Electronic Supplemental Information

Effect of Temperature on B(C$_6$F$_5$)$_3$-Catalysed Reduction of Germanium Alkoxides by Hydrosilanes – A New Route to Germanium Nanoparticles

Slawomir Rubinsztajn*, Urszula Mizerska, Joanna Zakrzewska, Pawel Uznański Marek Cypryk, and Witold Fortuniak

Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland
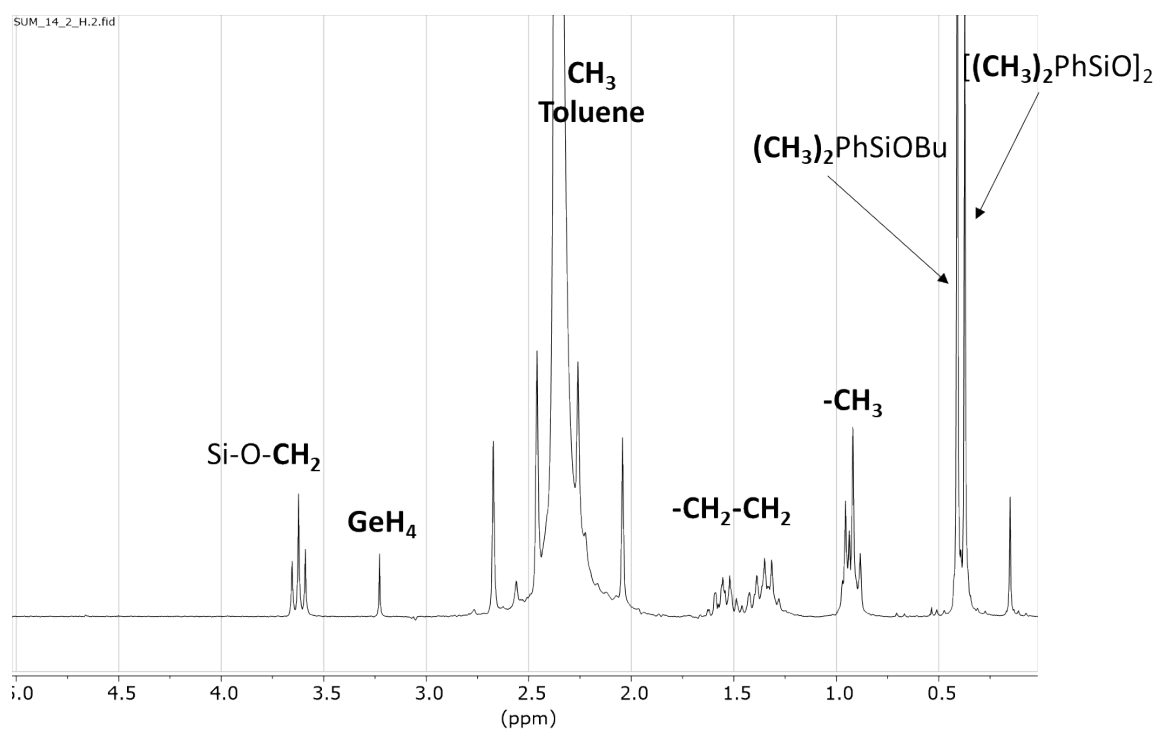
Figure S1. ^{1}H NMR spectrum of the reaction mixture of 5 mol eq. of PhMe$_2$SiH and 1 mol eq. of Ge(OBu)$_4$ in the presence of 2 × 0.5 mol% of B(C$_6$F$_5$)$_3$ in toluene at 20 °C after 4 h. of reaction.

