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Facile synthesis of digermylene oxide and its reactivity towards vanadocene: the first example of Cp_2V–germylene coordination

Kseniya V. Arsenyeva,[a] Maxim G. Chegerev,[b] Anton V. Cherkasov,[a] Kira I. Pashanova,[a] Irina V. Ershova,[a] Olesya Yu. Trofimova[a] and Alexandr V. Piskunov*[a]

[a] *G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, 603950 Nizhnii Novgorod, Russian Federation. E-mail: pial@iomc.ras.ru*
[b] *Institute of Physical and Organic Chemistry, Southern Federal University, 344090 Rostov-on-Don, Russian Federation*

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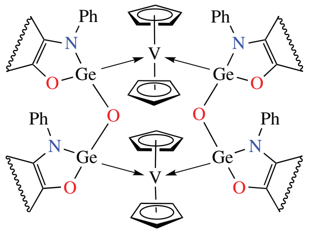
Digermylene oxide was prepared by hydrolysis of O,N-heterocyclic germylene, and its reactivity was examined *in situ*. Its treatment with N-heterocyclic carbene produces dianionic digermylene oxide while its reaction with vanadocene gives the dinuclear derivative, a rare example of a compound containing the vanadium–germylene coordination bond. The product structures were confirmed by X-ray diffraction analysis.

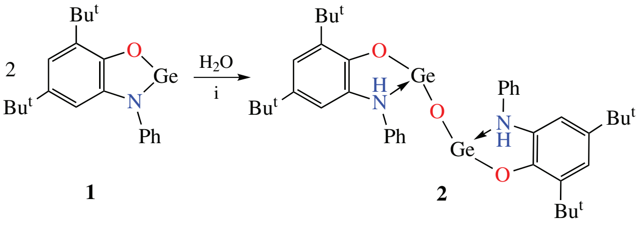


Keywords: N-heterocyclic carbene, germylene, vanadocene, *o*-amidophenolate, X-ray diffraction.

N-Heterocyclic carbenes (NHCs) are widely used ligands in organometallic chemistry, which can stabilize the unusual redox or coordination state of metal centers and provide a high catalytic activity to complexes.[1] The investigations of heavy analogues of carbenes is another promising direction in this chemistry.[2] One of the undeniable advantages of ligands based on low valent 14 group elements is the rich possibilities for modifying their electronic and steric structure. Not only classical methods of organic chemistry are available for various functionalizations of heavy carbene analogues but also additional transformations that are engendered by the organoelement chemistry of these derivatives. Germylenes are known to give oxide compounds which retain their two low-valent centres with the ability to coordinate with metals. The first examples of digermylene oxides were prepared in 2011[3] by the oxidation Ge$^{\text{I}}$ species with pyridine or trimethylamine *N*-oxides. The similar compounds form in the course of prolonged heating of aminotroponoiminato germanium(II) chloride with potassium hydroxide[4] or during the reduction of carbon dioxide with bulky amido-substituted digermyne LGeGeL [L is N(Ar*)$SiMe_3$, Ar* is $C_6H_2\{C(H)Ph_2\}_2$Me-2,6,4)].[5] The related amidogermylene oxides were observed during hydroboration of carbon dioxide in the presence of Ge$^{\text{II}}$ hydride complex[6] or prolonged storage of tetrameric amido-germanium(I) compound in CO_2 atmosphere.[7] More conveniently, digermylene oxide is formed as a side-product in the course of the uncontrolled hydrolysis of acyclic phosphinoamido-germylene.[8] However, attempts to accomplish the targeted hydrolysis for neat preparation of Ge$^{\text{II}}$–O–Ge$^{\text{II}}$ compounds were unsuccessful.[8]

In our recent investigations, we reported the chemistry of heavy carbene analogues bearing a redox-active *o*-amidophenolate backbone. Different germylenes,[9] stannylenes,[10] and plumbylenes[11] have been synthesized and examined. They demonstrated high aromaticity of chelated five-membered heterocycle,[12] underwent multiple oxidative[9(*a*),10(*a*),13] and reductive[9(*b*)] transformations. The present paper shows the facile preparation of digermylene oxide employing such O,N-heterocyclic germylene hydrolysis at the first stage. Thus synthesized Ge$^{\text{II}}$–O–Ge$^{\text{II}}$ compound was involved in the reaction with vanadocene to give the Ge–V organometallics.

