Synthesis and crystal structures of the first germanium-containing alkylidene complexes of molybdenum R₃Ge–CH=Mo(NAr)(OR′)₂ (R = Me, Ph) with direct germanium–carbene carbon bond

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Abstract

The novel germanium-containing alkylidene complexes of molybdenum R₃Ge–CH=Mo(NAr)(OCMe₂CF₃)₂ (Ar = 2,6-i-Pr₂C₆H₃; R = Me, Ph) have been prepared by the reaction of organogermanium vinyl reagents R₃GeCH=CH₂ with known alkylidene compounds Alkyl–CH=Mo(NAr)(OCMe₂CF₃)₂ (Alkyl = Bu^t, PhMe₂C). The titled compounds were isolated as crystalline solids and characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR spectroscopy and X-ray diffraction studies. The geometry of the Mo atoms in the compounds can be described as a distorted tetrahedron.
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1. Introduction

Molybdenum and tungsten alkylidene complexes of the type Alkyl–CH=M(NAr)(OR′)₂ (M = Mo, W; Alkyl = Bu^t, PhMe₂C; Ar = 2,6-i-Pr₂C₆H₃; R′ = CMe₂-CF₃) synthesized by Schrock and co-workers [1] are widely used as effective catalysts for olefine metathesis reactions [2]. Majority of such compounds differ from each other mainly by the nature of alkoxy groups and almost all complexes contain alkyl group (Me₃C or PhMe₂C) bonded to carbene carbon atom [1c]. Very few complexes of the type with group 14 element-con-taining substituents attached to carbene carbon atom have been synthesized [1c]. We have recently reported the synthesis and structural characterization of tungsten alkylidene complexes with organosilicon and organoger-manium groups attached to carbene carbon atom Ph₃E–CH=WCl₂(OBu^t)₂ (E = Si, Ge) [3] prepared via proton-ation of triple W≡C bond in the appropriate alkylidyne compounds Ph₃E–C≡W(OBu^t)₃ (E = Si, Ge) [4]. Knowledge about the relationship between composition and structure of the substituent bonded to carbene car-bon and catalytic activity of these complexes in olefin metathesis reactions is highly restricted.

Herein we report the synthesis and structural charac-terization of the first alkylidene complexes of molybde-num containing organogermanium groups bound to the carbene carbon atom.

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2. Results and discussion

It is known that stoichiometrical metathetical reaction of molybdenum alkylidene compounds of the type Bu^t–CH=Mo(NAr)(OR$'$)$_2$ (R$'$ = Bu^t, CMe$_2$CF$_3$, CMe(CF$_3$)$_2$) with trimethylvinylsilane yields silyl-substituted alkylidene complexes Me$_3$Si–CH=Mo(NAr)(OR$'$)$_2$ [1a]. We used this synthetic approach for preparation of germyl-substituted alkylidene complexes of molybdenum. It was found that the reactions of Alkyl–CH=Mo(NAr)(OCMe$_2$CF$_3$)$_2$ (Alkyl = Bu^t (1), PhMe$_2$C (2)) with organogermanium vinyl reagents proceeded smoothly at room temperature and yielded the titled compounds R$_3$Ge–CH=Mo(NAr)(OCMe$_2$CF$_3$)$_2$ (Ar=2,6-i-Pr$_2$C$_6$H$_3$; R = Me (3), Ph (4)):