Figure S2. ^{1}H NMR spectrum of the reaction mixture of 5 mol eq. of PhMe$_2$SiH and 1 mol eq. of Ge(OBu)$_4$ in the presence of 2 × 0.5 mol% of B(C$_6$F$_5$)$_3$ in toluene at 100 °C after 4 h. of reaction.
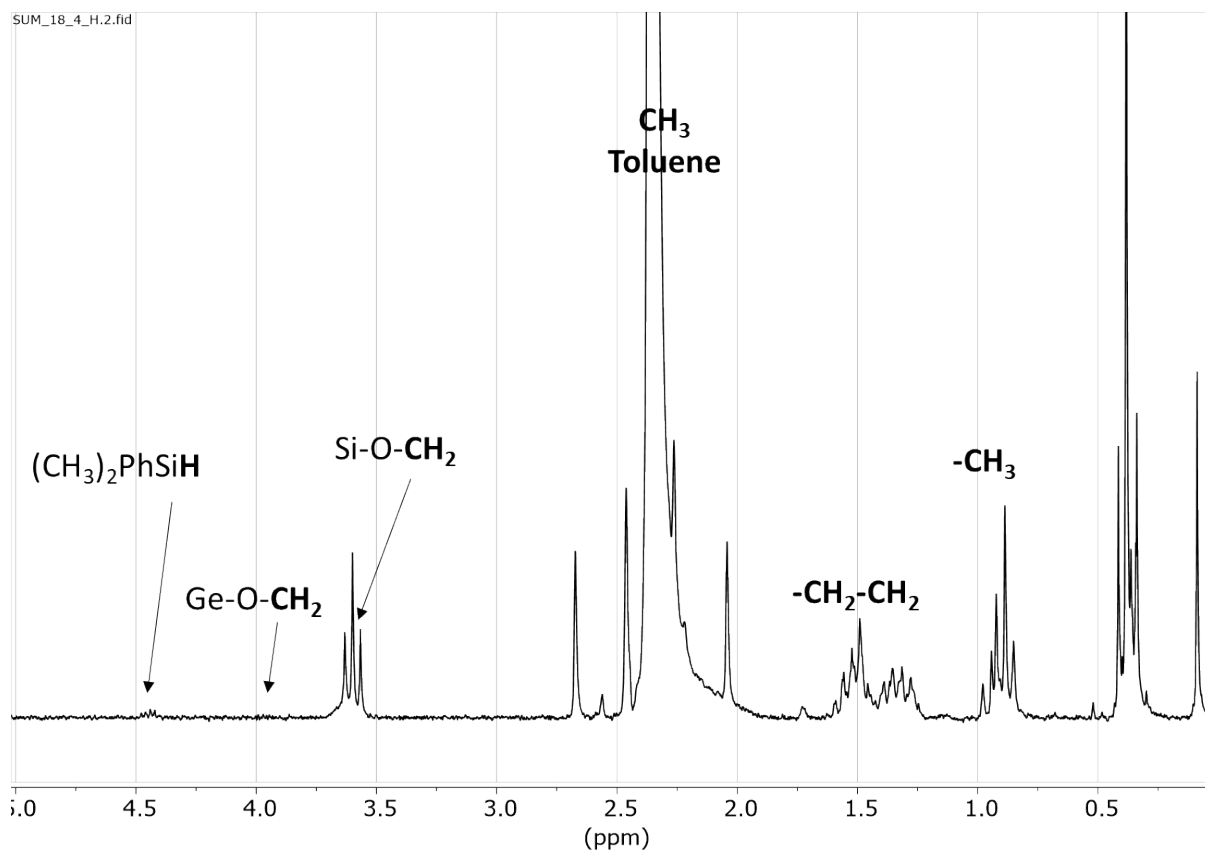
SUM_13_3_Si.22.fid

(CH$_3$)$_2$Ph**Si**OBu

((CH$_3$)$_2$Ph**Si**)$_2$O

(CH$_3$)$_2$Ph**Si**H

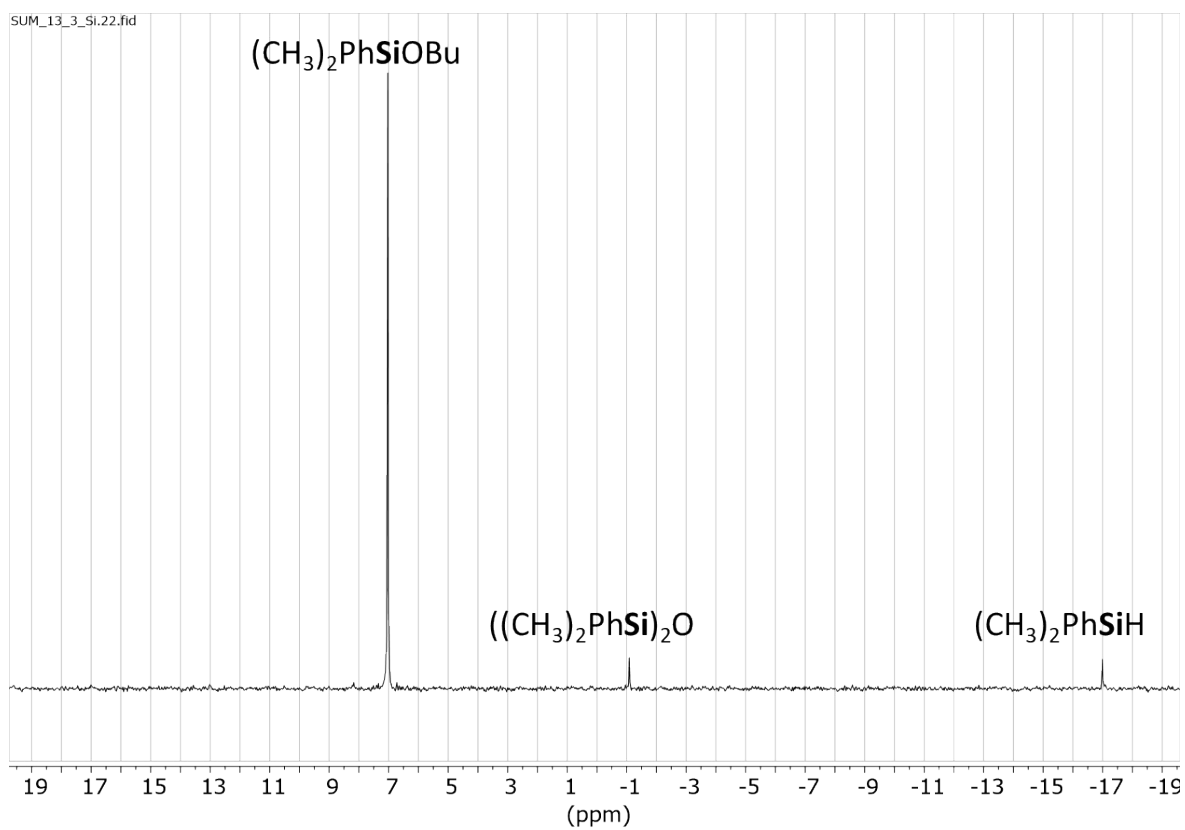19 17 15 13 11 9 7 5 3 1 -1 -3 -5 -7 -9 -11 -13 -15 -17 -19

