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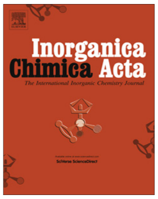

Synthesis, characterization and *Twin Polymerization* of a novel dioxagermine

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ABSTRACT

The synthesis of 6-bromo-2,2-di-*tert*-butyl-4*H*-1,3,2-benzo[*d*]dioxagermine (**1**) via an alcohol/alkoxide exchange starting from di-*tert*-butyl-di-ethoxy germane is reported. Characterization of the title compound including single crystal X-ray diffraction and TGA/DSC analysis, mass spectrometry, ^{1}H NMR, ^{13}C{^{1}H} NMR and IR spectroscopy is reported. DFT-D calculations have been carried out to assign the absorption band maxima of the IR spectrum to the corresponding vibrational modes. The suitability for *Twin Polymerization* of the novel dioxagermine **1** has been studied by TGA/DSC analysis and mass spectrometry. Proton-assisted *Twin Polymerization* of **1** results in an organic–inorganic hybrid material composed of a phenolic resin and [^{t}Bu$_2$GeO]$_n$.

1. Introduction

Germanium compounds derived from *ortho*-hydroxybenzyl alcohol are known in the literature for 50 years now, with the first report dating back to 1963, when Wieber et al. reported the synthesis of 2,2-dimethyl-4*H*-1,3,2-benzo[*d*]dioxagermine [1]. Later on Gragg et al. described the preparation of 2,2-di-*n*-butyl-4*H*-1,3,2-benzo[*d*]dioxagermine and 2,2-diphenyl-4*H*-1,3,2-benzo[*d*]dioxagermine applying the same synthesis strategy as reported by Wieber et al. starting from the corresponding dichlorogermane and *ortho*-hydroxybenzyl alcohol in the presence of a tertiary amine base. The latter compounds were characterized by elemental analysis, boiling point, refractive index and mass spectrometry [2]. Since then no additional reports appeared in the literature and hence detailed structural studies are still lacking. Here we report a straightforward synthesis and the full characterization of a new representative of these cyclic germanium compounds, 6-bromo-2,2-di-*tert*-butyl-4*H*-1,3,2-benzo[*d*]dioxagermine (**1**). The latter compound **1** attracted our interest with regard to a novel synthetic concept, the so called *Twin Polymerization*, which is defined as the concerted generation of two polymers in one synthetic step starting from a single monomer. An important aspect of this new type of polymerization is the formation of organic–inorganic hybrid materials, which exhibit a nanostructured composite of two interpenetrating networks [3]. Hence further treatment of these hybrid materials might give access to highly porous materials as was reported recently by Spange et al. for the *Twin Polymerization* of 2,2-dimethyl-4*H*-1,3,2-benzo[*d*]dioxasiline, which is structurally related to compound **1** [4,5]. We have chosen the bromo-substituted salicyl alcoholate rather than the non-substituted one as ligand, because of the lower reactivity of the alcohol with regard to Lewis acid promoted polymerization. The polymerization of the alcohol was identified as major problem in attempts to synthesize well defined monomers, for example, germanium alcoholates starting from different salicyl alcohols [6]. The ^{t}Bu$_2$Ge-derivative was identified as a good candidate for *Twin Polymerization*, because it is a solid material easy to purify and exhibits solubility and a low melting point. Its thermal behavior and fragmentation pattern derived from mass spectrometry were studied in order to probe suitability for thermally induced *Twin Polymerization* and proton-assisted *Twin Polymerization*, which both were expected to provide organic–inorganic hybrid materials composed of a phenolic resin and [^{t}Bu$_2$GeO]$_n$.