Treatment of germylene **1** with a stoichiometric quantity of water in toluene gave digermylene oxide **2** (Scheme 1). The reaction proceeds at room temperature and reaches its completion within several minutes. The colour of the initial light-yellow solution of germylene **1** disappeared immediately. We failed to obtain compound **2** in a solid state, while prolonged manipulations lead to its decomposition allowing only isolation of the corresponding *o*-aminophenol. Luckily, treatment of the initial filtered reaction mixture with 1,3-diisopropyl-4,5-dimethyl-imidazol-2-ylidene caused deprotonating of the initial digermylene oxide with the formation of ionic derivative **3** as a colourless well-formed crystals in 74% yield† (Scheme 2).



Scheme 1 *Reagents and conditions*: i, H_2O, toluene, room temperature.

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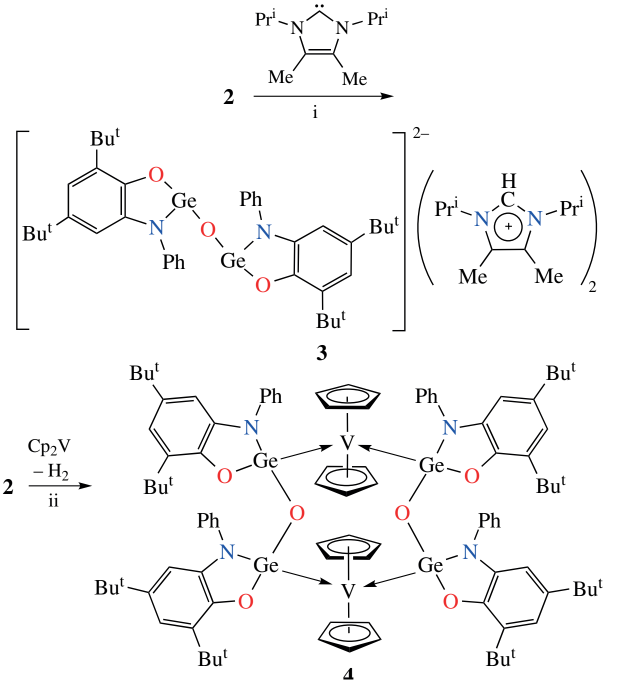
† All reactants were purchased from Aldrich. All manipulations on complexes were performed under Schlenk line conditions, in which oxygen and moisture were excluded. Solvents were purified by standard methods.[14] Germylene **1** was prepared according to the previously described method.[9(*a*)] NMR spectra were recorded using a Bruker Avance III 400 MHz instrument. Elemental analyses were performed with an Elementar Vario EL cube instrument.



Scheme 2 *Reagents and conditions*: i, toluene, room temperature; ii, Cp_2V, toluene/THF, room temperature, 3 days.

A single-crystal X-ray diffraction study examined the molecular structure of salt **3**.[‡] Its anion part is presented in Figure 1. Two imidazolium cations are practically identical to the reported earlier.[18] According to the X-ray diffraction data, the central fragment Ge(1)O(3)Ge(2) is disordered in two sites with the ratio of 0.94 : 0.06. Below we discuss the geometric characteristics of only the prevailing part with higher occupancy.