(ppm)

Figure S3. ^{29}Si NMR spectrum of the reaction mixture of 5 mol eq. of PhMe$_2$SiH and 1 mol eq. of Ge(OBu)$_4$ in the presence of 2 × 0.5 mol% of B(C$_6$F$_5$)$_3$ in toluene at 100 °C after 4 h. of reaction.
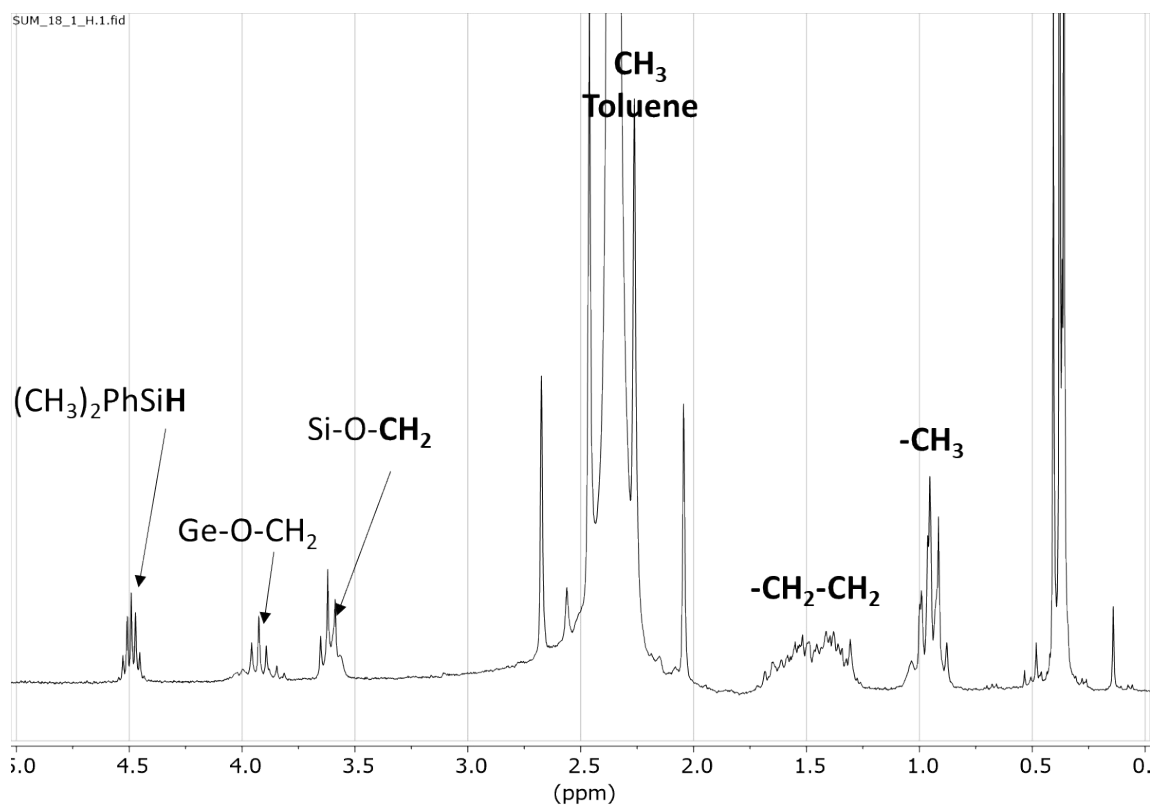
Figure S4. ^{1}H NMR spectrum of the reaction mixture of 5 mol eq. of PhMe$_2$SiH and 1 mol eq. of Ge(OBu)$_4$ in the presence 0.5 mol% of B(C$_6$F$_5$)$_3$ in toluene at 100 °C after 2 h. of reaction.
