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Selective synthesis of tetraarylgermanes and triarylgermanium halides

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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

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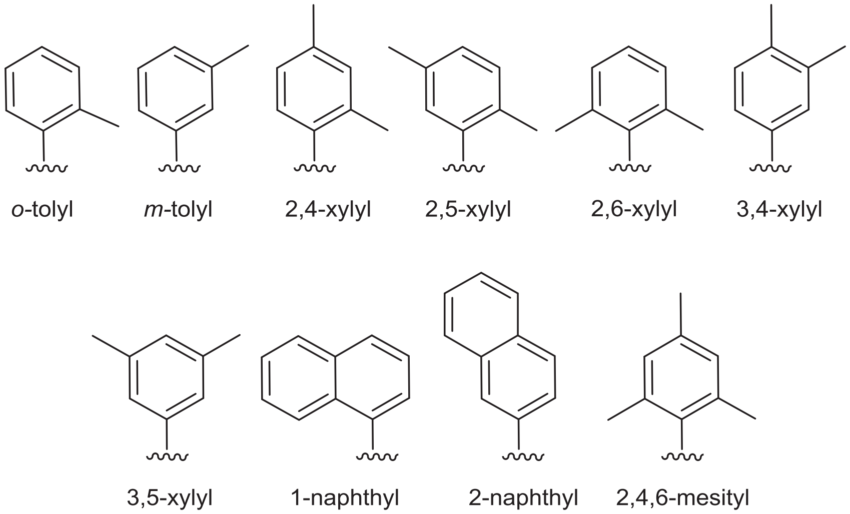

Fig. 1. Aromatic residues employed for the preparation of organogermanium compounds.

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 Kα 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