Dianion of **3** contains two tri-coordinated germylene centers linked by μ^2-oxygen bridge. The central Ge(1)–O(3)–Ge(2) bending angle is 132.92(9)°. It is significantly less than that for known (more than 145°) related compounds with tri-coordinated germylene atom.[3(b),4] The distances between germanium and oxide atoms are essentially long [1.815(2) and 1.818(2) Å] and exceed the values for related derivatives.[3–8] The sums of angles around Ge(1) (283.7°) and Ge(2) (273.2°) atoms are close to 270°. It means a low rate of involvement of lone pair located on s-orbital into the hybridization. The angles between six-membered rings of *o*-amidophenolate ligands and the corresponding *N*-phenyl substituents [41.3(2)°, 42.1(2)°] are significantly smaller than in the initial germylene **1** [59.39(9)°, 63.80(9)°].[9(a)] The bond lengths distribution in the *o*-amidophenolate fragment is typical of such types of ligands and are close to those in compound **1**.[9(a)] Simultaneously, the significant elongation up to 0.14 Å of Ge–O [1.917(2), 1.933(2) Å] and Ge–N [1.971(2), 1.997(2) Å] distances is observed in the five-membered metallacycles of **3** in contrast to **1** [Ge–O: 1.832(2)–1.834(2) Å; Ge–N: 1.858(2), 1.859(2) Å]. These heterocycles are completely flat in **1**, but one of the cycles is noticeably distorted in **3**. Thus, the bend angles of the Ge(1) and Ge(2) metallacycles along the O···N lines are 175.4(2)° and 156.7(2)°, respectively.

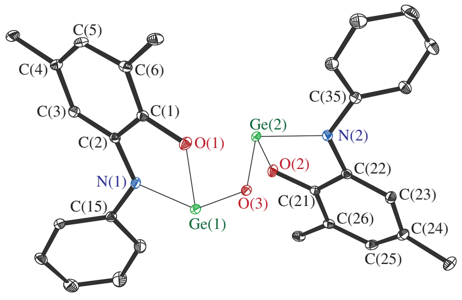


Figure 1 Molecular structure of dianionic part of **3**. Thermal ellipsoids are shown with 30% probability. The Me groups of Bu^t substituents and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg.): Ge(1)–O(1) 1.933(2), Ge(1)–N(1) 1.997(4), Ge(1)–O(3) 1.815(2), Ge(2)–O(2) 1.917(2), Ge(2)–N(2) 1.971(2), Ge(2)–O(3) 1.818(2), O(1)–C(1) 1.346(2), N(1)–C(2) 1.392(3), C(1)–C(2) 1.420(3), O(2)–C(21) 1.349(2), N(2)–C(22) 1.404(3), C(21)–C(22) 1.418(3); O(3)–Ge(1)–O(1) 100.19(7), O(3)–Ge(1)–N(1) 101.45(7), O(1)–Ge(1)–N(1) 82.03(6), O(3)–Ge(2)–O(2) 96.55(7), O(3)–Ge(2)–N(2) 94.03(7), O(2)–Ge(2)–N(2) 82.61(7), Ge(1)–O(3)–Ge(2) 132.92(9).

Synthesis of **3**. A drop of water (6.04 μl, 3.36 mmol) was added to toluene (15 ml) using micropipette. This solution was degassed and slowly added to a solution of compound **1** (0.247 g, 6.73 mmol) in the same solvent (15 ml). The mixture was stirred for 10–15 min. The slightly turbid resulting solution was passed through 0.45 μm syringe filter and treated with the 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (0.242 g, 13.4 mmol) in the same solvent. The volume of the reaction mixture was halved and it was stored overnight. Colourless crystals of **3** were collected and dried under reduced pressure. Yield 0.36 g (74%). Found (%): C, 69.11; H, 8.54; N, 7.42. Calc. for $C_{62}H_{92}Ge_2N_6O_3$ (%): C, 68.80; H, 8.32; N, 7.54. ^{1}H NMR (toluene-d_8, 20 °C) δ: 1.16 (d, 12 H, CH_3 of Pr^i, J 8.0 Hz), 1.34 (s, 18 H, Bu^t), 1.47 (s, 18 H, Bu^t), 1.83 (s, 12 H, C–Me), 3.81 (m, 4H, C*H*Me_2), 7.35–6.66 (m, 10 H, H_{Ph}), 7.59 (d, 2 H, H_{AP}, J 2.1 Hz), 7.71 (d, 2 H, H_{AP}, J 2.1 Hz), 10.0 (s, 2H, CH).

