mg, 1.04 mmol, 85%) was found in the volatile products by GLC analysis. Complex **2** decomposed at 107–110 °C without melting. Anal. Calc. for C₂₇H₃₄O₂Cl₂GeW: C, 45.17; H, 4.77. Found: C, 45.58; H, 4.69. IR (KBr, cm⁻¹): 3030, 1460, 1080, 735, 690, 460 (Ph₃Ge), 1150, 930 (W–O–C), 1350, 1230 (Bu^t), 1000 (HC≡). ¹H NMR (200 MHz, toluene-d⁸) δ 11.89 (s, 1H, HC≡, ¹*J*_{HαC} = 137.8, ²*J*_{HαW} = 7.2), 7.60–7.64 (m, 6H, *H*(2)), 7.14–7.19 (m, 9H, *H*(3,4)), 1.46 (s, 9H, CH₃), 1.06 (s, 9H, CH₃). ¹³C NMR (50 MHz, toluene-d⁸) δ 266.87 (W=C, ¹*J*_{C-183W} = 152.9), 137.94 (C(1)), 135.73 (CH(2)), 129.61 (CH(4)), 128.59 (CH(3)),

91.75 (WOCMe₃, ²J_{C-183W} = 8.7), 91.05 (WOCMe₃, ²J_{C-183W} = 8.8), 29.66 (CH₃), 29.26 (CH₃).

5.4. Reaction of Ph₃Sn–C≡W(OBu^t)₃ with HCl

Gaseous HCl (5.80 mL, 0.26 mmol) was condensed to a solution of Ph₃Sn–C≡W(OBu^t)₃ (0.10 g, 0.13 mmol) in toluene-d⁸ (1 mL) at –78 °C in NMR tube. ¹H NMR (200 MHz, toluene-d⁸) δ 12.04 (s, 1H, HC=, ¹J_{HxC} = 142.0, ²J_{HxW} = 13.8).

5.5. Single crystal X-ray diffraction study of **1** and **2**

Single crystals of **1** and **2** for X-ray structure analysis were obtained from pentane. The data were collected on a SMART APEX diffractometer (graphite-monochromated, Mo K_α-radiation, φ–ω-scan technique, λ = 0.71073 Å). The intensity data were integrated by SAINT program [8]. The structures were solved by direct methods and were refined on F² using all reflections with SHELXL-97 [9]. All non-hydrogen atoms were refined anisotropically. The part of hydrogen atoms were placed in calculated positions and refined in the “riding-model” and part of them were found from Fourier synthesis and refined isotropically. SADABS [10] was used to perform area-detector scaling and absorption corrections. The details of crystallographic, collection and refinement data are shown in Table 1.

6. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 214431 and 214432 for complexes **1** and **2**, respectively. Copies of these data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge

CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk).

Acknowledgements

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