Journal of Organometallic Chemistry 851 (2017) 143–149

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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

Selective synthesis of tetraarylgermanes and triarylgermanium halides

Melanie Wolf, Astrid Falk, Michaela Flock, Ana Torvisco, Frank Uhlig*

Institute of Inorganic Chemistry, Graz University of Technology, Stremayrgasse 9/V, 8010 Graz, Austria

ARTICLE INFO

Article history:
Received 12 July 2017
Received in revised form
15 September 2017
Accepted 16 September 2017
Available online 21 September 2017

Keywords:
Tetraarylgermanes
Triarylgermanium halides
Solid state structure
DFT calculations

ABSTRACT

A series of novel and previously published tetraarylgermanes aryl$_4$Ge (aryl = *m*-tolyl, 3,4-xylyl, 3,5-xylyl, 2-naphthyl) and triarylgermanium halides aryl$_3$GeX (aryl = *o*-tolyl, 2,4-xylyl, 2,5-xylyl, 2,6-xylyl, 1-naphthyl, 2,4,6-mesityl, X = Cl, Br) were synthesized and characterized. All solids were investigated using single crystal X-ray diffractometry in order to elucidate the molecular structures. Effects of the substitution pattern of the aryl residue employed have been studied in terms of the impact on the product formation.

1. Introduction

Despite tetraarylgermanes and organogermanium halides rarely finding straightforward use in direct applications, they represent powerful starting materials for the preparation of other organogermanium compounds [1–3]. Since the synthesis of organogermanium compounds does not follow the usual pattern known for the silicon and tin derivatives, numerous synthetic pathways have been studied thus far, including reactions with organometallic substances such as organolithium or organomagnesium compounds, comproportionation reactions or halogenations starting from organogermanes [2,4–12]. Thus, there is a multiplicity of different methods known, but unfortunately until now, no versatile pathway could be found for the preparation of these compounds, a problem which has been discussed repeatedly in literature [13–15].

Due to our need for different aryl substituted germanium derivatives and the lack of crystallographic data and reliable synthetic pathways, it was our aim to study the influence of the aromatic system on the product formation and behavior of different arylgermanium compounds. Therefore, various organogermanium compounds were synthesized and characterized using NMR, IR, single crystal X-ray and GCMS methods. In all cases, the germanium atom is bonded to at least one aromatic ligand. The ligands were chosen carefully concerning their steric bulkiness, bearing either one or two methyl groups in different positions towards the germanium atom, or include even larger polyaromatic systems presented in Fig. 1.

2. Experimental

2.1. Materials and methods

All reactions, unless otherwise stated, were carried out using standard Schlenk line techniques or in a glovebox under nitrogen atmosphere. All dried and deoxygenated solvents were obtained from a solvent drying system (Innovative Technology Inc.). Germanium tetrachloride was purchased at ABCR and stored under nitrogen. All other chemicals from commercial sources were utilized without further purification. Elemental analysis was performed on an Elementar vario EL or an Elementar vario MICRO cube. Melting point measurements were carried out by threefold determination with a Stuart Scientific SMP 10.

^{1}H (300.2 MHz), ^{13}C (75.5 MHz) NMR spectra were recorded on a Mercury 300 MHz spectrometer from Varian at 25 °C. Chemicals shifts are given in parts per million (ppm) relative to TMS ($\delta = 0$ ppm).

GCMS measurements were carried out on an Agilent Technologies 7890A GC system coupled to an Agilent Technologies 5975C VLMSD mass spectrometer or MS data were collected on a Waters

---

* Corresponding author. 6330 Institute of Inorganic Chemistry, Graz University of Technology, Stremayrgasse 9/V, 8010 Graz, Austria.

E-mail address: frank.uhlig@tugraz.at (F. Uhlig).

http://dx.doi.org/10.1016/j.jorganchem.2017.09.027
0022-328X/

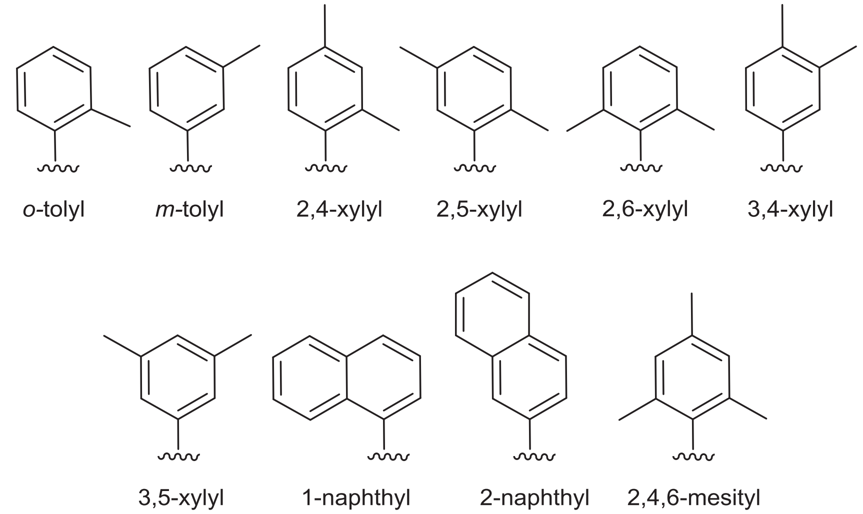

Fig. 1. Aromatic residues employed for the preparation of organogermanium compounds.

GCT Premier with EI ionization.

2.2. Crystal structure determination

All crystals suitable for single crystal X-ray diffractometry were removed from a vial or a Schlenk under N_2 and immediately covered with a layer of silicone oil. A single crystal was selected, mounted on a glass rod on a copper pin, and placed in the cold N_2 stream provided by an Oxford Cryosystems cryostream. XRD data collection was performed on a Bruker APEX II diffractometer with use of an Incoatec microfocus sealed tube of Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) and a CCD area detector. Empirical absorption corrections were applied using SADABS or TWINABS [16,17]. The structures were solved with use of the intrinsic phasing option in SHELXT and refined by the full-matrix least-squares procedures in SHELXL [18–20]. The space group assignments and structural solutions were evaluated using PLATON [21,22]. The solvent of crystallization of toluene for compound 2,4,6-mesityl$_3$GeBr (**10**) and 1-naphthyl$_3$GeBr (**9**) was removed from the refinement by using the "squeeze" option available in the PLATON program suite [23,24]. Non-hydrogen atoms were refined anisotropically. All other hydrogen atoms were located in calculated positions corresponding to standard bond lengths and angles and refined using a riding model. Disorder was handled by modeling the occupancies of the individual orientations using free variables to refine the respective occupancy of the affected fragments (PART) [25]. In some cases, the similarity SAME restraint, the similar-ADP restraint SIMU and the rigid-bond restraint DELU, as well as the constraints EXYZ and EADP were used in modeling disorder to make the ADP values of the disordered atoms more reasonable. In some cases, the distances between arbitrary atom pairs were restrained to possess the same value using the SADI instruction and in some cases distance restraints (DFIX) to certain target values were used. In some tough cases of disorder, anisotropic U^{ij}-values of the atoms were restrained (ISOR) to behave more isotropically. In compound 3,4-xylyl$_4$Ge (**2**), disordered positions for one of the 3,4-xylyl residues were refined using 50/50 positions. For compound 1-naphthyl$_3$GeBr · $CHCl_3$ (**9b**), several restraints and constraints (FRAG 17, AFIX 66) were used to afford idealized naphthalene geometry for one of the naphthyl residues. Compound 2,6-xylyl$_3$GeBr (**8**) was twinned and was refined using the matrix (-1 0 0 0 -1 0 0 0 -1). The main contributions of the two twin components refined to a BASF of 0.02. Compound 1-naphthyl$_3$GeBr · naphthyl (**9c**) was twinned and was refined using the matrix (0 1 0 1 0 0 0 0 -1). The main contributions of the two twin components refined to a BASF of 0.03. CCDC 1546216-1546226 contain the supplementary crystallographic data for compounds **1**-**5**, **7**-**10** respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif. Tables containing crystallographic data and details of measurements and refinement for compounds **1**-**5**, **7**-**10** can be found in Supplementary Information.