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2. Material and methods

All reactions were performed by using Schlenk techniques under argon. Solvents were purified and dried by applying standard techniques. All reactions were carried out with freshly distilled, dried solvents. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker "Avance III 500" spectrometer at ambient temperature. ATR-FT-IR spectra were recorded with a BioRad "FTS-165 spectrometer". Melting point evaluation was carried out with a "Melting Point B-540" apparatus from Büchi. Elemental analyses were determined using a "vario MICRO" from Elementar Analysensysteme GmbH. TGA/DSC experiments were determined by using a Mettler Toledo "TGA/DSC1 1600 system" with an MX1 balance. The measurement was performed from 40 to 800 °C with a rate of 10 K/min in Ar atmosphere and a volume flow of 60 mL/min. GC–MS analysis was performed on a gas chromatograph "17 A" with a quadruple pole mass spectrometer "QP-5000" from Shimadzu. A non-polar column, type "OPTIMA-5" from Machery Nagel consisting of polymethylphenylsiloxane (95% methyl-, 5% phenyl-groups) was used. The injector temperature was set to 230 °C, a split of 1:34 and a volume flow of the carrier gas helium of 1.4 mL/min was used. After 5 min at 50 °C the temperature was increased to 320 °C with a rate of 10 K/min and then kept at this temperature for 10 min. A solution of **1** in *n*-hexane was injected for GC–MS analysis. The solid state NMR spectrum was collected at 9.4 T on a Bruker Avance 400 spectrometer equipped with double tuned probes capable of MAS (magic angle spinning). $^{13}C\{^1H\}$ CP-MAS NMR spectra were measured at 100.6 MHz in 3.2 mm standard zirconium oxide rotors (BRUKER) spinning at 20 kHz. Cross polarization with a contact time of 5 ms was used to enhance sensitivity. The recycle delay was 5 s. The spectrum was referenced externally to tetramethylsilane (TMS) as well as to adamantane as secondary standard (38.48 ppm for ^{13}C). The spectra were collected with ^1H decoupling using a TPPM pulse sequence.

Tetraethoxy germane (98%), 5-bromo-2-hydroxybenzaldehyde and 1.9 M *tert*-butyllithium in *n*-pentane were purchased from ABCR GmbH & Co. KG, Merck Schuchardt OHG and Acros Organics, respectively. All starting materials were used without further purification.

2.1. Synthesis of 5-bromo-2-hydroxybenzyl alcohol [7]

The compound was prepared according to the literature using a modified synthetic procedure: 5-bromo-2-hydroxybenzaldehyde (10.1 g, 50 mmol) was dissolved in 250 mL of ethanol at 0 °C. $NaBH_4$ (1.88 g, 50 mmol) was added in portions (~0.3 g) to the stirred solution. The mixture was stirred at room temperature for 18 h. After removal of ethanol under reduced pressure (10^{-2} mbar) the resulting pale yellow solid was dissolved in 200 mL of a saturated, aqueous NH_4Cl solution. The crude product was extracted with diethyl ether (three times 80 mL). The organic phase was washed with brine (three times 20 mL) and dried with $MgSO_4$ for 2 h. After removal of $MgSO_4$ by filtration and excess solvent under reduced pressure (10^{-2} mbar) the product was purified by flash chromatography with silica (eluent: *n*-hexane/ethyl acetate – volume ratio of 8/2) to give a colorless solid after evaporation of the solvent (8.52 g, 84%); mp 104–107 °C; ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.21$ (s, H; $OH(CH_2OH)$), 4.84 (s, 2H, CH_2), 6.77 (d, H, H_α/C_6H_3, $^3J_{ortho} = 8.6$ Hz), 7.16 (d, H, H_γ/C_6H_3, $^4J_{meta} = 2.4$ Hz), 7.30 (s, H, $OH(C_6H_3)$), 7.30 ppm (dd, H, H_β/C_6H_3, $^3J_{ortho} = 8.6$ Hz, $^4J_{meta} = 2.4$ Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 64.2$ (CH_2), 111.9 (C_6H_3), 118.5 (C_6H_3), 126.4 (C_6H_3), 130.3 (C_6H_3), 132.2 (C_6H_3), 155.3 ppm (C_6H_3).

2.2. Synthesis of di-tert-butyl-di-ethoxy germane [8]

The compound was prepared according to the literature using a modified synthetic procedure: Tetraethoxy germane (4.41 mL, 5.02 g, 19.5 mmol) was slowly added to 20.50 mL (39 mmol) of a stirred solution of 1.9 M *tert*-butyl lithium in *n*-pentane at 0 °C. The mixture was stirred at room temperature for 24 h. The resulting precipitate was removed by filtration. Excess of *n*-pentane was removed under reduced pressure. The crude product was purified by distillation at $8 * 10^{-2}$ mbar and 45–50 °C to give di-*tert*-butyl-di-ethoxy germane as colorless liquid (5.08 g, 94%); ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.19$ (s, 18H; $CH_3–^tBu$), 1.22 (t, 6H, CH_3–OEt, $J = 6.9$ Hz), 3.88 ppm (q, 4H, CH_2–OEt, $J = 6.9$ Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 19.3$ (CH_3–OEt), 28.1 ($CH_3–^tBu$), 30.5 ($C_q–^tBu$), 60.4 ppm (CH_2–OEt).

