Synthesis and structures of silicon-, germanium- and tin-containing tungsten imido alkyl complexes $(ArN)_2W(CH_2EMe_3)_2$ (E = Si, Ge, Sn)

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Abstract

The novel silicon-, germanium- and tin-containing imido alkyl complexes of tungsten of the type $(ArN)_2W(CH_2EMe_3)_2$ (Ar = 2,6-$Pr^i_2C_6H_3$; E = Si (**1**), Ge (**2**), Sn (**3**)) have been prepared by the reactions of $(ArN)_2WCl_2(dme)$ (dme = 1,2-dimethoxyethane) with heteroelement-containing alkyllithium or Grignard reagents Me_3ECH_2Li (E = Si, Ge), Me_3ECH_2MgCl (E = Ge, Sn). The title compounds were isolated in high yields as crystalline solids and characterized by elemental analysis, IR, ^1H, ^{13}C, ^{29}Si and ^{119}Sn NMR spectroscopy and X-ray diffraction studies. The geometry of the W atoms in the compounds can be described as a distorted tetrahedron.
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Keywords: Imido alkyl complexes; Tungsten; Silicon; Germanium; Tin; X-ray diffraction; Synthesis
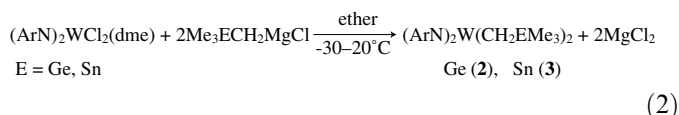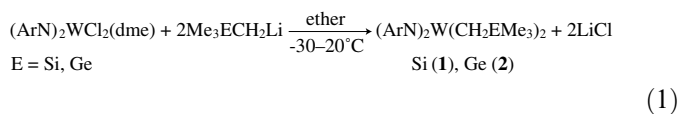
1. Introduction

Imido alkyl complexes of tungsten of the type $(ArN)_2W(CH_2R)_2$ (R = Bu^t, CMe_2Ph) [1] are known to be applicable as starting materials for the preparation of tungsten alkylidene complexes – efficient catalysts for olefin metathesis reactions [2]. Similar tungsten compounds with heteroelement-containing alkyl groups and their transformations into alkylidene complexes are rare [3].

Herein, we report the synthesis and structural characterization of tungsten imido alkyl complexes containing trimethylsilylmethyl, trimethylgermylmethyl and trimethylstannylmethyl substituents.

2. Results and discussion

The title compounds **1**–**3** were synthesized by the reactions of $(ArN)_2WCl_2(dme)$ with heteroelement-containing alkyllithium or Grignard reagents Me_3ECH_2Li (E = Si, Ge), Me_3ECH_2MgCl (E = Ge, Sn):

$$(ArN)_2WCl_2(dme) + 2Me_3ECH_2Li \xrightarrow[-30–20\,°C]{ether} (ArN)_2W(CH_2EMe_3)_2 + 2LiCl$$
$$E = Si, Ge \qquad\qquad\qquad Si\,(\mathbf{1}),\,Ge\,(\mathbf{2})$$

$$\tag{1}$$

$$(ArN)_2WCl_2(dme) + 2Me_3ECH_2MgCl \xrightarrow[-30–20\,°C]{ether} (ArN)_2W(CH_2EMe_3)_2 + 2MgCl_2$$
$$E = Ge, Sn \qquad\qquad\qquad Ge\,(\mathbf{2}),\quad Sn\,(\mathbf{3})$$

$$\tag{2}$$

Complexes **1**–**3** were isolated in 71–76% yields as air unstable orange crystalline solids well soluble in common organic solvents. They were characterized by elemental analysis, IR, ^1H, ^{13}C, ^{29}Si and ^{119}Sn NMR spectroscopy and X-ray diffraction studies.