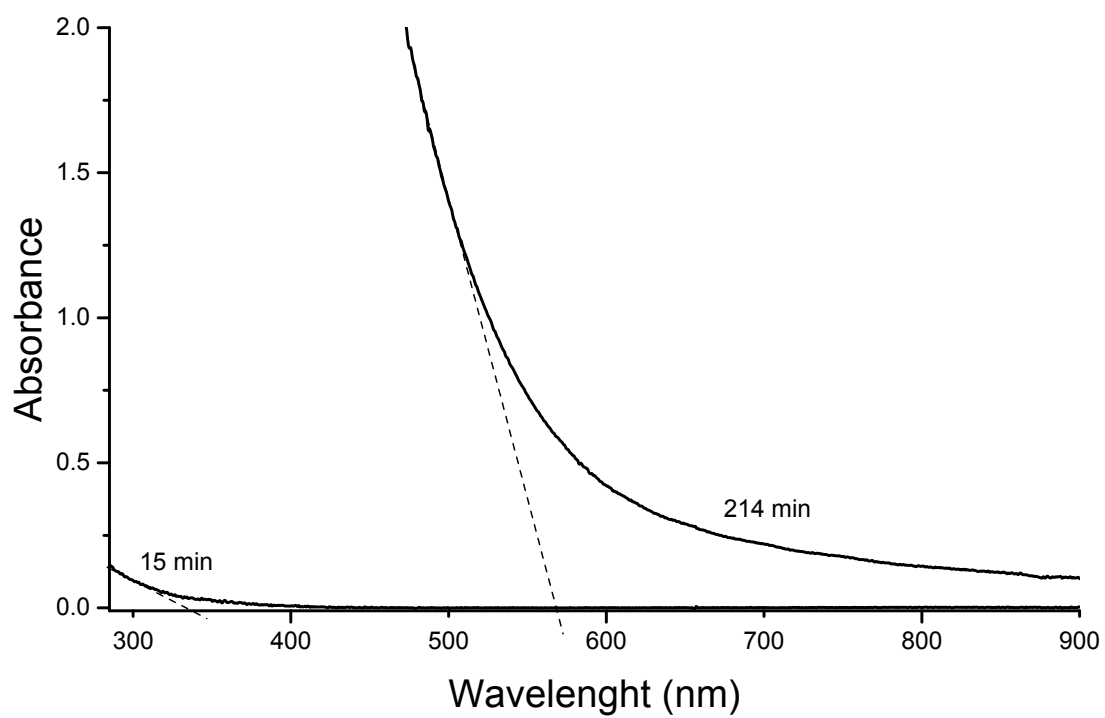
Figure S5. UV-Vis spectra of the reaction mixture of 1 mol eq. Ge(OBu)$_4$ with 5 mol eq. PhMe$_2$SiH in the presence 2 × 0.5mol% B(C$_6$F$_5$)$_3$ collected after 15 min and 214 min of reaction at 100 °C in toluene.
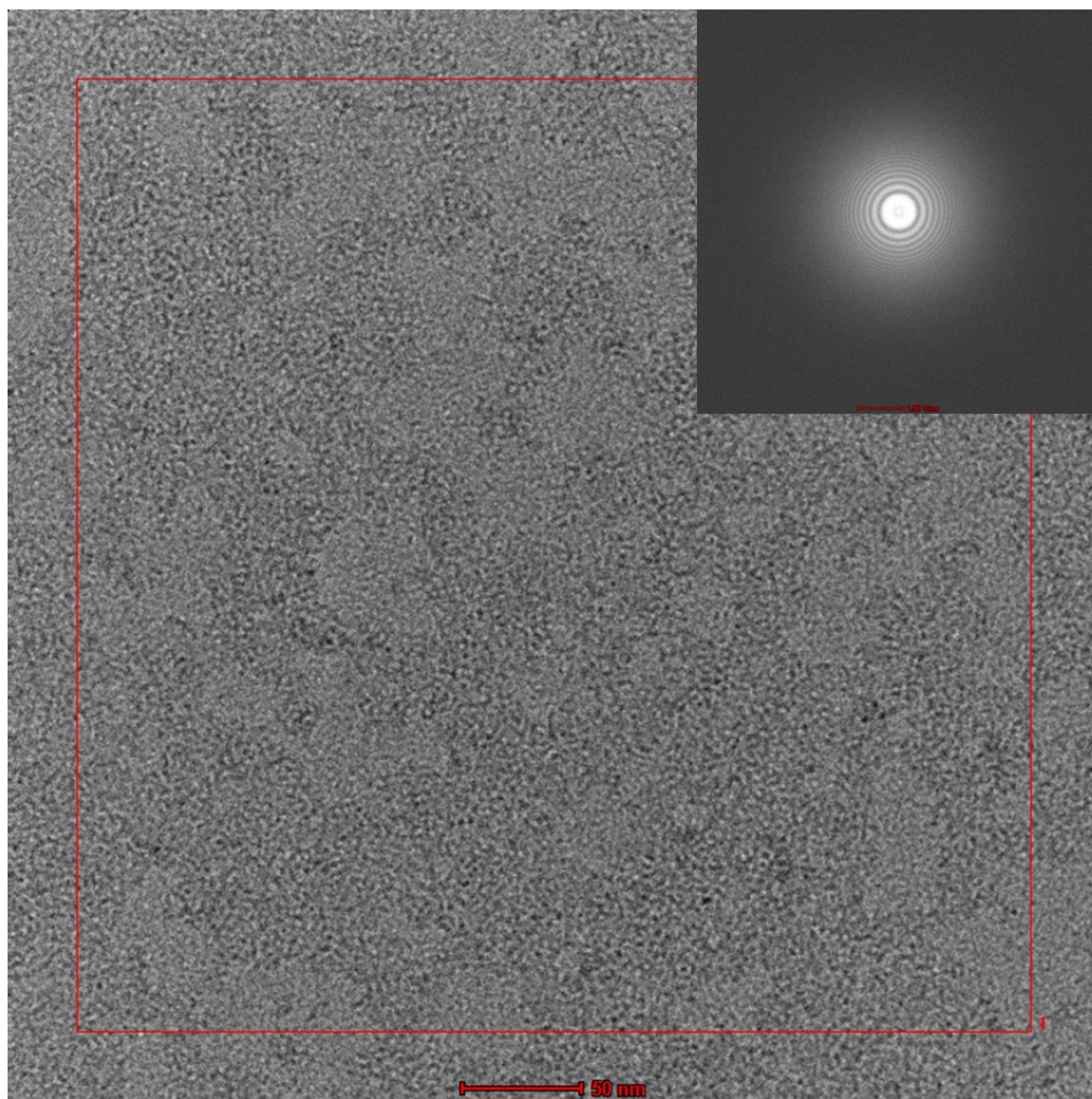
Figure S6. TEM images of the Ge NPs prepared in the reaction of 1 molar eq. of Ge(OBu)$_4$ with 5 molar eq. of PhMe$_2$SiH in the presence of 2 × 0.5 mol% B(C$_6$F$_5$)$_3$ in toluene at 100 °C. The inset in the upper right corner of the TEM image shows the FFT of the selected area.
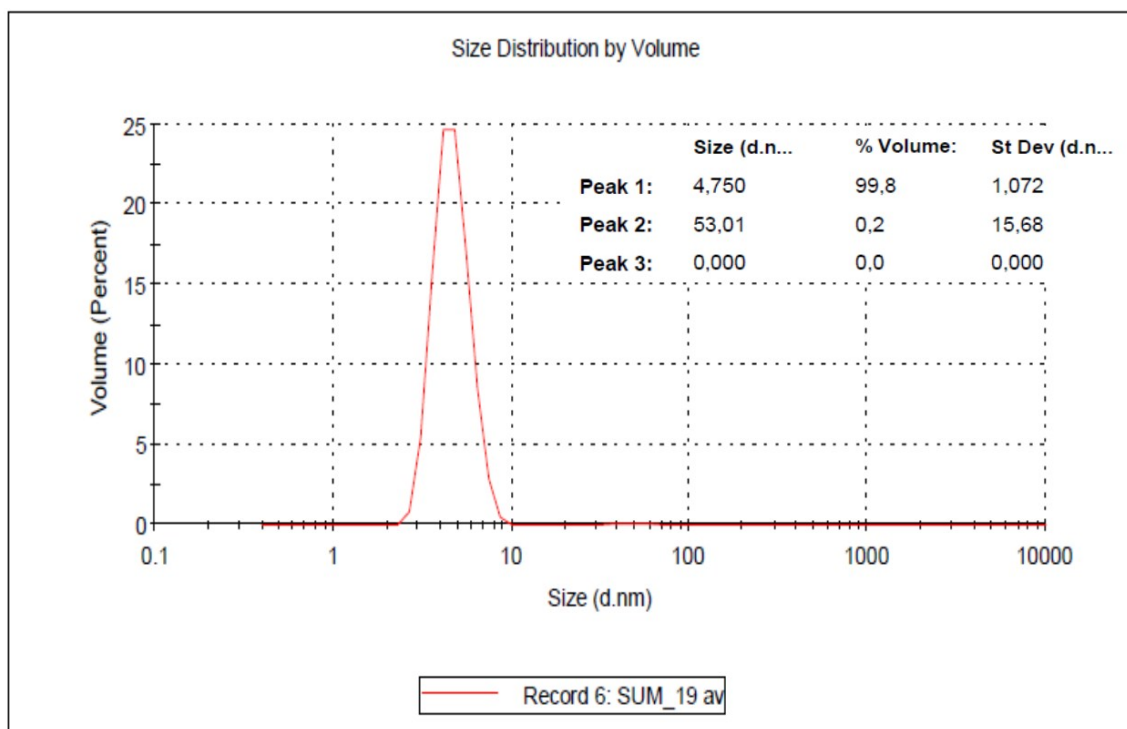
Figure S7. DLS analysis of the final reaction mixture of 1 mol eq. Ge(OBu)$_4$ with 5 mol eq. PhMe$_2$SiH in the presence 2 × 0.5 mol% B(C$_6$F$_5$)$_3$ carried out at 100 °C in toluene.