$$1(2) + R_3GeCH=CH_2 \xrightarrow{\text{Benzene}} 3(4) + Alkyl{-}CH=CH_2$$
$$(R = Me, Ph)$$
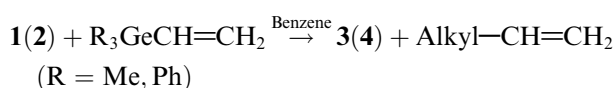
The course of the reactions was monitored by ^{1}H NMR. Trimethylvinylgermane was found to react with 1 and 2 in 0.5 h. The reactions with triphenylvinylgermane were completed in 30 h. The molybdenum alkylidene complexes 3 and 4 were isolated as air-sensitive yellow-orange crystalline solids. They were characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR spectroscopy and X-ray diffraction studies. According to X-ray data the complexes 3 and 4 have a *syn*-conformation. The Mo and Ge atoms have a typical tetrahedral coordination environment (Figs. 1, 2). The bond angles around Mo atoms vary in the range of 102.40(7)–111.34(6)° for 3 and 102.5(1)–112.46(8)° for 4. The bond angles around Ge atoms vary in the range of 107.6(1)–111.6(1)° for 3 and 106.7(1)–111.6 (1)° for 4. The Mo(1)–N(1)–C(13) (for 3) and Mo(1)–N(1)–C(1) (for 4) angles in diisopropylphenylimido ligands are 167.8(1)° and 175.0(2)°, respectively. The Mo(1)–N(1) distances are 1.731(1) and 1.721(2) Å for 3 and 4, respectively. The geometries of the MoCGe fragments are slightly different in 3 and 4. The Mo(1)–C(1) and Ge(1)–C(1) distances are 1.889(2) and 1.945(2) Å in 3 and are longer than the analogous Mo(1)–C(21) (1.876(2) Å), and Ge(1)–C(21) (1.935(2) Å) distances in 4. It should be noted that the Mo(1)–C(1)–Ge(1) angle is 137.6(1)° in 3 which is smaller than the similar Mo(1)–C(21)–Ge(1) (144.1(1)°) angle in 4. Apparently the bigger value of the MoCGe angle in 4 is due to the shortening of C(1)···C(39) and C(2)···C(38) distances between C(1–6) and C(34–39) planes which are 3.376(5) and 3.405(5) Å, respectively that are close to the sum of Van der Waals radii of carbon atoms (3.4 Å [5]). The Mo–C distances in 3 (1.889(2) Å) and 4 (1.876(2) Å) are shorter than the analogous distances in Mo(=CH–t-Bu)(=NAr)[OCMe$_2$(CF$_3$)]$_2$(C$_4$H$_7$N) (1.948(7)/1.909(9) Å [6]) and in Mo(=CH–t-Bu)(=NAr)(OTf)$_2$(dme) (1.90(1)/1.93(1) Å [1a]) complexes. The or-
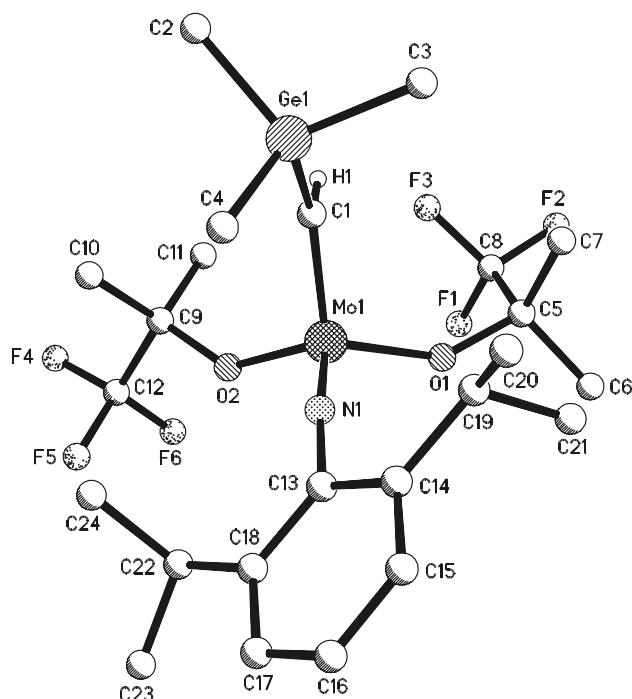
Fig. 1. The molecular structure of 3. Selected bond lengths (Å) and angles (°): Mo(1)–N(1), 1.731(1); Mo(1)–C(1), 1.889(2); Mo(1)–O(1), 1.908(1); Mo(1)–O(2), 1.912(1); Ge(1)–C(1), 1.945(2); N(1)–C(13), 1.403(2) and N(1)–Mo(1)–C(1), 102.40(7); N(1)–Mo(1)–O(1), 111.34(6); C(1)–Mo(1)–O(1), 110.74(6); N(1)–Mo(1)–O(2), 113.10(6); C(1)–Mo(1)–O(2), 108.26(6); O(1)–Mo(1)–O(2), 110.68(5); C(4)–Ge(1)–C(1), 109.82(8); C(4)–Ge(1)–C(3), 111.6(1); C(1)–Ge(1)–C(3), 108.3(1); C(4)–Ge(1)–C(2), 107.6(1); C(1)–Ge(1)–C(2), 109.02(9); C(3)–Ge(1)–C(2), 110.5(1); C(13)–N(1)–Mo(1), 167.8(1).