3. Crystal structures of compounds 1–3

According X-ray data, the complexes **1**–**3** are isostructural (Fig. 1). The W and E (E = Si, Ge, Sn) atoms in

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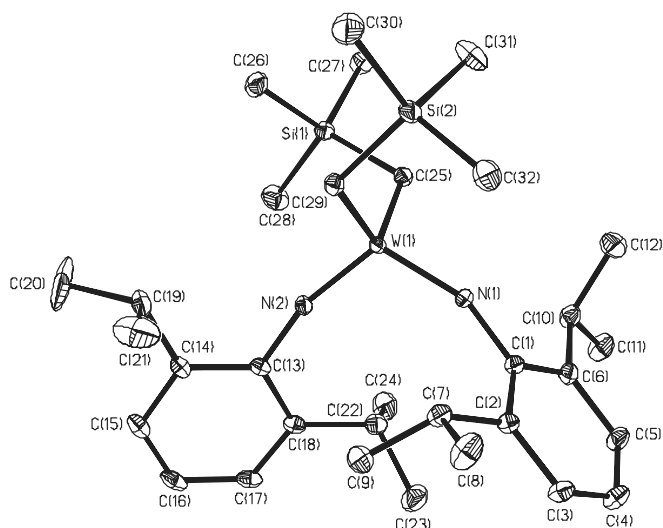
Fig. 1. Molecular structure of the complex **1** (Si). The structures of **2** (Ge) and **3** (Sn) are similar.

Table 1
Selected distances (Å) and angles (°) for **1–3**

	1 (E = Si)	**2** (E = Ge)	**3** (E = Sn)
Distance			
W(1)–N(1)	1.761(2)	1.751(2)	1.762(2)
W(1)–N(2)	1.751(2)	1.765(2)	1.755(2)
W(1)–C(25)	2.110(2)	2.104(3)	2.091(3)
W(1)–C(29)	2.114(2)	2.104(3)	2.084(3)
E(1)–C(25)	1.868(2)	1.965(2)	2.091(3)
E(2)–C(29)	1.878(2)	1.959(3)	2.166(3)
N(1)–C(1)	1.395(3)	1.391(3)	1.395(3)
N(2)–C(13)	1.400(2)	1.389(3)	1.395(3)
Angle			
N(2)W(1)N(1)	112.55(8)	112.9(1)	113.0(1)
N(2)W(1)C(25)	104.74(8)	107.1(1)	105.3(1)
N(1)W(1)C(25)	107.61(8)	107.1(1)	108.0(1)
N(2)W(1)C(29)	107.44(8)	107.9(1)	107.4(1)
N(1)W(1)C(29)	108.22(8)	105.2(1)	107.1(1)
C(25)W(1)C(29)	116.38(8)	116.9(1)	116.2(1)
C(28)E(1)C(27)	109.8(1)	110.6(2)	109.2(2)
C(28)E(1)C(25)	109.9(1)	108.7(1)	107.2(1)
C(27)E(1)C(25)	108.4(1)	107.8(1)	107.3(1)
C(28)E(1)C(26)	108.1(1)	109.5(2)	109.6(2)
C(27)E(1)C(26)	109.1(1)	108.8(2)	111.6(2)
C(25)E(1)C(26)	111.6(1)	111.4(2)	111.8(1)
C(1)N(1)W(1)	157.2(1)	165.1(2)	158.6(2)
C(32)E(2)C(31)	108.9(2)	108.2(2)	112.0(2)
C(32)E(2)C(30)	109.6(2)	109.6(2)	111.1(2)
C(31)E(2)C(30)	108.5(2)	110.3(1)	108.8(2)
C(32)E(2)C(29)	110.0(1)	109.0(1)	106.8(1)
C(31)E(2)C(29)	110.7(1)	111.6(1)	111.4(2)
C(30)E(2)C(29)	109.1(1)	108.0(1)	106.6(1)
C(13)N(2)W(1)	164.8(2)	158.2(2)	165.6(2)