[‡] The X-ray suitable crystals of **3**·2PhMe and **4**·2PhMe were obtained after storage of the appropriate toluene solutions at room temperature in a glowebox. The X-ray data were collected with a Bruker D8 Quest diffractometer (MoK_α-radiation, ω-scans technique, λ = 0.71073 Å, T = 100 K) using APEX3[15] software package. SADABS[16] was used to perform absorption corrections. The structures were solved *via* intrinsic phasing algorithm and were refined by full-matrix least squares on F^2 for all data using SHELX.[17] All non-hydrogen atoms and H(45A), H(56A) in **3** were found from the Fourier syntheses of electron density (all non-hydrogen atoms were refined anisotropically). All other hydrogen atoms in **3** and **4** were placed in calculated positions and were refined in the 'riding' model with $U(H)_{iso} = 1.2\,U_{eq}$ of their parent atoms [$U(H)_{iso} = 1.5\,U_{eq}$ for methyl groups].

Crystal data for **3**. $C_{76}H_{108}Ge_2N_6O_3$, M = 1298.86, space group $P2_1/c$, a = 14.7192(6), b = 15.3988(7) and c = 16.9345(7) Å, β = 107.992(2)°, V = 3537.8(3) Å^3, Z = 2, d_{calc} = 1.219 g cm^{-3}. Colourless single crystal with dimensions 0.35×0.30×0.03 mm was selected and intensities of 54123 reflections were collected (μ = 0.900 mm^{-1}, $2\theta_{max}$ = 50.24°). After merging of equivalence and absorption corrections, 20810 independent reflections (R_{int} = 0.0439) were used for the structure solution and refinement. Final R factors R_1 = 0.0512 [for reflections with $I > 2\sigma(I)$], wR_2 = 0.1187 (for all reflections), S = 1.018, largest diff. peak and hole are 0.52 and –0.44 e Å^{-3}, respectively. The unit cell of **3** contains two toluene molecules per molecule of the complex. The Ge(1)O(3)Ge(2) fragment is disordered in two sites with ratio of 0.94 : 0.06.

Crystal data for **4**. $C_{114}H_{136}Ge_4N_4O_6V_2$, M = 2050.50, space group $P\bar{1}$, a = 12.5194(5), b = 13.3822(5) and c = 17 .8560(6) Å, α = 71.0540(10)°, β = 88.5860(10)°, γ = 64.6500(10)°, V = 2534.05(16) Å^3, Z = 1, d_{calc} = 1.344 g cm^{-3}. Red single crystal with dimensions 0.34×0.21×0.18 mm was selected and intensities of 34471 reflections were collected (μ = 1.404 mm^{-1}, $2\theta_{max}$ = 52.19°). After merging of equivalence and absorption corrections, 9988 independent reflections (R_{int} = 0.0449) were used for the structure solution and refinement. Final R factor R_1 = 0.0508 [for reflections with $I > 2\sigma(I)$], wR_2 = 0.0929 (for all reflections), S = 1.069, largest diff. peak and hole are 0.59 and –0.68 e Å^{-3}, respectively. The unit cell of **4** contains two toluene molecules per molecule of the complex. All N–Ph fragments are disordered in two sites with ratios 0.64 : 0.36 and 0.51 : 0.49.