2.3. Theoretical calculations

Density functional calculations were performed using the Gaussian09 program package for all calculations at the mPW1PW91 hybrid functional level together with 6-311 + G(d) basis sets [26,27]. All structures were optimized and verified to be minima by vibrational frequency calculations.

2.4. Preparation of aryl$_4$Ge

A flask equipped with a dropping funnel and a reflux condenser was charged with Mg in THF or Et_2O. The dropping funnel was charged with arylbromide in THF or Et_2O, about 10% of the solution was added to the reaction vessel and the solution was heated carefully or dibromoethane was added to start the reaction. The arylbromide was subsequently added dropwise. After complete addition, the reaction was refluxed for 3-12 h. Residual Mg was filtered off using a filter cannula or a Schlenk-frit charged with Celite®. Germanium tetrachloride ($GeCl_4$) in toluene was added slowly to the ethereal Grignard solution at 0 °C. The solution was placed under vacuum and THF removed. In some cases, additional toluene was added. The reaction was stirred for 1 h, heated to reflux for several hours and was subsequently allowed to cool down to room temperature. After quenching with 10% degassed HCl at 0 °C under inert atmosphere, the water layer was washed twice with boiling toluene and the organic layers were dried over Na_2SO_4. After removal of solvent under reduced pressure, the product was washed several times with pentane and purified *via* recrystallization.

***m*-tolyl$_4$Ge (1)**: 10.0 g (411 mmol, 15.4 eq.) Mg in 100 ml Et_2O, 64.3 g (376 mmol, 14.1 eq.) 3-bromotoluene in 50 ml Et_2O, 5.70 g (26.6 mmol, 1.00 eq.) $GeCl_4$ in 60 ml toluene at 0 °C, refluxed for 12 h. The resulting oil was recrystallized from toluene at room temperature to obtain colorless crystals. Yield: 65%. M.p.: 145 °C. Elemental analysis (%) for $C_{28}H_{28}Ge$: C, 76.93; H, 6.46. Found: C, 77.68; H, 6.57. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.13 (m, 16H, ArH), 2.21 (s, 12H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 137.71, 136.34, 136.04, 132.65, 129.93, 128.14, 21.72 (CH_3) ppm. GCMS: Method 1: $t_R = 24.67$ min, *m*/*z*: 438.1 ($M^{+\cdot}$), 347.1 ($M^{+\cdot}$ -*m*-tolyl), 256.0 ($M^{+\cdot}$ - *m*-tolyl$_2$), 165.0 ($M^{+\cdot}$ - *m*-tolyl$_3$) 91.1 ($M^{+\cdot}$ - *m*-tolyl$_3$Ge).

3,4-xylyl$_4$Ge (2): 4.94 g (204 mmol, 13.8 eq.) Mg in 100 ml THF, 34.3 g (185 mmol, 12.5 eq.) 4-bromo-*o*-xylene in 50 ml THF, 3.17 g (14.8 mmol, 1.00 eq.) $GeCl_4$ in 60 ml toluene at 0 °C, refluxed for 3 h. The resulting solid was washed several times with pentane and recrystallized from toluene at -30 °C to obtain colorless crystals. Yield: 76%. M.p.: 172 °C. Elemental analysis (%) for $C_{32}H_{36}Ge$: C, 77.92; H, 7.36. Found: C, 77.95; H, 7.16. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.25 (d, 8H, 5,6- H, ArH), 7.11 (d, 4H, 2-H, ArH), 2.25 (s, 12H, CH_3), 2.20 (s, 12H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 137.44, 136.63, 133.92, 133.26, 129.59, 19.97 (CH_3), 19.96 (CH_3) ppm. GCMS: Method 2: $t_R = 22.90$ min, *m*/*z*: 494.2 ($M^{+\cdot}$), 389.1 ($M^{+\cdot}$ - 3,4-xylyl), 284.1 ($M^{+\cdot}$ - 3,4-xlyl$_2$), 179.0 ($M^{+\cdot}$ - 3,4-xylyl$_3$), 105.1 ($M^{+\cdot}$ - 3,4-xylyl$_3$Ge), 77.1 ($M^{+\cdot}$ - 3,4-xylylGe$_3$Me$_2$).

3,5-xylyl$_4$Ge (3): 10.0 g (411 mmol, 12.5 eq.) Mg in 100 ml THF, 60.9 g (329 mmol, 9.97 eq.) 4-bromo-*o*-xylene in 50 ml THF, 7.04 g (33.0 mmol, 1.00 eq.) $GeCl_4$ in 60 ml toluene at 0 °C, refluxed for 4.5 h. The resulting solid was washed several times with pentane and recrystallized from toluene at -30 °C to obtain colorless crystals. Yield: 70%. M.p.: 195 °C. Elemental analysis (%) for $C_{32}H_{36}Ge$: C, 76.60; H, 7.12. Found: C, 77.92; H, 7.36. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.12 (s, 8H, 2,6-H, ArH), 7.01 (s, 4H, 4-H, ArH), 2.27 (s, 24H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 137.50, 136.55, 133.28, 130.88, 21.64 (CH_3) ppm. GCMS: Method 1: $t_R = 25.49$ min, *m*/*z*: 494.3 ($M^{+\cdot}$), 389.1 ($M^{+\cdot}$ - 3,5-xylyl), 284.1 ($M^{+\cdot}$ - 3,5-xlyl$_2$), 179.0 ($M^{+\cdot}$ - 3,5-xylyl$_3$), 105.1 ($M^{+\cdot}$ - 3,5-xylyl$_3$Ge), 77.1 ($M^{+\cdot}$ - 3,5-xylylGe$_3$Me$_2$).

2-naphthyl$_4$Ge (4): 3.23 g (133 mmol, 5.50 eq.) Mg in 100 ml THF, 25 g (121 mmol, 5.00 eq.) 2-bromonaphthalene in 50 ml THF, 5.17 g (24.1 mmol, 1.00 eq.) $GeCl_4$ in 60 ml toluene at 0 °C, refluxed for 3 h. The resulting solid was washed several times with pentane and recrystallized from toluene at -30 °C to obtain colorless crystals. Yield: 68%. M.p.: 190 °C. Elemental analysis (%) for $C_{40}H_{28}Ge$: C, 82.65; H, 4.86. Found: C, 82.11; H, 4.82. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.12 (s, 4H, 1-H, ArH), 7.87 (d, 4H, 3-H, ArH), 7.85 (d, 4H, 4-H, ArH), 7.74 (t, 8H, 5,8-H, ArH), 7.48 (m, 8H, 6,7-H, ArH) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 136.47, 134.01, 133.78, 133.47, 131.80, 128.35, 128.02, 127.86, 126.78, 126.26 ppm. DI/MS EI *m*/*z*: 582.14 ($M^{+\cdot}$), 455.1 ($M^{+\cdot}$ - 2-naphthyl), 328.1 ($M^{+\cdot}$ -2-naphthyl$_2$), 201.0 ($M^{+\cdot}$ -2-naphthyl$_3$).