1–3 have a distorted tetrahedral coordination. The W–C distances in **1–3** are similar and fall over a narrow range between 2.084(3) and 2.114(2) Å. However, the values indicate a shortening of the W–C distances in the series of –SiMe$_3$, –GeMe$_3$ and –SnMe$_3$ derivatives. A similar trend of decreasing Mo–C distances was recently found for the molybdenum imido alkyl compounds (ArN)$_2$-Mo(CH$_2$EMe$_3$)$_2$ (E = Si, Ge, Sn) [4]. The E–C (methylene group) distances are 1.868(2)/1.878(2) Å for **1**, 1.965(2)/1.959(3) Å for **2** and 2.162(3)/2.166(3) Å for **3**. The differences between the average E–C (methylene group) distances are slightly bigger than the differences between the covalent radii of Si (1.13 Å [5]), Ge (1.19 Å [5]) and Sn (1.36 Å [5]) atoms. The same situation was observed in the similar Mo complexes [4]. The W=N distances in **1–3** are in the range of 1.751(2)–1.762(2) Å. The differences between the average W=N distances in **1–3** and the average distances Mo=N in Mo compexes [4] are close to the differences between ionic radii of W and Mo atoms (W^{6+} = 0.56 Å and Mo^{6+} = 0.55 Å for coordination number 4 [6]). The WNC and WCE angles in **1–3** (157.2(1)°–165.6(2)° and 113.6(1)°–117.5(1)°, respectively) (see Table 1) are close to the analogous angles in the corresponding Mo complexes [4].

4. Conclusion

The novel organosilicon-, germanium- and tin-containing imido alkyl complexes of tungsten (ArN)$_2$W(CH$_2$EMe$_3$)$_2$ (E = Si (**1**), Ge (**2**), Sn (**3**)) have been prepared in high yields by the reactions of (ArN)$_2$WCl$_2$(dme) with alkyllithium or Grignard reagents Me$_3$ECH$_2$Li (E = Si, Ge), Me$_3$E-CH$_2$MgCl (E =' Ge, Sn). All the compounds were characterized by elemental analysis, IR, ^{1}H, ^{13}C, ^{29}Si and ^{119}Sn NMR spectroscopy and X-ray diffraction studies. A trend of decreasing W–C distances was found on going from silicon- to germanium- and to tin-containing derivatives. The

reactions of compounds **1–3** with triflic acid and hydrogen chloride as a possible route to heteroelement-containing tungsten carbene complexes are now under detailed investigation.

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. Compounds (ArN)$_2$WCl$_2$(dme) [1], Me$_3$ECH$_2$Li (E = Si, Ge) [7], Me$_3$ECH$_2$MgCl (E = Ge, Sn) [8] were prepared according to the literature procedure. Infrared spectra were recorded with a "Perkin–Elmer-577" spectrometer. The samples were prepared under argon as Nujol mulls. 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 for ^{1}H, ^{13}C and ^{29}Si NMR, and tetramethylstannane (0.00 ppm) for ^{119}Sn NMR spectra.

5.2. Preparation of (ArN)$_2$W(CH$_2$SiMe$_3$)$_2$ (**1**)

To a solution of (ArN)$_2$WCl$_2$(dme) (1.5 g, 2.16 mmol) in 15 mL of ether at −30 °C 0.41 g (0.4.31 mmol) of Me$_3$Si-

CH_2Li in 5 mL of ether was added. The reaction mixture was stirred and allowed to warm slowly to room temperature. A white precipitate was formed and the solution became dark yellow-orange. The reaction solution was separated from the precipitate of LiCl by centrifugation. Slow evaporation of the solvent from the reaction solution at room temperature afforded 1.11 g (73.0%) of **1** as orange crystals. Anal. Found: C, 54.03; H, 7.93. Calc. for $C_{32}H_{56}N_2Si_2W$: C, 54.21; H, 7.97%. IR (KBr, cm^{-1}): 3050, 1430, 750 (2,6-$Pr^i_2C_6H_3$), 1245, 840, 680 (CH_2SiMe_3). ^1H NMR (200 MHz, toluene-d^8) δ 7.05–6.83 (m, 6, H_m and H_p), 3.63 (sept, 4 H, $CHMe_2$), 1.23 (s, 4 H, CH_2SiMe_3, $^2J_{HW} = 9.3\,Hz$), 1.13 (d, 24 H, $CHMe_2$), 0.22 (s, 18, CH_2SiMe_3). ^{13}C NMR (50 MHz, toluene-d^8) δ 151.88 (C_{ipso}, $^2J_{CW} = 32.1\,Hz$), 142.78 (C_o), 125.51 (C_p), 122.50 (C_m), 59.30 (CH_2SiMe_3, $J_{CW} = 95.3\,Hz$), 28.54 ($CHMe_2$), 23.60 ($CHMe_2$), 1.35 (CH_2SiMe_3). ^{29}Si NMR (39.7 MHz, toluene-d^8) δ 1.0 (CH_2SiMe_3).

