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New insights into the selective and systematic preparation of arylgermanium hydrides

Ana Torvisco, Melanie Wolf, Michael Traxler, Dietrich Gudat and Frank Uhlig

Experimental 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.). $GeCl_4$ and LiCl were purchased at ABCR and stored under nitrogen. DCM was dried over P_2O_5 and distilled prior to usage. All other chemicals from commercial sources were utilized without further purification. Mixed halides Ar_3GeHal (Ar = 2,4-$Me_2C_6H_3$, 2,5-$Me_2C_6H_3$, 2,6-$Me_2C_6H_3$, 1-naphthyl; Hal = Cl, Br) were synthesized according to literature procedure and included below.[S1] Celite® with a median particle size of 16.4 μm was used (Celite® 512). Elemental analysis was performed on an Elementar vario EL or an Elementar vario MICRO cube. Melting points were determined as the average of three measurements using a Stuart Scientific SMP 10 instrument. IR spectra were recorded on a Bruker APHA FT-IR spectrometer with platinum ATR diamond top.

^1H (300.2 MHz) and ^{13}C (75.5 MHz) NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer at 25 °C in $CDCl_3$. ^{73}Ge (13.96 MHz) NMR spectra were recorded on a Bruker AV400 spectrometer equipped with a normal broadband observation probe at 30 °C or 70 °C in toluene-d_8, using the ring pulse program in the Bruker pulse program library to minimize acoustic ringing effects. Chemical shifts in ^1H and ^{13}C NMR spectra were referenced to TMS using the signals of the residual protons or carbon atoms of the deuterated solvent (^1H: $\delta(CDCl_3) = 7.24$, $\delta(CD_3/\text{toluene-}d_8) = 2.09$; ^{13}C: $\delta(CDCl_3) = 77.23$) as secondary references. The ^{73}Ge NMR Spectra were referenced using the Ξ-scale[S2] with neat $GeMe_4$ ($\Xi = 3.488315$ MHz) as secondary reference.

GC-MS measurements were carried out on an Agilent Technologies 7890A GC system coupled to an Agilent Technologies 5975C VLMSD mass spectrometer using a HP5 column (30 m×0.250mm×0.025 μm) and a carrier helium gas flow of 0.92726 ml/min. A "hot-needle", manual injection method at an injector temperature of 240 °C was performed (40 °C for 2 minutes, Ramp 1 at 20 °C/min to 100 °C, Ramp 2 at 16 °C/min to 200 °C, Ramp 3 12 °C/min to 320 Hold time 20 minutes). The MS conditions included positive EI ionization at an ionization energy of 70 eV and a full scan mode (50-500 m/z).

Crystals suitable for single crystal X-ray diffractometry were removed from a vial or a Schlenk 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 for compounds **1a**, **2a**, and **3a**, on a Bruker APEX II diffractometer[S3] with use of an IμS microsource (Incoatec microfocus) sealed tube of Mo Kα radiation (λ= 0.71073 Å) and a CCD area detector. Data integration was carried out using SAINT.[3] Empirical absorption corrections were applied using SADABS.[S4,S5] CELL_NOW[S6] was used for the determination of the unit cell and twin law, while TWINABS[S7] was used for integration and generation of hkl4- and hkl5-files which were used in structure solution and refinement. The structures were solved with use of the intrinsic phasing option in SHELXT[S8] and refined by the full-matrix least-squares procedures in SHELXL[S8-S12] as implemented in the program SHELXLE.[S13] The space group assignments and structural solutions were evaluated using PLATON.[S14,S15] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to germanium atoms were located in a difference map and refined isotropically. All other hydrogen atoms were located in calculated positions corresponding to standard bond lengths and angles and refined using a riding model. Compound $(2,5\text{-}Me_2C_6H_3)_2Ge(Cl)H$ (**2a**) was refined as a 2-component inversion twin (BASF 0.02). All crystal structures representations were made with the program Diamond[S16] with all atoms displayed as 30% ellipsoids. CIF files were edited, validated and formatted either with the programs encifer,[S17] publCIF,[S18] or Olex2.[S19] CCDC 2116346-2116348 contain the supplementary crystallographic data for compounds **1a**, **2a** and **3a**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. Table 1 contains crystallographic data and details of measurements and refinement for compounds **1a**, **2a**, and **3a**. Table S2 contain selected bond lengths and angles for selected arylgermanium hydrides.