Chemical formula	mass%	Atom%
O	15.36	41.57
F	3.53	8.06
Si	2.09	3.23
Ge	79.02	47.14
Total	100	100

Figure S8. A – image of the powder obtained after removal of solvent and volatile compound from the reaction mixture of 1 mol eq. Ge(OBu)$_4$ with 5 mol eq. PhMe$_2$SiH in the presence 2 × 0.5 mol% B(C$_6$F$_5$)$_3$ carried out at 100 °C in toluene; B – SEM image of the powder; C – EDS spectrum of the powder.
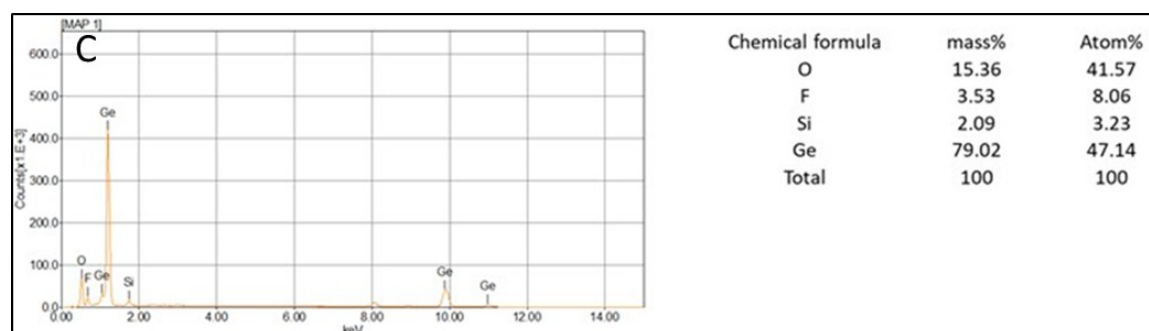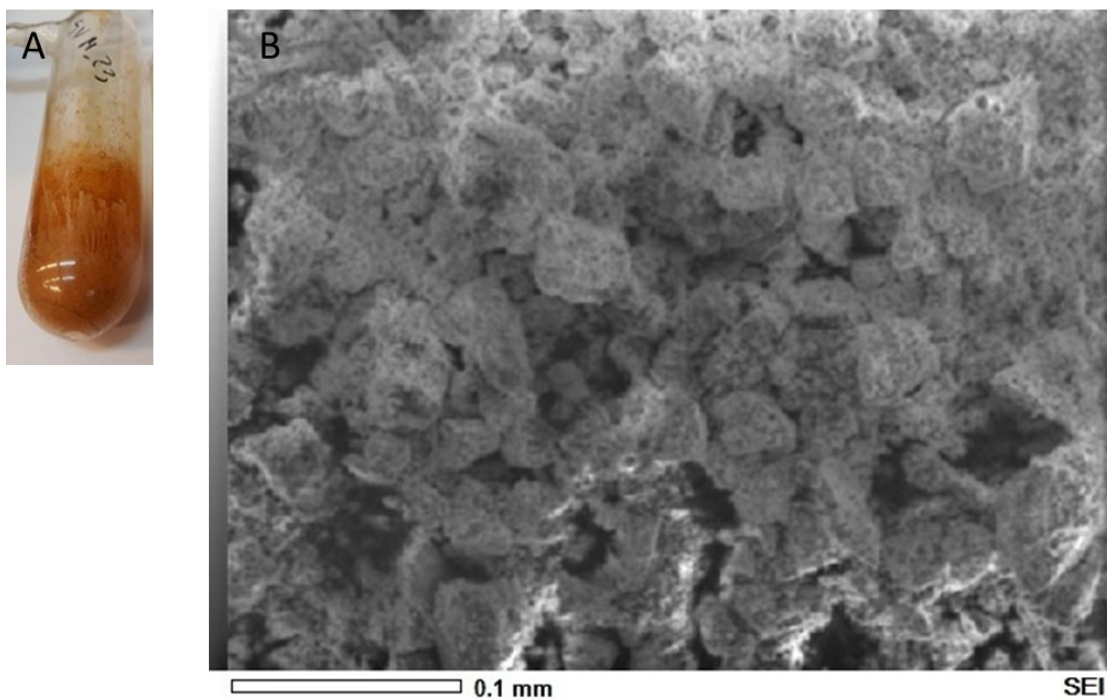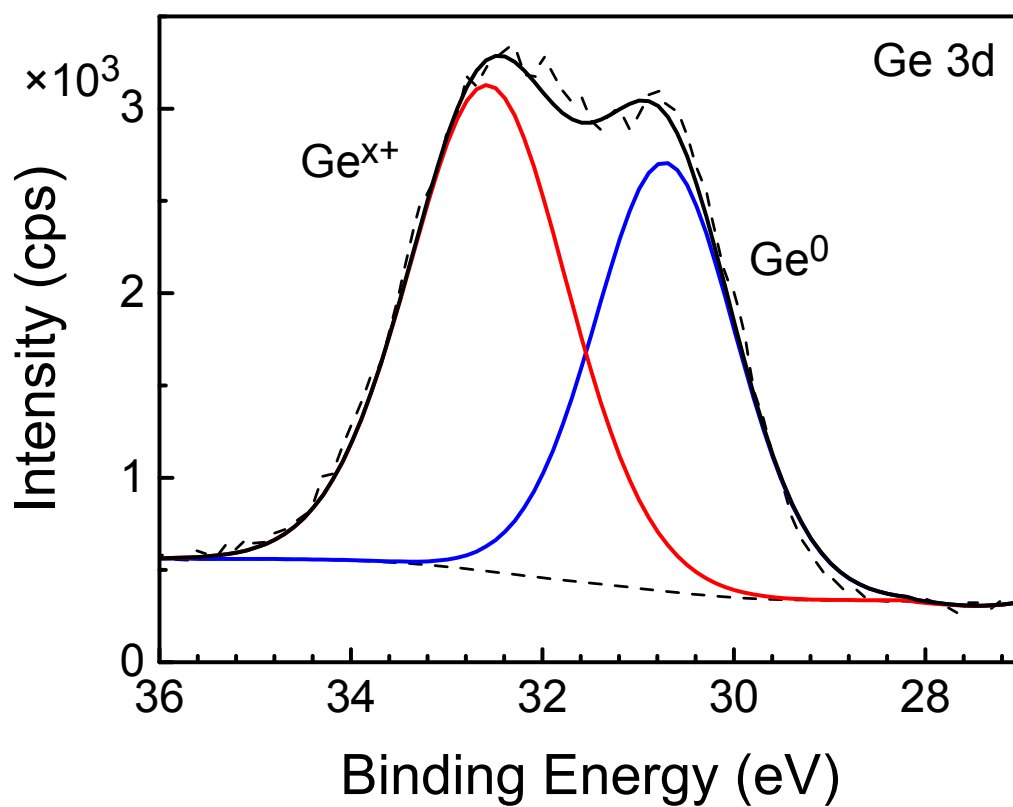