2.5. *Preparation of aryl$_3$GeX (X = Cl, Br)*

A flask equipped with a dropping funnel and a reflux condenser was charged with Mg in THF or Et_2O. The dropping funnel was charged with arylbromide in THF, about 10% of the solution was added to the reaction vessel and the solution was heated carefully or dibromoethane was added to start the reaction. The arylbromide was subsequently added dropwise. After complete addition, the reaction was refluxed for 3-12 h. Residual Mg was filtered off using a filter cannula or a Schlenk-frit charged with Celite®. Germanium tetrachloride ($GeCl_4$) in toluene was added slowly to the Grignard solution at 0 °C. The solution was placed under vacuum and THF removed. In some cases, additional toluene was added. The reaction was stirred for 1 h, heated to reflux for several hours and was subsequently allowed to cool down to room temperature. After quenching with 10% degassed HCl at 0 °C under inert atmosphere, the water layer was washed twice with boiling toluene and the organic layers were dried over Na_2SO_4. After removal of solvent under reduced pressure, the product was washed several times with pentane and purified *via* recrystallization or condensation.

***o*-tolyl$_3$GeX (5)**: 6.00 g (247 mmol, 12.2 eq.) Mg in 80 ml THF, 38.4 g (224 mmol, 11.1 eq.) 2-bromotoluene in 50 ml THF, 4.32 g (20.2 mmol, 1.00 eq.) $GeCl_4$ in 60 ml toluene at 0 °C. The resulting colorless solid (15-22% *o*- tolyl$_3$GeCl, 78-85% *o*-tolyl$_3$GeBr) was recrystallized from toluene at -30 °C to obtain colorless crystals. Yield: 85%. Elemental analysis (%) for $C_{21}H_{21}GeX$: Cl: C, 66.12; H, 5.55. Br: C, 59.22; H, 4.92. Found: C, 60.70; H, 4.92. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.46 (d, 3H, 6-H, ArH), 7.36 (t, 3H, 3-H, ArH), 7.21 (m, 6H, 4,5-H, ArH), 2.35 (s, 9H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 143.89, 135.15, 130.98, 130.84, 126.00, 23.42 (CH_3) ppm. GCMS: Method 2: Cl: $t_R = 18.25$ min, *m*/*z*: 382.1 ($M^{+\cdot}$), 347.1 ($M^{+\cdot}$ - Cl), 290.1 ($M^{+\cdot}$ - *o*-tolyl), 255.1 ($M^{+\cdot}$ - *o*-tolylCl), 199.0 ($M^{+\cdot}$ - *o*-tolyl$_2$), 181.1 ($M^{+\cdot}$ -*o*-tolylGeCl), 165.1 ($M^{+\cdot}$ - *o*-tolyl$_2$Cl), 91.1 ($M^{+\cdot}$ - *o*-tolyl$_2$GeCl). Br: $t_R = 18.87$ min, *m*/*z*: 426.0 ($M^{+\cdot}$), 347.1 ($M^{+\cdot}$ -Br), 334.0 ($M^{+\cdot}$ - *o*-tolyl), 255.0 ($M^{+\cdot}$ -*o*-tolylCl), 243.9 ($M^{+\cdot}$ -*o*-tolyl$_2$), 181.1 ($M^{+\cdot}$ - *o*-tolylGeCl), 165.1 ($M^{+\cdot}$ - *o*-tolyl$_2$Br), 91.1 ($M^{+\cdot}$ - *o*-tolyl$_2$GeBr).

2,4-xylyl$_3$GeX (6): 10.00 g (411 mmol, 11.0 eq.) Mg in 200 ml THF, 69.2 g (374 mmol, 10.0 eq.) 4-bromo-*m*-xylene in 100 ml THF, 8.00 g (37.4 mmol, 1.00 eq.) $GeCl_4$ in 100 ml toluene at 0 °C. A brown slurry was obtained (74-80% 2,4-xylyl$_3$GeCl, 26-20% 2,4-xylyl$_3$GeBr). After several crystallization attempts, 2,4-xylyl$_3$GeCl was obtained as a colorless liquid. Yield: 72%. Elemental analysis (%) for $C_{24}H_{27}GeCl$: Cl: C, 68.06; H, 6.43. Found: C, 67.97; H, 6.35. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.30 (d, 3H, 6-H, ArH), 7.07 (s, 3H, 3-H, ArH), 6.99 (d, 3H, 2-H, ArH), 2.33 (s, 9H, CH_3), 2.30 (s, 9H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 143.83, 140.77, 135.02, 131.78, 131.39, 126.70, 23.17 (CH_3), 21.59 (CH_3) ppm. GCMS: Method 2: Cl: $t_R = 20.15$ min, *m*/*z*: 424.1 ($M^{+\cdot}$), 389.1 ($M^{+\cdot}$ - Cl), 318.1 ($M^{+\cdot}$- 2,4-xylyl), 281.1 ($M^{+\cdot}$ - 2,4-xylylCl), 209.2 ($M^{+\cdot}$ - 2,4-xylylGeCl), 179.1 ($M^{+\cdot}$ - 2,4-xylyl$_2$Cl), 105.0 ($M^{+\cdot}$ - 2,4-xylyl$_2$GeCl), 77.1 ($M^{+\cdot}$ - 2,4-xylyl$_2$GeCl(CH_3)$_2$).