5.3. Preparation of $(ArN)_2W(CH_2GeMe_3)_2$ (2)

(a) The procedure was essentially the same as described above. From $(ArN)_2WCl_2(dme)$ (1.5 g, 2.16 mmol) and Me_3GeCH_2Li (0.6 g, 4.33 mmol) complex **2** was obtained as orange crystals (1.17 g, 68%). Anal. Found: C, 48.21; H, 7.06. Calc. for $C_{32}H_{56}N_2Ge_2W$: C, 48.17; H, 7.07%. IR (KBr, cm^{-1}): 3050, 1430, 750 (2,6-$Pr^i_2C_6H_3$), 1230, 590, 570 (CH_2GeMe_3). ^1H NMR (200 MHz, toluene-d^8) δ 7.03–6.85 (m, 6, H_m

and H_p), 3.65 (sept, 4 H, $CHMe_2$), 1.58 (s, 4 H, CH_2GeMe_3, $^2J_{HW} = 8.3\,Hz$), 1.14 (d, 24 H, $CHMe_2$), 0.35 (s, 18, CH_2GeMe_3). ^{13}C NMR, DEPT (50 MHz, toluene-d^8) δ 152.09 (C_{ipso}, $^2J_{CW} = 32.1\,Hz$), 142.63 (C_o), 125.33 (C_p), 122.47 (C_m), 61.31 (CH_2GeMe_3, $J_{CW} = 103.5\,Hz$), 28.53 ($CHMe_2$), 23.59 ($CHMe_2$), 1.52 (CH_2GeMe_3).

(b) To a solution of $(ArN)_2WCl_2(dme)$ (1.8 g, 2.59 mmol) in 15 mL of ether at $-30\,°C$ an ether solution of trimethylgermylmethylmagnesium chloride (0.39 M, 13.3 mL, 5.17 mmol) was added. The reaction mixture was stirred magnetically and allowed to warm slowly to room temperature. A white precipitate was formed and the solution became dark yellow-orange. The reaction solution was separated from precipitate of $MgCl_2$ by centrifugation. Slow evaporation of the solvent from the reaction solution at room temperature afforded 1.45 g (71.0%) of **2** as orange crystals.

5.4. Preparation of $(ArN)_2W(CH_2SnMe_3)_2$ (3)

To a solution of $(ArN)_2WCl_2(dme)$ (1.5 g, 2.16 mmol) in 15 mL of ether at $-30\,°C$ an ether solution of trimethylstannylmethylmagnesium chloride (0.43 M, 10 mL, 4.30 mmol) was added. The reaction mixture was stirred and allowed to warm slowly to room temperature. A white precipitate was formed and solution became dark yellow-orange. The reaction solution was separated from precipitate of $MgCl_2$ by

Table 2
The details of crystallographic, collection and refinement data for **1–3**