CCDC 2059875 (**3**·2PhMe) and 2059876 (**4**·2PhMe) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

Among the carbene complexes of transition metals, vanadium compounds are currently ones of the least studied objects. Against the background of the well-studied chemistry of vanadium vinylidene derivatives,[19] only a few publications is devoted to complexes involving NHC ligands.[18,20] The coordination of heavy carbene analogues with vanadium are even rarer. Weiss and co-workers observed the first example of such bonding in 1988[21] when the $[GeH_3]^-$ substituted carbonyl ligand in $CpV(CO)_4$ to give the corresponding anionic species. Dimethylgermylene released in the course of thermolysis of 7-germanorbornadiene was captured with decamethylvanadocene. The resulting vanadium-germylene complex was identified utilizing EPR spectroscopy.[22] Recently, the crystalline and solution-state structure of the dicyclopentadienylvanadium N-heterocyclic silylene (NHSi) complex was reported.[23] We have examined the reactivity of germylene **1** and new digermylene oxide **2** towards Cp_2V. Germylene **1** does not react with vanadocene either at room temperature or when heated in toluene. In the meantime, the reaction between digermylene oxide **2** and Cp_2V proceeds slowly at room temperature under ambient conditions.[§] The initial violet colour of vanadocene changes by deep-brown, and EPR signal for Cp_2V disappears during three days. The prolonged storage of the concentrated reaction mixture yields complex **4** as dark-red air-sensitive crystals. During this reaction, vanadocene reduces the amine protons to give dinuclear derivative, which contains two $[Cp_2V]^{2+}$ centers bonded by two dianionic parts of **3**. Compound **4** is silent in the X-band EPR region at room temperature and 100 K due to the antiferromagnetic interaction between two paramagnetic d^1-vanadium(IV) centers.[24] The comparable spectroscopic features were recently observed for the relative bis-vanadocene derivative containing –OPO– bridges between two V^{IV} centers which demonstrated well-resolved EPR spectrum at 4 K only.[25] Compound **4** demonstrates a resolved ^{1}H NMR spectrum except for Cp-protons which give broad signal at 4.99 ppm. The molecular structure of **4** is shown in Figure 2. According to the X-ray diffraction data, the geometry of all N–Ph fragments is slightly distorted due to the disorders of these fragments in two sites with different ratios.

Eight-membered metallocycle in **4** adopts 'chair' conformation. The $[Cp_2V]^{2+}$ fragments are separated by 6.856(2) Å and demonstrate the bent sandwich, which is characteristic of numerous related complexes.[25,26] The vanadium ion coordination geometry is a distorted tetrahedron with the Cp-ring centroids and two germanium atoms in the vertices. $V\cdots Cp_{centre}$ distances [1.919(2), 1.930(2) Å] and Cp_{centre}–V–Cp_{centre} angle [139.4(2)°] correlate favorably with the corresponding metric parameters in closely related molecules and cations.[25,26] The dihedral angle between the two Cp-rings is 42.0(2)°. The sums of N–Ge–O and O–Ge–O angles around Ge(1) and Ge(2) atoms lie in the range of 277.9–289.7° and remain close to 270°, indicating the preservation of the divalent oxidation state of germanium atoms. It is also evidenced by the lengths of the Ge–O [1.833(2)–1.837(2) Å] and Ge–N [1.954(2)–1.964(2) Å] bonds in five-membered heterocycles. They are somewhat shorter than those in **3** but significantly longer than in known Ge^{IV} *o*-amidophenolates.[27] Digermylene oxide fragment Ge–O–Ge is appreciably transformed during complexation, namely, the Ge–O bond [1.860(2), 1.875(2) Å] is elongated simultaneously with the increase in the Ge(1)–O(3)–Ge(2) angle [157.2(2)°] in contrast to the free dianion in **3**. The *o*-amidophenolate part keeps its structural characteristics herewith five-membered heterocycle is planar. Until now, only four compounds with germanium–vanadium covalent bonds were characterized structurally. In addition to the previously[21] mentioned $[CpV(CO)_3GeH_3]^-$, there are three organometallic derivatives with Cp_2V^{IV}–Ge^{IV} bonds.[28] Complex **4** demonstrates the first example of Cp_2V^{IV}–Ge^{II} coordination with the closest interaction between elements Ge–V [2.4548(7), 2.4558(6) Å].