2,5-xylyl$_3$GeX (7): 2.74 g (113 mmol, 5.70 eq.) Mg in 100 ml THF, 19.0 g (102 mmol, 5.20 eq.) 2-bromo-*p*-xylene in 50 ml THF, 4.50 g (19.7 mmol, 1.00 eq.) $GeCl_4$ in 60 ml toluene at 0 °C. The resulting colorless solid (16-50% 2,5- xylyl$_3$GeCl, 50-84% 2,5-xylyl$_3$GeBr) was recrystallized from toluene at -30 °C to obtain colorless crystals. Yield: 65-70%. Elemental analysis (%) for $C_{24}H_{27}GeX$: Cl: C, 68.06; H, 6.43. Br: C, 61.59; H, 5.82. Found: C, 62.97; H, 5.89. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.28 (s, 3H, 6-H, ArH), 7.14 (d, 6H, 3,4-H, ArH), 2.29 (s, 9H, CH_3), 2.25 (s, 9H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 140.59, 135.66, 135.28, 134.24, 131.52, 130.80, 22.88 (CH_3), 21.27 (CH_3) ppm. GCMS: Method 2: Cl: $t_R = 18.80$ min, *m*/*z*: 424.1 ($M^{+\cdot}$), 389.1 ($M^{+\cdot}$ - Cl), 318.0 ($M^{+\cdot}$- 2,5-xylyl), 283.1 ($M^{+\cdot}$ - 2,5-xylylCl), 209.1 ($M^{+\cdot}$ - 2,5-xylylGeCl), 179.1 ($M^{+\cdot}$ - 2,5-xylyl$_2$Cl), 105.1 ($M^{+\cdot}$ - 2,5-xylyl$_2$GeCl), 91.1 ($M^{+\cdot}$ - 2,5-xylyl$_2$GeClCH_3), 77.1 ($M^{+\cdot}$ - 2,5-xylyl$_2$GeCl(CH_3)$_2$) Br: $t_R = 19.31$ min, *m*/*z*: 468.1 ($M^{+\cdot}$), 389.1 ($M^{+\cdot}$ - Br), 362.0 ($M^{+\cdot}$ - 2,5-xylyl), 283.1 ($M^{+\cdot}$ - 2,5-xylylBr), 256.9 ($M^{+\cdot}$ - 2,5-xylyl$_2$), 209.1 ($M^{+\cdot}$ - 2,5-xylylGeBr), 179.1 ($M^{+\cdot}$ - 2,5-xylyl$_2$Br), 105.1 ($M^{+\cdot}$ - 2,5-xylyl$_2$GeBr), 91.1 ($M^{+\cdot}$ - 2,5-xylyl$_2$GeClCH_3), 77.1 ($M^{+\cdot}$ - 2,5-xylyl$_2$GeBr(CH_3)$_2$).

2,6-xylyl$_3$GeX (8): 10.00 g (411 mmol, 6.85 eq.) Mg in 100 ml THF, 69.2 g (374 mmol, 6.00 eq.) 2-bromo-*m*-xylene in 150 ml THF, 12.85 g (60.0 mmol, 1.00 eq.) $GeCl_4$ in 60 ml toluene at 0 °C. The resulting solid was recrystallized from toluene at -30 °C to obtain colorless crystals (17-21% 2,6-xylyl$_3$GeCl, 79-83% 2,6-xylyl$_3$GeBr). Yield: 55-70%. Elemental analysis (%) for $C_{24}H_{27}GeX$: Cl: C, 68.06; H, 6.43. Br: C, 61.59; H, 5.82. Found: C, 62.17; H, 5.95. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.19 (t, 3H, 4-H, ArH), 7.00 (d, 6H, 3,5-H, ArH), 2.31 (s, 18H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 143.60, 140.32, 129.89, 129.10, 25.19 (CH_3) ppm. GCMS: Method 2: Cl: $t_R = 19.92$ min, *m*/*z*: 424.1 ($M^{+\cdot}$), 389.1 ($M^{+\cdot}$ - Cl), 283.1 ($M^{+\cdot}$ - 2,6-xylylCl), 209.1 ($M^{+\cdot}$ - 2,6-xylylGeCl), 179.1 ($M^{+\cdot}$ - 2,6-xylyl$_2$Cl), 105.1 ($M^{+\cdot}$ - 2,6-xylyl$_2$GeCl), 77.1 ($M^{+\cdot}$ - 2,6-xylyl$_2$GeCl(CH_3)$_2$). Br:

$t_R = 20.57$ min, m/z: 468.1 ($M^{+\cdot}$), 389.1 ($M^{+\cdot}$ - Br), 362.0 ($M^{+\cdot}$ - 2,6-xylyl), 283.1 ($M^{+\cdot}$ - 2,6-xylylBr), 256.9 ($M^{+\cdot}$ - 2,6-xylyl$_2$), 209.1 ($M^{+\cdot}$ - 2,6-xylylGeBr), 179.1 ($M^{+\cdot}$ - 2,6-xylyl$_2$Br), 105.1 ($M^{+\cdot}$ -2,6-xylyl$_2$GeBr), 77.1 ($M^{+\cdot}$ - 2,6-xylyl$_2$GeBr(CH_3)$_2$).

1-naphthyl$_3$GeX (9): 8.00 g (329 mmol, 6.85 eq.) Mg in 70 ml THF, 61.9 g (299 mmol, 6.23 eq.) 1-bromonaphthalene in 200 ml THF, filtered hot over Celite® using a Schlenk frit. 10.3 g (48.0 mmol, 1.00 eq.) $GeCl_4$ in 60 ml toluene at RT. The resulting solid (10-35% 1-naphthyl$_3$GeCl, 65-90% 1- naphthyl$_3$GeBr) was washed several times with pentane and toluene and recrystallized from toluene, chloroform and THF at -30 °C to obtain colorless crystals of 1-naphthyl$_3$GeCl or 1- naphthyl$_3$GeBr, which were used for further analysis. Yield: 50-65%. Elemental analysis (%) for $C_{30}H_{21}$GeX: Br: C, 67.47; 3.96 H, 4.32. Found: C, 68.07; H, 3.96. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.28 (d, 3H, 8-H, ArH), 7.98 (d, 3H, 2-H, ArH), 7.90 (d, 3H, 4-H, ArH), 7.73 (d, 3H, 5-H, ArH), 7.47 (t, 3H, 7-H, ArH), 7.36 (m, 6H, 3,6-H, ArH) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 136.06, 135.45, 134.19, 133.30, 131.79, 129.10, 128.98, 126.58, 126.32, 125.48 ppm. GCMS: Method 2: Cl: $t_R = 29.02$ min, m/z: 490.1 ($M^{+\cdot}$), 455.1 ($M^{+\cdot}$ - Cl), 363.0 ($M^{+\cdot}$ - 1-naphthyl), 252.1 ($M^{+\cdot}$ - 1-naphthylGeCl), 127.1 ($M^{+\cdot}$ - 1-naphthyl$_2$GeCl), 77.1 ($M^{+\cdot}$ - 1-naphthyl$_2$GeCl(C_4H_4)). Br: $t_R = 30.55$ min, m/z: 534.0 ($M^{+\cdot}$), 455.1 ($M^{+\cdot}$ - Br), 406.9 ($M^{+\cdot}$ -1-naphthyl), 327.0 ($M^{+\cdot}$ -1-naphthylBr), 252.1 ($M^{+\cdot}$ - 1-naphthylGeBr), 201.0 ($M^{+\cdot}$ -1-naphthyl$_2$Br), 127.1 ($M^{+\cdot}$ -1-naphthyl$_2$GeBr), 77.1 ($M^{+\cdot}$ - 1-naphthyl$_2$GeBr(C_4H_4)).

