Journal of Organometallic Chemistry 813 (2016) 36–40

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Nitrile functionalized organogermane chalcogenide clusters with hetero-(nor-)adamantane cores

Samuel Heimann, Günther Thiele, Stefanie Dehnen*

Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse, D-35043 Marburg, Germany

ARTICLE INFO

Article history:
Received 19 January 2016
Received in revised form
5 March 2016
Accepted 22 March 2016
Available online 24 March 2016

Dedicated to Professor Heinrich Lang on the occasion of his 60th birthday.

Keywords:
Organo-germanium chemistry
Hybrid clusters
Germanium chalcogenide clusters
Nitrile ligands
X-ray diffraction
DFT calculations

ABSTRACT

By the synthesis of $Cl_3Ge(CH_2)_2CN$ (**1**) and subsequent reaction with sodium monochalcogenides, adamantane-type $[(NC(CH_2)_2Ge)_4Ch_6]$ (Ch = S (**2**), Se) and noradamantane-type $[(NC(CH_2)_2Ge)_4Te_5]$ (**3**) were obtained. The compounds represent the first nitrile-functionalized tetrel chalcogenide clusters and the first nitrile-functionalized clusters of the named architectures, and are thus potential precursor for novel reaction pathways to multifunctional core-shell compounds.

1. Introduction

Organotetrel chalcogenide clusters, that is, binary clusters of groups 14 and 16, have shown intriguing physical and chemical properties, in particular if the respective ligands comprise functional organic groups [1]. Such compounds can therefore be regarded as core-shell hybrids: via an appropriate choice of the elemental combination, the inorganic core can be designed for e.g. opto-electronic properties, while the organic periphery can be adjusted for further chemical derivatization or complexation towards transition metal compounds [2–4].

Certain restrictions exist for the integration of functional groups in the ligand shell of compounds of the general type $[(R^fTt)_xCh_y]$, with R^f = functionalized organic ligand, Tt = Si, Ge, Sn, and Ch = S, Se, Te. Strong coordination of a donor group at the ligand towards the core unit, or redox reactions with the chalcogenide source restrict the variety of potentially interesting organic substituents that can be directly attached to the Ge atoms. Hence, starting with $Cl_3Ge{-}R^f$ in a standard reaction with H_2Ch or TMS_2Ch, only keto and carboxylate groups [5], or silyl substituents [6] could so far be integrated in the ligand shell of R^fGe/E clusters that are known in one of three predominant core architectures: the adamantane type, the double-decker-type, both of the general formulae $[(RTt)_4Ch_6]$ [7,8], or the noradamantane-type structure $[(RTt)_4Ch_5]$ [9]. Even though the functional groups allow for further derivatization, e.g. via reaction with hydrazine, organic hydrazines, hydrazones or hydrazides [10], the follow-up chemistry is fairly restricted. Hence, novel functionalities are desirable in regard of new potential derivatization approaches of the organic ligand decoration. Here, we would like to present our results on the synthesis of Ge/E cluster compounds that are terminated by nitrile groups, and discuss their potential for further derivatization, e.g. with respect to click chemistry or hydrogenation, or upon utilization of the coordinating properties of the nitrogen lone pair for further (transition) metal ion coordination.

2. Materials and methods

2.1. General

All manipulations were performed under strict exclusion of oxygen and moisture, applying standard Schlenk and glovebox techniques. 1,1,3,3-Tetramethyldisiloxane (purchased from Sigma-

---

* Corresponding author.
E-mail address: dehnen@chemie.uni-marburg.de (S. Dehnen).

http://dx.doi.org/10.1016/j.jorganchem.2016.03.026
0022-328X/

Aldrich in 97% purity), $GeCl_4$ (purchased from Sigma-Aldrich in 99.99% purity) and $Na_2S\cdot 9H_2O$ (purchased from Acros Organics in 98+% purity) were used as received. Na_2Se and Na_2Te were synthesized from equimolar amounts of the elements in liquid ammonia according to known literature procedures [11]. Et_2O and THF were freshly distilled from sodium and benzophenone, MeOH was dried with Mg and subsequent distillation, H_2O has been degassed and saturated with Ar prior use. ESI spectra were recorded on a Finnigan MAT 95S. CHN analyses were performed on a Vario MicroCube, EDX on a Noran Instruments Vovayer 4.0 with a CamScan CS 4DV electron microscope with an acceleration voltage of 20 kV and an accumulation time of 100 s. NMR spectra were obtained from a Bruker DRX 300 (^1H, ^{13}C) or DRX 400 (^{125}Te) in $CDCl_3$. X-ray diffraction was performed at T = 100 K on a Stoe IPDS2, equipped with graphite monochromator. All structures were solved by direct methods in WinGX and Olex2 [12], and refined by full-matrix least-squares refinement against F^2 in SHELXL-2015 [13]. Absorption correction were performed numerically including shape optimization with Stoe X-Area. CCDC 1448281-1448283 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.2. Synthesis of 1