	1	2	3
Empirical formula	$C_{32}H_{56}N_2Si_2W$	$C_{32}H_{56}Ge_2N_2W$	$C_{32}H_{56}N_2Sn_2W$
Formula weight	708.82	797.82	890.02
Temperature (K)	100(2)	100(2)	100(2)
Crystal size (mm)	$0.30 \times 0.20 \times 0.10$	$0.20 \times 0.10 \times 0.05$	$0.10 \times 0.08 \times 0.02$
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
a (Å)	11.0719(6)	11.1080(7)	11.3302(8)
b (Å)	16.2061(9)	16.307(1)	16.302(1)
c (Å)	20.147(1)	20.026(1)	20.109(1)
β (°)	103.582(1)	103.266(1)	103.313(1)
Volume ($Å^3$)	3513.8(3)	3530.7(4)	3614.4(4)
Z	4	4	4
D_{calc} (g/cm^3)	1.340	1.501	1.636
Absorption coefficient (mm^{-1})	3.377	4.962	4.566
$F(000)$	1456	1600	1744
θ Range for data collection (°)	1.63–29.02	1.63–29.03	1.63–29.02
Index ranges	$-15 \leqslant h \leqslant 15$, $-21 \leqslant k \leqslant 20$, $-17 \leqslant l \leqslant 27$	$-15 \leqslant h \leqslant 14$, $-22 \leqslant k \leqslant 22$, $-27 \leqslant l \leqslant 27$	$-8 \leqslant h \leqslant 15$, $-20 \leqslant k \leqslant 22$, $-27 \leqslant l \leqslant 26$
Reflections collected	25220	36687	25999
Independent reflections [R_{int}]	9201 [0.0208]	9348 [0.0232]	9469 [0.0241]
Absorption correction	SADABS		
Max/min transmission	0.7288/0.4307	0.7895/0.4369	0.9142 and 0.6581
Refinement method	Full-matrix least-squares on F^2		
Data/restraints/parameters	9201/2/553	9348/0/546	9469/0/496
Goodness-of-fit on F^2	1.052	1.071	1.068
Final R indices [$I > 2sigma(I)$]	$R = 0.0252$, $R_w = 0.0602$	$R = 0.0251$, $R_w = 0.0622$	$R = 0.0298$, $R_w = 0.0680$
R indices (all data)	$R = 0.0293$, $R_w = 0.0622$	$R = 0.0284$, $R_w = 0.0637$	$R = 0.0338$, $R_w = 0.0696$
Largest difference peak and hole (e $Å^3$)	2.750/−1.242	2.266/−1.459	2.733/−1.531

centrifugation. Slow evaporation of the solvent from the reaction solution at room temperature afforded 1.46 g (76.1%) of **3** as orange crystals. Anal. Found: C, 43.09; H, 6.24. Calc. for $C_{32}H_{56}N_2Sn_2W$: C, 43.17; H, 6.35%. IR (KBr, cm^{-1}): 3050, 1430, 750 ($2,6-Pr_2^iC_6H_3$), 1180, 525, 510 (CH_2SnMe_3). ^1H NMR (200 MHz, toluene-d^8) δ 7.20–6.81 (m, 6, H_m and H_p), 3.65 (sept, 4 H, CHMe$_2$), 2.07 (s, 4 H, CH_2SnMe$_3$, $^2J_{HW} = 6.8$ Hz, $^2J_{H^{117/119}Sn} = 60.5/63.0$ Hz), 1.16 (d, 24 H, CHMe_2), 0.26 (s, 18, CH$_2$SnMe_3, $^2J_{H^{117/119}Sn} = 51.2/53.5$ Hz). ^{13}C NMR (50 MHz, toluene-d^8) δ 152.35 (C_{ipso}, $^2J_{CW} = 32.5$ Hz), 142.44 (C_o), 125.03 (C_p), 122.32 (C_m), 57.47 (CH_2SnMe_3, $J_{CW} = 110.0$ Hz, $J_{C^{117/119}Sn} = 146.7/153.6$ Hz), 28.55 (CHMe$_2$), 23.57 (CHMe_2), −6.78 (CH$_2$SnMe_3, $J_{C^{117/119}Sn} = 318.3/333.6$ Hz). ^{119}Sn NMR (74.6 MHz, toluene-d^8) δ 10.3 (CH$_2$$SnMe_3$, $^2J_{^{119}Sn^{183}W} = 10.3$ Hz)

5.5. Single crystal X-ray diffraction study of 1–3

Single crystals of **1–3** for X-ray structure analysis were obtained by crystallization from ether. The data were collected on a SMART APEX diffractometer (graphite-monochromator, Mo Kα-radiation, $\lambda = 0.71073$ Å). The intensity data were integrated with the SAINT program [9]. The structures were solved by direct methods and were refined on F^2 using all reflections with SHELXTL [10]. 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 [11] was used to perform area-detector scaling and absorption corrections. The details of crystallographic, collection and refinement data are shown in the Table 2.

6. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 263011, 263012 and 263013 for complexes **1–3**, respectively. Copies of this 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).

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