2,4,6-mesityl$_3$GeX (10): 7.50 g (309 mmol, 8.80 eq.) Mg in 70 ml THF, 55.9 g (281 mmol, 8.00 eq.) 2-bromo-1,3,5-trimethylbenzene in 300 ml THF, 7.52 g (35.1 mmol, 1.00 eq.) $GeCl_4$ in 100 ml toluene at RT. The resulting solid (25-40% 2,4,6-mesityl$_3$GeCl, 60-75% 2,4,6-mesityl$_3$GeBr) recrystallized from toluene at -30 °C to obtain colorless crystals of 2,4,6-mesityl$_3$GeBr. Yield: 55-65%. Elemental analysis (%) for $C_{30}H_{21}$GeX: Cl: C, 69.65; H, 7.14. Br: C, 63.58; H, 6.52. Found: C, 67.56; H, 6.97. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.78 (s, 6H, 3,5-H ArH), 2.24 (s, 9H, CH_3), 2.13 (s, 18H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 143.78, 138.32, 135.0, 128.89, 23.72, 21.20 ppm. GCMS: Method 2: Cl: $t_R = 29.02$ min, m/z: 466.1 ($M^{+\cdot}$), 431.1 ($M^{+\cdot}$ - Cl), 346.10 ($M^{+\cdot}$ - 2,4,6-mesityl), 237.2 ($M^{+\cdot}$ - 2,4,6-mesitylGeCl), 228.0 ($M^{+\cdot}$ - 12,4,6-mesityl$_2$), 119.1 ($M^{+\cdot}$ - 2,4,6-mesityl$_2$GeCl). Br: $t_R = 21.84$ min, m/z: 510.1 ($M^{+\cdot}$), 431.2 ($M^{+\cdot}$ - Br), 390.1 ($M^{+\cdot}$ - 2,4,6-mesityl), 311.1 ($M^{+\cdot}$ - 2,4,6-mesitylBr), 270.9 ($M^{+\cdot}$ - 2,4,6-mesityl$_2$), 237.2 ($M^{+\cdot}$ - 2,4,6-mesitylGeBr), 119.1 ($M^{+\cdot}$ - 2,4,6-mesityl$_2$GeBr).

3. Results and discussion

3.1. Synthesis and theoretical calculations

As previously mentioned, the most commonly used methods for the introduction of an aryl residue onto a metal center is the employment of Grignard or organolithium reagents [2,9–11]. In a typical Grignard reaction, excess of magnesium is reacted with an arylhalide in order to yield the corresponding Grignard reagent, which can be further reacted with a proportion of metal halide to yield the desired product. This is valid to some extent for other group 14 elements and smaller ligands [28]. However, in the case of organogermanium compounds bearing larger substituents, this route entails various disadvantages independent of the stoichiometry used [4–8,28]. These drawbacks include the formation of mixtures, from which the desired product is very difficult or in some cases impossible to separate, long and challenging work-up procedures and low yields, and as a consequence, cost intensive preparation over a number of steps [11].

In all cases, for the preparation of desired aryl substituted germanium compounds, the same Grignard method was employed (Fig. 2). A slight excess of magnesium was used for the Grignard reaction and removed *via* filtration before further reaction with $GeCl_4$, in order to avoid the formation of digermanes as described by Glockling et al. [29]. $GeCl_4$ in toluene was then added to the Grignard solution. When necessary, the reaction mixture was refluxed for at least 1 h, or stirred overnight at room temperature. After the reaction was complete, the mixture was quenched under acidic conditions and the organic layers were worked up. After removal of solvents and purification steps, products were crystallized from toluene either at lower temperatures or *via* evaporation techniques.

$$\text{aryl-Br} + \text{Mg} \xrightarrow{\text{Et}_2\text{O/ THF}} \text{aryl-Mg-Br} \xrightarrow[\text{toluene}]{+\ \text{GeX}_4} \text{aryl}_n\text{GeX}_{4-n}$$

Fig. 2. Grignard route for the preparation of aryl$_4$Ge and aryl$_3$GeX for R = *o*-tolyl (**5**), *m*-tolyl (**1**), 2,4-xylyl (**6**), 2,5-xylyl (**7**), 2,6-xylyl (**8**), 3,4-xylyl (**2**), 3,5-xylyl (**3**), 1-naphthyl (**9**) and 2-naphthyl (**4**).

For the synthesis of all presented tetraarylgermanes and triarylgermanium halides, varying excesses of Grignard reagent were employed. In some cases, very large excesses of Grignard reagent were used (14–10 equivalents of Grignard reagent to germanium halide) and were thought to be necessary in order to provide the tetraarylgermanes in high yields. However, we determined that ratios as low as 5:1 Grignard reagent to germanium halide were sufficient to provide acceptable yields. Following this pathway for 3,4-xylyl (**2**), 3,5-xylyl (**3**) and 2-naphthyl (**4**) residues, the tetraarylgermanes were obtained as has been reported for phenyl, *m*-tolyl (**1**) and *p*-tolyl moieties (Fig. 3). However, expanding these experiments to *o*-tolyl (**5**), did not result in formation of tetraarylgermanes, but rather the triarylgermanium halides, as was reported by Simons et al. [7]. Takeuchi et al. claimed to prepare *o*-tolyl$_4$Ge using the Grignard route, however this could not be reproduced within the course of this work [30]. It should be mentioned that it is possible to prepare *o*-tolyl$_4$Ge over other preparation pathways, *i.e.* by reacting the Grignard reagent with zinc chloride, forming the arylzinc, which can be further reacted with $GeCl_4$, although the formation of mixtures is observed [2].

In order to determine whether the formation of the product is determined by the size of the ligand or the substitution pattern of the aryl residue, two naphthyl moieties, distinguishable concerning their substitution pattern, were employed. Interestingly, while the 2-naphthyl moiety led to the formation of the tetraarylgermane (**4**), the 1-naphthyl residue once again lead to the formation of the triarylgermanium halide (**9**), thus indicating, that the substitution pattern and thus the orientation of the substituent plays a more important role on the number of residues that can accommodate around the germanium metal as compared to the size of the ligand. While other preparation pathways were conducted for the preparation of 1-naphthyl$_3$GeX (X = Cl, Br), the results were inconclusive [31]. In 1952, West reported that all attempts to synthesize 1-naphthyl$_4$Ge over organolithium or Grignard reagents were unsuccessful, agreeing with the results of this work. Interestingly, reaction of 1-naphthylLi with 1-naphthyl$_3$GeBr gave small amounts of 1-naphthyl$_4$Ge [32]. Preparation became very difficult upon employment of the 1-naphthyl residue due to solubility reasons and thus proved to be a time intensive preparation. Higher amounts of solvents had to be used to prevent solidification of the Grignard reagent. Moreover, the Grignard reagent was never allowed to cool to room temperature before reaction with germanium tetrahalide, thus cannulated hot or filtered off using a hot Schlenk frit. Work up procedures were rather challenging due to the fact that free naphthalene was present in most cases, which could not be removed upon sublimation due to the instability of the desired product. Nevertheless, extraction using a mixture of solvents including toluene and pentane was helpful for removal of side