Figure S9. XPS spectrum of the powder obtained after removal of solvent and volatile compound from the reaction mixture of 1 mol eq. $Ge(OBu)_4$ with 5 mol eq. $PhMe_2SiH$ in the presence 2×0.5 mol% $B(C_6F_5)_3$ carried out at 100 °C in toluene.
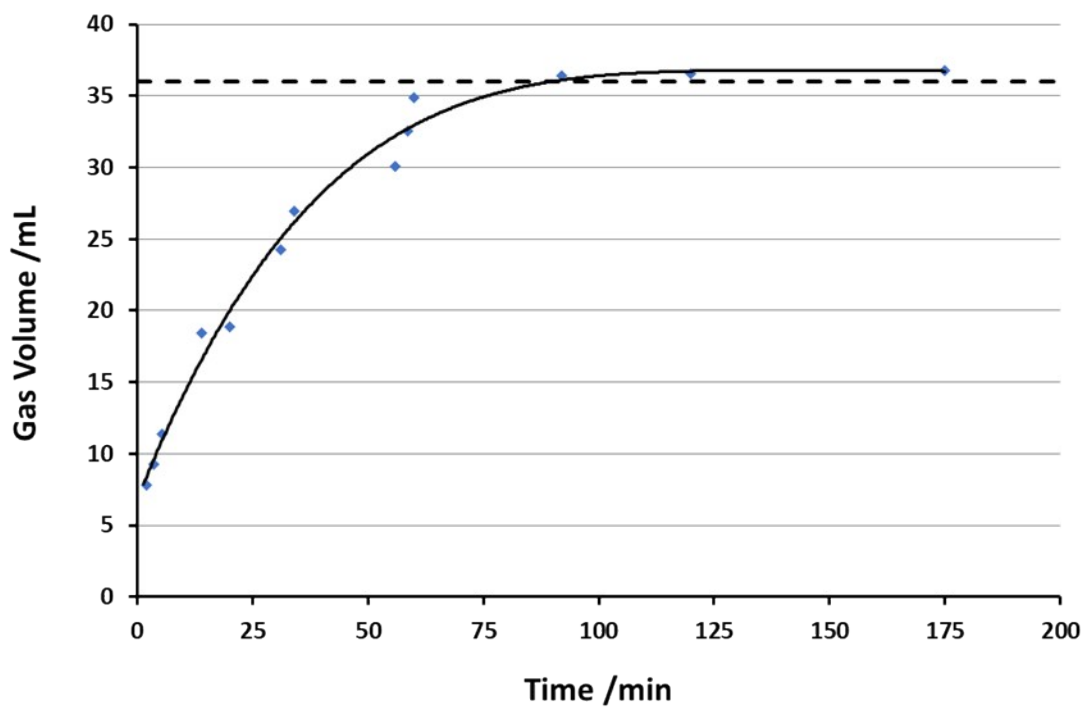
Figure S10. Plot of gas formation vs. time for the reaction mixture of 3.39 mmol eq. of PhMe$_2$SiH and 0.797 mmol eq. of Ge(OBu)$_4$ in the presence 3.4 × 10^{-2} mmol of B(C$_6$F$_5$)$_3$ in toluene at 100 °C. The dashed line represented expected volume of hydrogen generated.