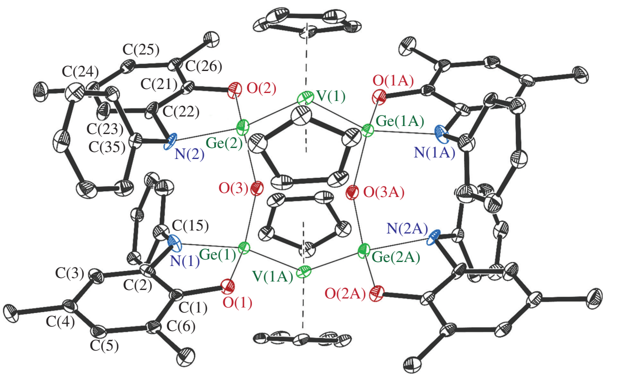


Figure 2 Molecular structure of **4**. Thermal ellipsoids are shown with 30% probability. The Me groups of Bu^t substituents and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg.): Ge(1)–O(1) 1.837(2), Ge(1)–O(3) 1.860(2), Ge(1)–N(1) 1.964(4), Ge(1)–V(1A) 2.4558(6), Ge(2)–O(2) 1.833(2), Ge(2)–O(3) 1.875(2), Ge(2)–N(2) 1.954(4), Ge(2)–V(1) 2.4548(7), $V(1)\cdots Cp_{centre}$ 1.919(2), 1.930(2); O(1)–Ge(1)–O(3) 99.2(2), O(1)–Ge(1)–N(1) 86.6(2), O(3)–Ge(1)–N(1) 102.2(7), O(1)–Ge(1)–V(1A) 122.32(7), O(3)–Ge(1)–V(1A) 114.68(7), N(1)–Ge(1)–V(1A) 125.8(6), O(2)–Ge(2)-O(3) 99.1(2), O(2)–Ge(2)–N(2) 87.7(2), O(3)–Ge(2)–N(2) 91.1(3), O(2)–Ge(2)–V(1) 119.23(7), O(3)–Ge(2)–V(1) 115.62(7), N(2)–Ge(2)–V(1) 135.7(2), Ge(2)–V(1)–Ge(1A) 84.74(2), Ge(1)–O(3)–Ge(2) 157.2(2).

In summary, hydrolysis of germanium(II) O,N-heterocyclic compound was found to be a simple way to prepare the germylene oxide derivative. The latter was identified as dianionic complex after double deprotonation with 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene. The reaction of digermylene oxide with vanadocene produces the rare example of an organometallic compound containing a V^{IV}–Ge^{II} bond.

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[§] *Synthesis of complex* **4**. The reaction mixture after hydrolysis of **1** was treated with the THF solution of Cp_2V (0.12 g, 6.73 mmol). The initial colour of vanadocene disappeared during three days and the prolonged storage of the concentrated reaction mixture resulted in the precipitation of complex **4** as dark-red air sensitive crystals. Crystals of **4** were collected and dried under reduced pressure. Yield 0.27 g (44%). Found (%): C, 64.72; H, 6.83; N, 2.87. Calc. for $C_{100}H_{120}Ge_4N_4O_6V_2$ (%): C, 64.35; H, 6.48; N, 3.00. ^{1}H NMR ($CDCl_3$, 20 °C) δ: 1.26 (s, 18H, Bu^t), 1.44 (s, 18H, Bu^t), 6.4–6.95 (m, 10H, H_{Ph}), 7.36 (d, 2H, H_{AP}, J 2.1 Hz), 7.04 (d, 2H, H_{AP}, J 2.1 Hz).

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