15.0 mL (84.9 mmol, 1.0 eq) of 1,1,3,3-tetramethydisiloxane are slowly added to a solution of 10.0 mL (87.6 mmol, 1.0 eq) $GeCl_4$ in 30 mL of Et_2O. The reaction mixture is heated to reflux for 1.5 h and allowed to cool to room temperature. The resulting reaction mixture is added to a solution of 6.3 mL (96.2 mmol, 1.1 eq) of acrylonitrile in 10 mL of Et_2O and stirred for 20 h. **1** can be obtained after vacuum distillation (80 °C, 10^{-3} mbar) as colorless liquid in quantitative yield (19.8 g, 84.9 mmol). After cooling, **1** forms a light-yellow solid. CHN (meas./calc.)/%: C (16.94/15.46), H (2.08/1.73), N (5.83/6.01). Crystallographic data for $C_3H_4Cl_3GeN$ (M_w = 233.01 g/mol): monoclinic space group $P2_1/m$, a = 6.1541(7) Å, b = 6.8845(4) Å, c = 9.4294(10) Å, β = 105.578(8)°. R_1 (refl.) = 0.0196 (980), wR_2 (refl.) = 0.0427 (1119), S = 0.944. ^1H NMR (300 MHz, $CDCl_3$) δ: 2.73–2.82 (m, 2H, CH_2), 2.28–2.38 (m, 2H, CH_2) ppm. ^{13}C (75 MHz, $CDCl_3$) δ: 25.8 (Ge–$\mathbf{C}H_2$), 11.1 (C–$\mathbf{C}H_2$), 116.3 ($\mathbf{C}$–N) ppm.

2.3. Synthesis of 2

A solution of 0.50 g (2.15 mmol) of **1** in 25 mL acetone is added to a solution of 1.09 g (4.54 mmol, 2.1 eq) of $Na_2S\cdot 9H_2O$ in a mixture of 25 mL H_2O and 25 mL of acetone and vigorously stirred for 5 h under exclusion of light. The volume of the reaction mixture was reduced to 25 mL, the resulting precipitate washed with 0.5 mL H_2O and solved in MeOH. The resulting solution was layered with Et_2O to yield **2** after 5 d as colorless crystals in 80% yield (0.30 g, 0.43 mmol) with respect to **1**. CHN (meas./calc.)/%: C (20.55/20.61), H (2.33/2.31), N (7.95/8.01). EDX ratio (meas./calc.) Ge:S (1:1.49/1:1.5). Crystallographic data for $C_{12}H_{16}Ge_4N_4S_6$ (M_w = 699.01 g/mol): tetragonal space group $I4_1/a$, a = 10.4630(4) Å, c = 21.3857(15) Å. R_1 (refl.) = 0.0288 (946), wR_2 (refl.) = 0.0432 (1577), S = 0.723. ^1H NMR (300 MHz, $CDCl_3$) δ: 1.78–1.85 (m, 2H, CH_2), 2.45–2.54 (m, 2H, CH_2) ppm. ^{13}C (75 MHz, $CDCl_3$) δ: 36.5 (Ge–$\mathbf{C}H_2$), 14.4 (C–$\mathbf{C}H_2$) 118.8 ($\mathbf{C}$–N) ppm.

2.4. Synthesis of $[(NC(CH_2)_2Ge)_4Se_6]$

A solution of 0.50 g (2.15 mmol) of **1** in 50 mL of THF is added to a suspension of 0.30 g (2.40 mmol, 1.1 eq) Na_2Se in 100 mL of THF under constant stirring. The reaction mixture is stirred for 30 h under exclusion of light. After filtration, the resulting solution is evaporated to a final volume of 75 mL and left for 15 h. **3** forms as colorless blocks. MS (ESI^+) m/z = 981.33 (M^+). CHN (meas./calc.)/%: C (14.67/14.70), H (1.65/1.64), N (5.68/5.71). EDX ratio (meas./calc.) Ge/Se (1:1.56/1:1.5). The crystal quality has so far not been good enough for the collection of a satisfying and publishable data set; however, the cluster composition and structure was unambiguously identified. According to ^1H and ^{13}C NMR data, the CH_2CH_2CN ligands are retained on the cluster molecules in solution. ^{77}Se NMR data could not be detected within the experimental noise.