dinary Ge–C(Me) and Ge–C(Ph) distances in 3 and 4 vary in the range of 1.939(2)–1.954(2) and 1.940(3)–1.948(3) Å, respectively. The comparison of the Ge–C(Me, Ph) and Ge–C(CH) distances in 3 and 4 allow to note a shortening of Ge(1)–C(21) bond in 4. Apparently it is due to the more efficient electron density delocalization in the MoCGe fragment in 4 than in 3.

The preliminary study have shown that complexes 3 and 4 are active catalysts for metathesis of hex-1-ene. The detailed investigation of catalytic properties of the titled compounds in olefine metathesis reactions will be published in due course.

3. Experimental

3.1. General

All manipulations were carried out in evacuated sealed ampoules using standard Schlenk techniques. The solvents were thoroughly dried and degassed. Compounds 1 and 2 [1a] and R$_3$GeCH=CH$_2$ (R = Me, Ph) [7] were prepared according to a literature procedure. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker
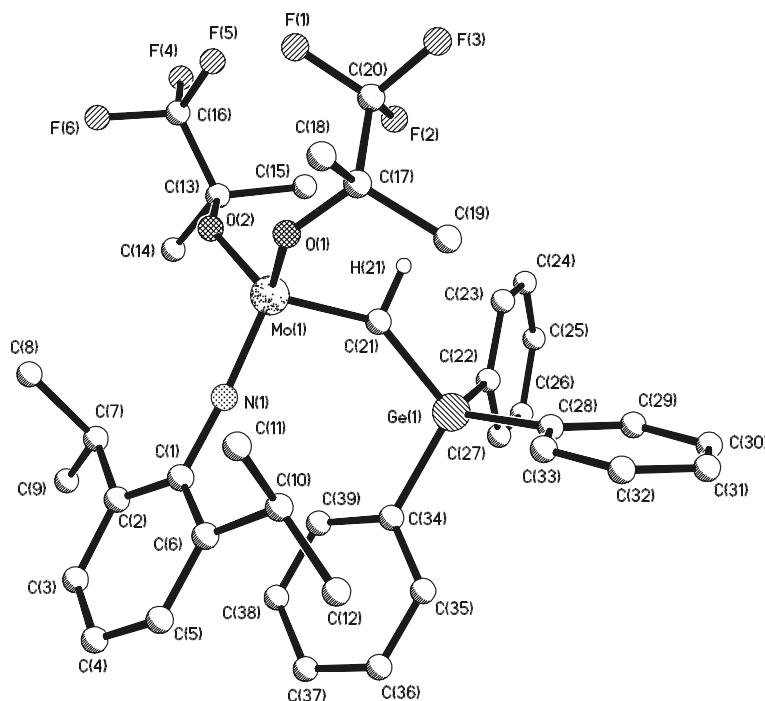
Fig. 2. The molecular structure of **4**. Selected bond lengths (Å) and angles (°): Mo(1)–N(1), 1.721(2); Mo(1)–C(21), 1.876(2); Mo(1)–O(1), 1.904(2); Mo(1)–O(2), 1.903(2); Ge(1)–C(21), 1.935(2); N(1)–C(1), 1.396(3) and N(1)–Mo(1)–C(21), 102.5(1); N(1)–Mo(1)–O(1), 111.55(9); C(21)–Mo(1)–O(1), 107.43(9); N(1)–Mo(1)–O(2), 113.01(9); C(21)–Mo(1)–O(2), 109.3(1); O(2)–Mo(1)–O(1), 112.46(8); C(21)–Ge(1)–C(22), 106.7(1); C(21)–Ge(1)–C(34), 110.9(1); C(22)–Ge(1)–C(34), 111.6(1); C(21)–Ge(1)–C(28), 110.5(1); C(22)–Ge(1)–C(28), 109.7(1); C(34)–Ge(1)–C(28), 107.5(1); C(1)–N(1)–Mo(1), 175.0(2).