Experimental section

Materials
Phenyldimethylsilane (Fluorochem, 98 %), germanium n-butoxide (ABCR, 95 %), tris(pentafluorophenyl)borane (TCI, >97 %), toluene (drybox system) was used without further purification.

NMR spectroscopy
^1H, ^{13}C, ^{29}Si NMR spectra in $CDCl_3$ were obtained with a Bruker 500 MHz spectrometer. ^{29}Si NMR spectra was recorded with broadband proton decoupling. A heteronuclear gated decoupling with 20 s delay technique was used to acquire ^{29}Si NMR spectra.

IR spectroscopy.
FTIR spectra were recorded by a Nicolet 380 spectrophotometer. Analyzed sample was placed between two KBr plates or in cuvette with ZnSe windows. FTIR-ATR spectra were recorded using the Nicolet 6700 apparatus equipped with iD7 ATR accessory.

UV spectroscopy
UV spectra were recorded using a Specord S600 (Zeiss, Jena, Analytik Jena AG, Jena, Germany) UV–VIS spectrometer equipped with 8-cell changer position with temperature control unit. Analysis were completed under dry nitrogen using 0.1cm quartz cuvette equipped with Teflon stopcock.

DLS measurements
Size and size distribution of colloidal nanoparticles were measured using Zeta Sizer 3000 HAS (Malvern Instrument) in dry toluene.

SEM and EDS measurements
Scanning electron microscopy (SEM) observations were performed on a low vacuum Scanning Electron Microscope JSM 5500 by JEOL, equipped with energy-dispersive X-ray spectrometer EDX.

TEM measurements
Transmission electron microscopy (TEM) imaging of nanoparticles were conducted using Talos F200x by FEI, equipped with a scanning system (STEM) and energy-dispersive X-ray spectrometer EDX. Due to the amorphous nature of the formed Ge NPs high-angle annular dark-field imaging (HAADF) STEM technique was used to image the Ge NPs. TEM samples were prepared by drop-casting of the toluene suspension of Ge NPs onto TEM grids (Carbon Films on 200 Mesh Grids of Copper, Agar Scientific).

X-ray Fluorescence Spectroscopy (XRF)
Content of the Ge in toluene was determined by XRF. Germanium content measurement was performed using WDXRF spectrometer Panalytical Axios mAX, equipped with Rh SST-mAX, 4kW lamp. Measurements were made in helium atmosphere. The detection time of germanium has been significantly extended to obtain a small statistical error due to the number of fluorescent photon counts. The measurement results were calculated using the Omnian resident program and calibration of the spectrometer based on a series of synthetic standards.

Photoluminescence
Photoluminescence measurements of toluene dispersions of Ge NPs were performed using Fluorolog-3 22 instrument (Horiba Jobin-Yvone).

XPS analysis

XPS analysis of the selected samples of Ge powders was performed using AXIS Ultra photoelectron spectrometer (XPS, Kratos Analytical Ltd.) equipped with a monochromatic Al-Ka X-ray source (1486.6 eV). The main component of the C 1s line was used to calibrate collected spectra.

Synthesis of Ge NPs by reaction of Ge(OBu)$_4$ with SiH functional silanes in the presence B(C$_6$F$_5$)$_3$

All operations in preparation of the reaction mixture were performed under the atmosphere of nitrogen. The solution of germanium (IV) butoxide (0.83 g, 2.28 mmol) dissolved in 11.4 mL of dried toluene was placed in a flask purged with nitrogen, equipped with magnetic stirrer, nitrogen gas inlet and gaseous products outlet through a bubbler. Separately the solution of phenyldimethylsilane (1.54 g, 11.3 mmol) and tris(pentafluorophenyl)borane (0.029 g, 0.05 mmol) were dissolved in 53 mL of dried toluene. This solution was introduced to the stirred solution of germanium (IV) butoxide at 100°C by means of a syringe through septum over a period of 20 min. Weak gas evolution was observed during the silane addition. Color of the reaction mixture gradually changed from colorless to yellow over a period of 2 h. At that point, a second portion of tris(pentafluorophenyl)borane (0.029 g, 0.05 mmol) dissolved in 3 mL of dried toluene was added. An addition gas evolution was observed, and the color of the reaction mixture changed from yellow to orange and finally to dark red. Reaction mixture was hold at 100 °C for an additional 12 h and finally cooled down to RT. The final solution and isolated solids were analyzed by ^{1}H, ^{29}Si NMR, DSL, FTIR, XRF, SEM/EDS, TEM and HAADF-STEM. Photoluminescence of the selected samples was studied using Fluorolog-3 22 instrument.

Theoretical DFT calculations

All quantum mechanical calculations were performed using the Gaussian 16 suite of programs [1]. Geometries of the bases and base pair model systems were optimized using the hybrid B3LYP density functional [2] corrected for dispersion interactions using Grimme GD3 empirical term [3], with Def2-SVP basis set [4] in the gas phase. All stationary points were identified as stable minima by frequency calculations. The vibrational analysis provided thermal enthalpy and entropy corrections at 298 K within the rigid rotor/harmonic oscillator/ideal gas approximation [1]. Thermochemical corrections were scaled by a factor of 0.985 [5]. More accurate single point electronic energies were obtained using the B3LYP functional, including Grimme GD3 dispersion correction [3], with the larger Def2-TZVP basis set for the Def2-SVP optimized geometries [6]. This level of theory is denoted as B3LYP-GD3/Def2TZVP//B3LYP-GD3/Def2SVP. Integration grid was set to ultrafine.

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