2.3. Synthesis of 6-bromo-2,2-di-tert-butyl-4H-1,3,2-benzo[d]dioxagermine (1)

Di-*tert*-butyl-di-ethoxy germane (1.65 mL, 2.00 g, 7.22 mmol) was slowly added to a stirred solution of 5-bromo-2-hydroxybenzyl alcohol (1.47 g, 7.22 mmol) in xylene (50 mL) under reflux. The mixture was stirred under reflux for 36 h. After removal of the xylene under reduced pressure (10^{-2} mbar, 90 °C) the crude product was dissolved in *n*-pentane (20 mL). Filtration and evaporation of *n*-pentane gave 6-bromo-2,2-di-*tert*-butyl-4*H*-1,3,2-benzo[*d*]dioxagermine as yellow solid (2.55 g, 91%); mp 59–62 °C; ^1H NMR (500 MHz, C_6D_6, 25 °C, TMS): $\delta = 1.06$ (s, 18H, $CH_3–^tBu$), 4.67 (s, 2H, CH_2), 6.75 (d, H, H_α/C_6H_3, $^3J_{ortho} = 8.8$ Hz), 6.93 (d, H, H_γ/C_6H_3, $^4J_{meta} = 2.5$ Hz), 7.17 ppm (dd, H, H_β/C_6H_3, $^3J_{ortho} = 8.8$ Hz, $^4J_{meta} = 2.5$ Hz); $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, 25 °C, TMS): $\delta = 27.8$ ($CH_3–^tBu$), 32.5 ($C_q–^tBu$), 66.5 (CH_2), 112.3 (C_6H_3), 121.9 (C_6H_3), 130.7 (C_6H_3), 132.4 (C_6H_3), 132.6 (C_6H_3), 158.0 ppm (C_6H_3); *m/z*: 390, 388, 386 and 384 [$M^{+\cdot}$]; ATR-FT-IR: 3079 w (C_{aryl}–H), 2934 m (CH_3), 2857 m (CH_2), 1472 s (CH_2), 1260 s (O–C_{aryl}), 1183 s (CH_2–C_{aryl}), 812 s (C–CH_3), 791 s (C_6H_3), 675 s (Ge–OC_{aryl}), 615 cm^{-1} s (Ge–OCH_2); *Anal.* Calc. for $C_{15}H_{23}BrGeO_2$: C, 46.45; H, 5.98. Found: C, 46.29; H, 5.91%.

2.4. Polymerization of compound 1

Trifluoromethanesulfonic acid (0.042 mL, 0.480 mmol) was added to a stirred solution of 6-bromo-2,2-di-*tert*-butyl-4*H*-1,3,2-benzo[*d*]dioxagermine (1.862 g, 4.800 mmol) in dichloromethane (50 mL) at 0 °C. The mixture was stirred at room temperature for 4 days. The resulting precipitate was filtered off and washed with *n*-hexane (10 mL) and diethyl ether (10 mL) three times, respectively. Removal of residual solvent in air at 60 °C gave an amorphous brown powder. Yield based on **1** (0.71 g, 38%); $^{13}C\{^1H\}$ CP-MAS NMR (100.6 MHz, 25 °C, TMS, adamantane): $\delta = 27$ ($CH_3–^tBu$), 33 (CH_2), 114 (C_6H_3), 130 (C_6H_3), 149 ppm (C_6H_3); ATR-FT-IR: 3210 b (OH), 2940 m (CH_3), 2863 m (CH_2), 1466 s, 1449 s, 1207 s, 1175 s, 1026 s, 862 s, 633 s (Ge–O), 513 s (Ge–C) cm^{-1}.

2.5. X-ray diffraction analysis of compound 1

Single crystals suitable for X-ray structural analysis were grown from a saturated solution in *n*-hexane at room temperature. X-ray crystallographic data were collected on an Oxford diffractometer of the type Gemini S using Cu Kα-radiation ($\lambda = 1.54$ Å) at 100 K using oil-coated shock-cooled crystals [9–11]. The structure was solved by direct methods using SIR-92 and refined by full matrix least-square procedures on F^2 using SHELXL-97 [12,13]. All non-hydrogen atoms were refined anisotropically and a riding model