DPX-200 NMR spectrometer. The chemical shifts are reported in parts per million with tetramethylsilane (0.00 ppm) as the internal standard.

3.2. Preparation of $Me_3Ge–CH\!\!=\!\!Mo(NAr)(OCMe_2CF_3)_2$ (3)

A solution of $Me_3GeCH\!\!=\!\!CH_2$ (1.1 g, 7.4 mmol) in 3 mL of benzene was added to a solution of **1** (1.3 g, 2.1 mmol) in 3 mL of benzene. The reaction mixture was kept at room temperature for 0.5 h. Evaporation of the solvent and volatiles in vacuo and crystallization of the solid residue from pentane (3 mL) afforded 0.7 g (50%) of **3** as yellow-orange crystals. Dec. p. >80 °C. Anal. Calc. for $C_{24}H_{39}F_6GeMoNO_2$: C, 43.93; H, 6.00. Found: C, 44.00; H, 5.97%. ^{1}H NMR (200 MHz, toluene-d_8) δ 13.34 (s, 1H, MoC*H*GeMe$_3$), 7.12–6.90 (m, 3H, H$_{arom}$), 3.67 (sept, 2H, C*H*Me$_2$), 1.34 and 1.27 (s, 6H each, OC*Me$_2$*CF$_3$), 1.19 (d, 12H, CH*Me$_2$*), 0.20 (s, 9H, MoCHGe*Me$_3$*). ^{13}C NMR (50 MHz, toluene-d_8) δ 275.5 (Mo*C*HGeMe$_3$), 154.6 (C_{ipso}), 145.7 (C_o), 128.0 (C_p), 123.1 (C_m), 78.4 (q, $^2J_{CF} = 29.8$, O*C*Me$_2$CF$_3$), 24.3 (*C*HMe$_2$), 24.8 (O*C*Me$_2$CF$_3$), 23.8 (CH*Me$_2$*), 1.1 (MoCHGe*Me$_3$*). The reaction of $Me_3GeCH\!\!=\!\!CH_2$ with **2** was carried out in a similar way. The yield of **3** was 52%.