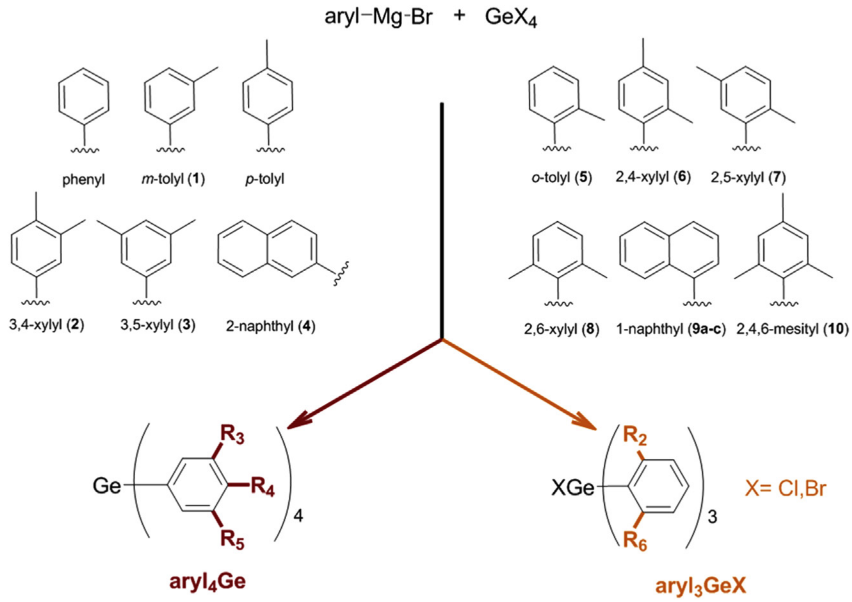

Fig. 3. Influence of substituent position on the aryl residue on product formation using the Grignard route for aryl = phenyl [9,10,38], *o*-tolyl (**5**) [2], *m*-tolyl (**1**) [2], *p*-tolyl [2], 2,4-xylyl (**6**), 2,5-xylyl (**7**) [35,36], 2,6-xylyl (**8**) [34], 3,4-xylyl (**2**), 3,5-xylyl (**3**), 1-naphthyl (**9a-c**) [31], 2-naphthyl (**4**), 2,4,6-mesityl (**10**) [34].

products.

Expanding this research to subsequently higher substituted residues such as 2,4-xylyl, 2,5-xylyl, 2,6-xylyl, the effect of the substitution pattern becomes even more apparent. While 3,4-xylyl (**2**) and 3,5-xylyl (**3**) exclusively yielded the tetraarylgermane, the 2,4-xylyl (**6**), 2,5-xylyl (**7**), 2,6-xylyl (**8**) residues lead to the formation of the triarylgermanium halide without any side products present [33–36]. Therefore, it can be concluded that the number of residues around the germanium central atom is controlled by the position of the substituents on the aryl residue used [37]. A sterically demanding substituent, i.e. the methyl group, on at least one *ortho* position results in preferred formation of triarylgermanium halides rather than the tetraarylgermane derivatives. Dumler et al. observed similar results for the preparation of 2,5-xylyl$_3$GeBr [35]. This is also supported by the fact, that in both cases, the 2,6-xylyl (**8**) and also the previously reported larger 2,4,6-mesityl (**10**) residue the expected triarylgermanium halide was obtained [33,34,37].

Compulsory approximations, namely DFT calculations, were conducted and compared to the results by direct means confirming that the outcome of the reaction indeed depends on the steric bulk of the ligand used. The reaction mechanism was investigated and the reaction enthalpies ΔH were calculated ($\Delta H = H(\text{aryl}_4\text{Ge}) + H(\text{MgBr}_2) - H(\text{aryl}_3\text{GeBr}) - H(\text{arylMgBr})$) (Fig. 4, Table 1).

It can be observed in Table 1 that the reaction enthalpy varies in value depending on the functional group introduced. It was possible to isolate and even recrystallize all systems showing a reaction enthalpy higher than -100 kJ/mol over the Grignard route. In contrast, all reactions showing lower values ($\Delta H < -100$ kJ/mol) seemed to stop at the trisubstituted stage and the triarylgermanium halide was formed. Therefore, DFT calculations support the observation that formation of tetraarylgermanes is highly dependent on the substituent position of the residue used, since with increasing steric demand around the metal center, the reaction enthalpy decreases noticeably, showing the lowest value for the crowded 2,6-xylyl$_4$Ge.

$$\text{aryl}_3\text{GeBr} + \text{arylMgBr} \xrightarrow{\qquad} \text{aryl}_4\text{Ge} + \text{MgBr}_2$$

Fig. 4. Base reaction for the calculation of the enthalpies ΔH, in dependence of the aryl substituents.

Table 1
DFT calculated reaction enthalpy ΔH values in kJ/mol for the preparation of aryl$_4$Ge in dependence of the aryl substituent.

aryl	ΔH (kJ/mol)
2-naphthyl	−103.5
phenyl	−102.9
m-tolyl	−102.4
3,5-xylyl	−102.3
3,4-xylyl	−101.4
2,5-xylyl	−90.5
1-naphthyl	−85.5
o-tolyl	−68.0
2,4-xylyl	−54.1
2,4,6-mesityl	−41.5
2,6-xylyl	−36.0

In the case of the triarylgermanium halides, occurrence of halogen-metal exchange presents another complication, a problem that was reported for other group 14 elements as well [1–3]. Nevertheless, it must be mentioned that separation and characterization of aryl$_3$GeX (X = Cl, Br) proves to be very difficult using standard techniques. While this might be problematic, this issue could be neglected since halide mixtures of aryl$_3$GeX (X = Cl, Br) could be used as educts for subsequent reactions.

3.2. X-ray crystallography

All solid compounds were characterized using single X-ray crystallography. Crystallization from toluene at low temperatures or *via* evaporation techniques worked best in most cases, with the exception of 2,4-xylyl$_3$GeX (**6**) (X = Cl, Br) which was a brown oil from which it was not possible to obtain a crystal structure and 1-naphthyl$_3$GeBr (**9a-c**) which cocrystallizes with various recrystallization solvents.

Compounds *m*-tolyl$_4$Ge (**1**), 3,4-xylyl$_4$Ge (**2**), 3,5-xylyl$_4$Ge (**3**) and 2-naphthyl$_4$Ge (**4**) (Fig. 5) are comparable to previously

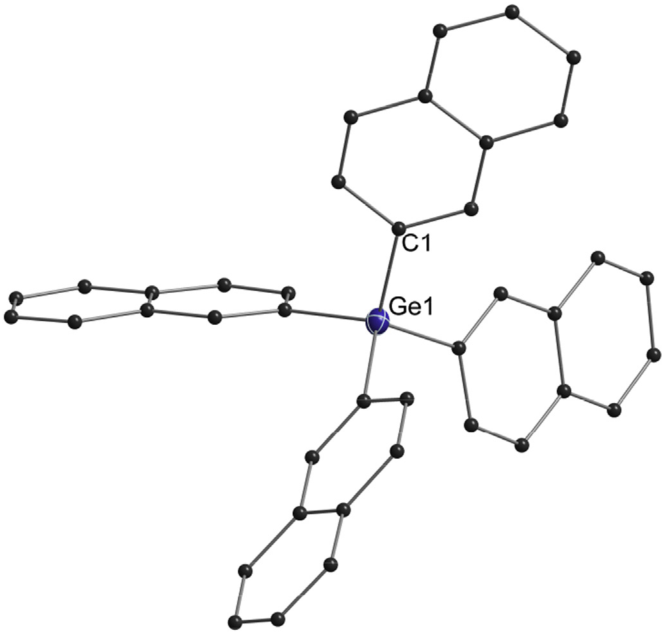

Fig. 5. Crystal structure of 2-naphthyl$_4$Ge (**4**). All non-carbon atoms shown as 50% shaded ellipsoids. Hydrogen atoms removed for clarity.

reported tetraaryl substituted germanes (Table 2). Each molecule is in a near tetrahedral environment with average C–Ge–C angles of 109°. With respect to averaged Ge–C bond lengths, these fall within a narrow range of 1.94–1.96 Å and are not affected by the degree of bulkiness afforded by the organic substituent onto the germanium atom.