2.5. Synthesis of 3

Same procedure as for $[(NC(CH_2)_2Ge)_4Se_6]$, applying 0.50 g (2.15 mmol) of **1** and 0.42 g (2.42 mmol, 1.1 eq) Na_2Te with the same amount of solvents. After reduction of the solvent volume, **3** crystallizes after 4 h as orange blocks in approx. 34% yield (0.21 g, 0.18 mmol) with respect to **1**. MS (ESI^+) m/z = 1145.35 (M^+). CHN (meas./calc.)/% C (12.52/12.58), H (1.40/1.41), N (4.88/4.89). EDX ratio (meas./calc.) Ge/Te (1:1.18/1:1.25). Crystallographic data for $C_{12}H_{16}Ge_4N_4Te_5$ (M_w = 1144.65 g/mol): triclinic space group $P\bar{1}$, a = 10.8179(6) Å, b = 11.0425(6) Å, c = 12.0025(6) Å, α = 102.642(4)°, β = 113.904(4)°, γ = 94.980(4). R_1 (refl.) = 0.0524 (3729), wR_2 (refl.) = 0.1374 (5244), S = 0.953. ^1H NMR (300 MHz, $CDCl_3$) δ: 2.60–3.11 (m, 2H, CH_2), 1.92–2.25 (m, 2H, CH_2) ppm. ^{13}C (75 MHz, $CDCl_3$) δ: 35.7–38.5 (Ge–$\mathbf{C}H_2$), 15.7–22.7 (C–$\mathbf{C}H_2$), 119.7–121.7 ($\mathbf{C}$–N) ppm. ^{125}Te NMR δ: 21.71 ppm (Te1), −96.05 ppm (Te2 − Te4).

Density functional theory (DFT) calculations were done with the program system TURBOMOLE [14a] employing the Becke–Perdew 86 (BP86) functional [14b,c] with def2-TZVP bases [14d] and respective fitting bases [14e] for the evaluation of the Coulomb matrix. Effective core potentials (ECPs) were used for Te atoms (ECP-28) [14f]. Contour plots were generated with gOpenMol.[14g]

3. Results and discussion

Starting out from our synthetic protocol that proved successful for the generation of keto-functionalized chlorogermanes [15,16], we reacted $GeCl_4$ with acrylonitrile to yield $Cl_3Ge(CH_2)_2CN$ (**1**) in almost quantitative yield after work-up procedure. Further reactions with chalcogenide sources $Na_2S\cdot 9H_20$, Na_2Se, or Na_2Te, respectively, in appropriate solvents (see Materials and Methods section) yielded adamantane-type $[(NC(CH_2)_2Ge)_4Ch_6]$ (Ch = S (**2**), Se [17]) and noradamantane-type $[(NC(CH_2)_2Ge)_4Te_5]$ (**3**), as illustrated in Scheme 1.

Compound **1** crystallizes in the monoclinic space group $P2_1/m$ with two formulae units in the unit cell. Its molecular structure is depicted in Fig. 1. The Ge–Cl and Ge–C bond lengths in **1** (Ge–Cl 2.1232(7), 2.1265(4) Å; Ge–C 1.928(2) Å) are slightly or even noticeably shorter than average values for reported single-bond distances (Ge–Cl 2.150 Å, Ge–C 2.004 Å) [18], whereas the C≡N bond length (1.141(3) Å) is in good agreement with those reported (C_{alk}–C≡N 1.137 Å, C_{ar}–C≡N 1.138 Å; see also below) [18].

Compound **2** crystallizes in the tetragonal space group $I4_1/a$ with four formulae units in the unit cell, depicted in Fig. 2. The comparably short chain length of the organic substituents inhibits intramolecular coordination of the functional group in a C≡N→Sn fashion. Consequently, the adamantane-type cluster architecture is energetically clearly preferred with respect to the isomeric double-decker motif. It should be noted that for Ge/S sesquichalcogenide clusters $[(RGe)_4S_6]$, even potentially back-coordinating ligands do not cause the formation of this isomeric cluster structure, as five-coordinated Ge atoms are disfavored due to sterical restrictions at the R–GeS_3 unit [5,15,16,19]. For this, the adamantane-type