3.3. Preparation of $Ph_3Ge–CH\!\!=\!\!Mo(NAr)(OCMe_2CF_3)_2$ (4)

A solution of $Ph_3GeCH\!\!=\!\!CH_2$ (0.4 g, 1.1 mmol) in 3 mL of benzene was added to a solution of **1** (0.7 g, 1.1 mmol) in 3 mL of benzene. The reaction mixture was kept at room temperature for 30 h. Evaporation of the solvent in vacuo and crystallization of the residue from pentane (3 mL) afforded 0.5 g (50%) of **4** as yellow-orange crystals. Dec. p. >85 °C. Anal. Calc. for $C_{39}H_{45}F_6GeMoNO_2$: C, 55.65; H, 5.35. Found: C, 55.46; H, 5.41%. ^{1}H NMR (200 MHz, C$_6$D$_6$) δ = 13.34 (s, 1H, MoC*H*GePh$_3$), 7.80–6.80 (m, 18H, H$_{arom}$), 3.56 (sept, 2H, C*H*Me$_2$), 1.36 and 1.25 (s, 6H each, OC*Me$_2$*CF$_3$), 1.03 (d, 12H, CH*Me$_2$*). ^{13}C NMR (50 MHz, C$_6$D$_6$) δ 261.6 (Mo*C*HGePh$_3$), 154.3, 153.7, 145.7, 145.4, 135.3, 129.1, 123.4, 122.7 (C_{arom}), 79.4 (q, $^2J_{CF} = 28.5$, O*C*Me$_2$CF$_3$), 24.8 (*C*HMe$_2$), 24.1 (CH*Me$_2$*), 24.5 (O*C*Me$_2$CF$_3$). The reaction of $Ph_3GeCH\!\!=\!\!CH_2$ with **2** was carried out in a similar way. The yield of **4** was 65%.

3.4. Crystallographic data for 3 and 4

The suitable crystals of **3** and **4** for X-ray diffraction were prepared by slow evaporation of concentrated

Table 1
Crystallographic data and structure refinement details for **3** and **4**

	3	**4**
Empirical formula	$C_{24}H_{39}F_6GeMoNO_2$	$C_{39}H_{45}F_6GeMoNO_2$
Formula weight	656.09	842.29
Crystal size (mm^3)	$0.5 \times 0.08 \times 0.02$	$0.16 \times 0.14 \times 0.05$
T (K)	100(2)	100(2)
λ (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
Unit cell dimensions		
a (Å)	10.2895(15)	11.0773(16)
b (Å)	30.665(4)	19.261(3)
c (Å)	10.6380(16)	18.272(3)
β (°)	118.052(2)	96.073(3)
Volume ($Å^3$)	2962.3(8)	6164.3(4)
Z	4	4
Density (calculated) (g/cm^3)	1.471	1.443
Absorption coefficient (mm^{-1})	1.495	1.161
$F(000)$	1336	1720
θ range for data collection (°)	2.24–25.00	2.06–29.13
Index ranges	$-12 \leqslant h \leqslant 12, -36 \leqslant k \leqslant 36, -12 \leqslant l \leqslant 12$	$-15 \leqslant h \leqslant 14, -26 \leqslant k \leqslant 17, -24 \leqslant l \leqslant 22$
Reflections collected	23 098	28 232
Independent reflections (R_{int})	5221 (0.0274)	10 296 (0.0496)
Data/restraints/parameters	5221/0/472	10 296/12/583
Goodness-of-fit on F^2	1.051	0.979
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0248, wR_2 = 0.0591$	$R_1 = 0.0430, wR_2 = 0.0910$
R Indices (all data)	$R_1 = 0.0286, wR_2 = 0.0603$	$R_1 = 0.0742, wR_2 = 0.1020$
Largest difference peak and hole (e $Å^3$)	0.744 and -0.525	0.847 and -0.547

pentane solutions of the complexes at room temperature. The data were collected on a Bruker AXS "SMART APEX" diffractometer (graphite-monochromated, Mo Kα-radiation, φ–ω-scan technique, $\lambda = 0.71073$ Å). The intensity data were integrated by SAINT program [8], while the program SADABS [9] was utilized for the scaling of diffraction data, application of a decay correction and an empirical absorption correction based on redundant reflections. The structures were solved by direct methods and were refined on F^2 using all reflections with SHELXL [10]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms in **3** were found from Fourier synthesis and refined isotropically. One part of the hydrogen atoms in **4** were found from Fourier synthesis and refined isotropically but other part one were placed in calculated positions and refined in the "riding-model". The details of crystallographic, collection and refinement data are shown in the Table 1.

4. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 252706 and 252707 for complexes **3** and **4**, 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 336 033, e-mail: deposit@ccdc. cam.ac.uk, or on the web http://www.ccdc.cam.ac.uk.

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