3.3. *Triarylgermanium bromides or aryl$_3$GeBr*

In contrast to the tetraarylgermanes, the substituent position on the residue around the central germanium atom in the triarylgermanium derivatives does seem to have an effect on averaged Ge–C bond lengths (Table 3). As compared to phenyl$_3$GeBr (1.934(1) Å) [44], a slight increase in the average Ge–C bond lengths is seen for *o*-tolyl$_3$GeBr (**5**) (1.947(2) Å) and 2,5-xylyl$_3$GeBr (**7**) (1.948(2) Å) due to the presence of substituents on the *ortho* position of the aryl residue.However, with the increase of steric bulk around the germanium center due to methyl groups at both the 2- and 6 positions of the aryl residue, this bond elongation becomes more pronounced, with averaged Ge–C distances of 1.977(3) Å in 2,6-xylyl$_3$GeBr (**8**) and 1.971(6) Å in 2,4,6-mesityl$_3$GeBr (**10**). Finally, as expected, the larger ^{t}butyl substituent on the *ortho* position of the aryl residue in 2-^{t}butylphenylGe$_3$Br causes the longest Ge–C bond length of 1.997(2) Å [45]. Consequently, 2-^{t}butylphenylGe$_3$Br displays a wider C–Ge–Br angle of 110.66(6)° and narrower C–Ge–C angle of 108.26(6)°, whereas all other molecules display wider C–Ge–C angles than C–Ge–Br angles, highlighting the steric strain from the ^{t}butyl substituent of the aryl residue on the central germanium atom environment [45]. This increased steric bulk around the germanium center is also manifested by an increased Ge–Br bond in 2-^{t}butylphenylGe$_3$Br (2.362(1) Å) and 2,4,6-mesityl$_3$GeBr (10) (2.364(4) Å) as compared to phenyl$_3$GeBr (2.318(7) Å) [44,45].

Curiously, all three trinaphthylgermanium bromides crystallize in the presence of either a solvent of crystallization as seen for 1-naphthyl$_3$GeBr · toluene (**9a**), 1-naphthyl$_3$GeBr · CHCl$_3$ (**9b**), or with a naphthyl molecule as seen in 1-naphthyl$_3$GeBr · naphthalene (**9c**) (Fig. 6) This highlights the inherent difficulties with isolating naphthyl derivatives of germanium. Both Ge–C and Ge–Br bond lengths do not seem to be affected by the solvent of crystallization or cocrystallized naphthyl molecule, and compare well to other triarylgermanium bromides with aryl residues substituted at the *ortho* position.

4. Conclusion

Tetraarylgermanes and triarylgermanium halides were prepared and fully characterized to gather new information on this challenging compound class. Aryl residues with different steric demands were applied, having *ortho*, *meta* or *para* substitution on the phenyl ring, as is the case for *o*-tolyl, *m*-tolyl, 2,4-xylyl, 2,5-

Table 2
List of selected bond lengths and angles for selected tetraaryl substituted germanes.

		Space Group	Ge–C (Å) (avg.)	C–Ge–C (°) (avg.)
	phenyl$_4$Ge [39–41]	$P\text{-}42_1c$	1.960(2)	109.5(2)
	o-tolyl$_4$Ge [2,42]	$P\text{-}1$	1.954(4)	109.5(2)
1	*m*-tolyl$_4$Ge [2]	$I4_1/a$	1.956(3)	109.47(9)
	p-tolyl$_4$Ge [43]	Pc	1.949(5)	109.5(2)
2	3,4-xylyl$_4$Ge	$P2_1/c$	1.943(7)	109.45(9)
3	3,5-xylyl$_4$Ge	$P2/c$	1.953(2)	109.48(9)
4	2-naphthyl$_4$Ge	$P2_1/n$	1.953(2)	109.47(6)

Table 3
List of selected bond lengths and angles for selected triaryl substituted germanium bromides.

		Space Group	Ge–C (Å) (avg.)	Ge–Br (Å)	C–Ge–C (°) (avg.)	C–Ge–Br (°) (avg.)
	phenyl$_3$GeBr [44]	$P2_1/c$	1.934(1)	2.318(7)	112.4(4)	106.3(4)
5	*o*-tolyl$_3$GeBr	$P2_1/c$	1.947(2)	2.339(3)	111.79(8)	107.05(5)
7	2,5-xylyl$_3$GeBr	$P2_1/c$	1.948(2)	2.357(4)	113.11(10)	105.50(7)
8	2,6-xylyl$_3$GeBr	$P\text{-}1$	1.977(3)	2.345(5)	115.01(14)	103.12(10)
9a	1-naphthyl$_3$GeBr · toluene	$R\text{-}3$	1.946(5)	2.346(4)	110.84(7)	108.07(7)
9b	1-naphthyl$_3$GeBr · CHCl$_3$	$P\text{-}1$	1.945(6)	2.346(8)	111.67(19)	107.18(17)
9c	1-naphthyl$_3$GeBr · naphthalene	$R\text{-}3$	1.946(3)	2.357(5)	111.03(13)	107.86(9)
10	2,4,6-mesityl$_3$GeBr	$P\text{-}1$	1.971(6)	2.364(4)	115.28(2)	102.77(4)
	2-^{t}butylphenylGe$_3$Br [45]	$R\text{-}3$	1.997(2)	2.362(1)	108.26(6)	110.66(6)

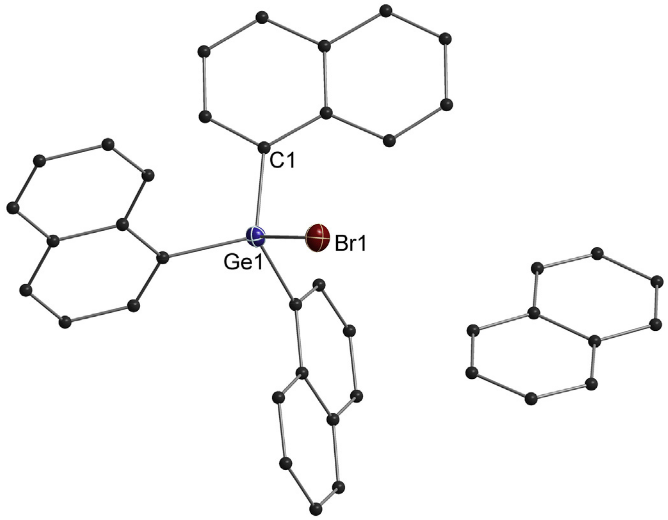

Fig. 6. Crystal structure of 1-naphthyl$_3$GeBr • naphthalene (**9c**). All non-carbon atoms shown as 50% shaded ellipsoids. Hydrogen atoms removed for clarity.

xylyl, 2,6-xylyl, 3,4-xylyl and 3,5-xylyl or even larger polyaromatic systems such as 1-naphthyl, 2-naphthyl and 2,4,6-mesityl.

The synthesis of tetraarylgermanes and triarylgermanium halides could be achieved by preparation of the corresponding Grignard and subsequent reaction with a germanium tetrahalide. It could be shown that excess of Grignard reagent towards germanium halides lead exclusively to either the tetraarylgermane compound or the triarylgermanium halide derivative. Thus, depending on the aryl residue substitution pattern and thus the steric demand afforded by the ligand, the number of aryl residues around the germanium central atom can be controlled. This confirmed by DFT compulsory approximations supporting previously made observations by experimental methods and previous publications.

Presented solid aryl substituted germanes and germanium halides have been fully characterized with X-ray crystallography. The effects of aryl residue substitution pattern and thus steric bulk on the germanium metal environment was discussed. All trinaphthylgermanium halide derivatives crystallize in the presence of either a solvent of crystallization as seen for 1-naphthyl$_3$GeBr · toluene (**9a**), 1-naphthyl$_3$GeBr · $CHCl_3$ (**9b**), or with a naphthyl molecule as seen in 1-naphthyl$_3$GeBr · naphthalene (**9c**). This highlights the inherent difficulties with isolating naphthyl derivatives of germanium.

Acknowledgements

This work was supported by the NAWI Graz project, a collaboration between the Graz University of Technology and the Graz University.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jorganchem.2017.09.027.

References

[1] P. Brown, M.F. Mahon, K.C. Molloy, J. Organomet. Chem. 435 (1992) 265–273.
[2] J.K. Simons, E.C. Wagner, J.H. Muller, J. Am. Chem. Soc. 55 (1933) 3705–3712.
[3] U. Krueerke, E. Wittouck, Chem. Ber. 95 (1962) 174–182.
[4] J.A. Cooke, C.E. Dixon, M.R. Netherton, G.M. Kollegger, K.M. Baines, Synthesis and Reactivity in Inorganic and Metal-organic Chemistry 26, 1996, pp. 1205–1217.
[5] M.A. Chaubon, B. Dittrich, J. Escudie, H. Ramdane, H. Ranaivonjatovo, J. Satge, Synth. React. Inorg. Met.-Org. Chem. 27 (1997) 519–533.
[6] C.R. Samanamu, C.R. Anderson, J.A. Golen, C.E. Moore, A.L. Rheingold, C.S. Weinert, J. Organomet. Chem. 696 (2011) 2993–2999.
[7] M.L. Amadoruge, E.K. Short, C. Moore, A.L. Rheingold, C.S. Weinert, J. Organomet. Chem. 695 (2010) 1813–1823.
[8] S.P. Komanduri, F.A. Shumaker, K.D. Roewe, M. Wolf, F. Uhlig, C.E. Moore, A.L. Rheingold, C.S. Weinert, Organometallics 35 (2016) 3240–3247.
[9] G.T. Morgan, H.D.K. Drew, J. Chem. Soc. Trans. 127 (1925) 1760–1768.
[10] C.A. Kraus, L.S. Foster, J. Am. Chem. Soc. 49 (1927) 457–467.
[11] D.M. Harris, W.H. Nebergall, O.H. Johnson, Inorg. Synth. 5 (1957) 70–72.
[12] S.N. Bhattacharya, P. Raj, R.C. Srivastava, J. Organomet. Chem. 105 (1976) 45–49.
[13] E.K. Schrick, T.J. Forget, K.D. Roewe, A.C. Schrick, C.E. Moore, J.A. Golen, A.L. Rheingold, N.F. Materer, C.S. Weinert, Organometallics 32 (2013) 2245–2256.
[14] O.H. Johnson, D.M. Harris, J. Am. Chem. Soc. 72 (1950) 5564–5566.
[15] S. Roller, D. Simon, M. Draeger, J. Organomet. Chem. 301 (1986) 27–40.
[16] Bruker, Bruker AXS Inc., Madison, Wisconsin, USA, 2012.
[17] R. Blessing, Acta Crystallogr. Sect. A 51 (1995) 33–38.
[18] G. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467–473.
[19] G. Sheldrick, Acta Crystallogr. Sect. A 64 (2008) 112–122.
[20] G.M. Sheldrick, Acta Crystallogr. Sect. A Found. Adv. 71 (2015) 3–8.
[21] A.L. Spek, J. Appl. Crystallogr. 36 (2003) 7–13.
[22] A.L. Spek, Acta Crystallogr. Sect. D. 65 (2009) 148–155.
[23] P. van der Sluis, A.L. Spek, Acta Crystallogr. Sect. A 46 (1990) 194–201.
[24] A.L. Spek, Acta Crystallogr. Sect. C. Struct. Chem. 71 (2015) 9–18.
[25] P. Müller, R. Herbst-Irmer, A.L. Spek, T.R. Schneider, M.R. Sawaya, Crystal Structure Refinement, A Crystallographer's Guide to SHELXL Oxford University Press, 2006.
[26] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, in, Gaussian, Inc., Wallingford, CT, USA, 2009.
[27] C. Adamo, V. Barone, J. Chem. Phys. 108 (1998) 664–675.
[28] P. Thornton, Sci. Synth. 5 (2003) 55–73.
[29] F. Glockling, K.A. Hooton, J. Chem. Soc. (1962) 3509–3512.
[30] Y. Takeuchi, H. Yamamoto, K. Tanaka, K. Ogawa, J. Harada, T. Iwamoto, H. Yuge, Tetrahedron 54 (1998) 9811–9822.
[31] G. Cerveau, C. Chuit, R.J.P. Corriu, C. Reye, Organometallics 10 (1991) 1510–1515.
[32] R. West, J. Am. Chem. Soc. 74 (1952) 4863–4865.
[33] M.J.S. Gynane, M.F. Lappert, P. Riviere, M. Riviere-Baudet, J. Organomet. Chem. 142 (1977) C9–C11.
[34] M.J.S. Gynane, M.F. Lappert, P.I. Riley, P. Rivière, M. Rivière-Baudet, J. Organomet. Chem. 202 (1980) 5–12.
[35] V.A. Dumler, V.D. Kolbasina, N.E. Evstafeeva, V.I. Proshutinskii, I.I. Lapkin, Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol. 20 (1977) 1797–1799.
[36] I.I. Lapkin, V.A. Dumler, N.E. Evstafeeva, V.D. Kolbasina, L.M. Konyukhova, Zh. Obshch. Khim. 53 (1983) 1828–1831.
[37] I.I. Lapkin, V.A. Dumler, E.S. Ponosova, Zh. Obshch. Khim. 39 (1969) 1455–1459.
[38] D.L. Tabern, W.R. Orndorff, L.M. Dennis, J. Am. Chem. Soc. 47 (1925) 2039–2044.
[39] P.C. Chieh, J. Chem. Soc. A (1971) 3243–3245.
[40] A. Karipides, D.A. Haller, Acta Crystallogr. Sect. B Struct. Sci. 28 (1972) 2889–2892.
[41] K. Claborn, B. Kahr, W. Kaminsky, CrystEngComm 4 (2002) 252–256.
[42] V.K. Belsky, A.A. Simonenko, V.O. Reikhsfeld, J. Organomet. Chem. 265 (1984) 141–143.
[43] M. Charissé, S. Roller, M. Dräger, J. Organomet. Chem. 427 (1992) 23–31.
[44] H. Preut, F. Huber, Acta Crystallogr. Sect. B 35 (1979) 83–86.
[45] C.R. Samanamu, C.R. Anderson, J.A. Golen, C.E. Moore, A.L. Rheingold, C.S. Weinert, J. Organomet. Chem. 696 (2011) 2993–2999.