Table S1. Crystallographic data and details of measurements for compounds **1a**, **2a** and **3a** Mo Kα (λ=0.71073Å). $R_1 = \Sigma / |F_o| - |F_c| / |\Sigma| F_d$; $wR_2 = [\Sigma_w (F_o^2 - F_2^2)^2 / \Sigma_w (F_o^2)^2]^{1/2}$

Compound	$(2,5\text{-}Me_2C_6H_3)_3GeH$ **(1a)**	$(2,5\text{-}Me_2C_6H_3)_2Ge(Cl)H$ **(2a)**	$(2,5\text{-}Me_2C_6H_3)_2GeH_2$ **(3a)**
Formula	$C_{24}H_{28}Ge$	$C_{16}H_{19}ClGe$	$C_{16}H_{20}Ge$
Fw (g mol^{-1})	389.05	319.35	284.91
a (Å)	5.1734(4)	4.9390(2)	4.9200(4)
b (Å)	34.197(3)	12.9382(7)	11.5407(9)
c (Å)	11.2239(12)	11.2907(6)	12.5031(10)
α (˚)	90	90	96.550(2)
β (˚)	95.674(3)	94.166(2)	96.532(2)
γ (˚)	90	90	94.905(2)
V (Å^3)	1976.0(3)	719.59(6)	697.22(10)
Z	4	2	2
Crystal size (mm)	0.09 × 0.08 × 0.06	0.10 × 0.09 × 0.07	0.10 × 0.09 × 0.08
Crystal habit	Block, colourless	Block, colourless	Block, colourless
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1$	*P*-1
d_{calc} (mg/m^3)	1.308	1.474	1.357
μ (mm^{-1})	1.55	2.29	2.17
T (K)	100(2)	100(2)	100(2)
2*θ* range (˚)	2.4–33.3	2.4–28.3	2.6–33.2
F(000)	816	328	296
R_{int}	0.108	0.057	0.049
independent reflns	7543	2368	5349
No. of params	236	172, 1	166
R_1, wR_2 (all data)	$R_1 = 0.1004$ $wR_2 = 0.1010$	$R_1 = 0.0259$ $wR_2 = 0.0525$	$R_1 = 0.0188$ $wR_2 = 0.0494$
R_1, wR_2 (>2σ)	$R_1 = 0.0569$ $wR_2 = 0.0910$	$R_1 = 0.0245$ $wR_2 = 0.0521$	$R_1 = 0.0184$ $wR_2 = 0.0491$

Table S2. List of selected bond lengths and angles for selected arylgermanium hydrides.

	Space Group	**Ge–C (Å)**	**Ge—Cl (Å)**	**Ge–H (Å)**	**C–Ge–C (°)**	**H–Ge–H (°)**	**C–Ge–H (°)**	**C—Ge—Cl (°)**	**Cl—Ge—H (°)**
Ph_3GeH [S20]	*P*-1 $P2_1/c$	1.944(5) 1.944(4)	–	1.45(3) 1.50(5)	109.27(2) 110.77(1)	–	108.33(2) 109.67(2)	–	–
***o*-Tol_3GeH [S21]**	*C*2/*c*	1.961(2)	–	1.71(2)	106.57(2)	–	112.69(2)	–	–
$(2,5\text{-}Me_2C_6H_3)_3GeH$ (1a)	$P2_1/c$	1.956(2) 1.958(2) 1.967(2)	–	1.42(2)	109.15(9) 109.58(9) 110.20(9)	–	108.9(9) 109.1(9) 109.9(9)	–	–
$(2,4,6\text{-}Me_3C_6H_2)_3GeH$ [S22]	*C*2/*c*	2.045(3)	–	*	109.2(3)	–	*	–	–
$(4\text{-}Bu^nC_6H_4Ge)_2GeH$ [S23]	*P*-1	1.984(2)	–	1.37(2)	108.10(9)	–	111(1)	–	–
$(2,5\text{-}Me_2C_6H_3)_2GeH_2$ (3a)	*P*-1	1.952(2) 1.954(2)	–	1.40(2) 1.41(2)	113.75(6)	110.1(12)	105.5(8) 108.1(8) 108.8(8) 113.8(6)	–	–
$(2,4,6\text{-}Me_3C_6H_2)_2GeH_2$ [S23]	*C*2/*c*	1.965(2)	–	1.43(3)	113.2(1)	107.35(3)	109.06(3)	–	–
$(2,5\text{-}Me_2C_6H_3)_2Ge(Cl)H$ (2a)	$P2_1$	1.936(4) 1.945(4)	2.193(2)	1.49(4)	114.24(17)	–	112.0(16) 112.6(19)	105.83(12) 105.92(12)	105(2)

*Hydrogen atom not found on difference map

A) Synthesis of Ar_3GeH

i) Grignard Route towards Ar_3GeHal (Hal = Cl, Br)[S1]

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 aryl bromide 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 aryl bromide was subsequently added dropwise. After complete addition, the mixture was refluxed for 3-12 hours. 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, and the solvent was switched for toluene. The mixture was stirred for 1 hour, heated to reflux for several hours and was subsequently allowed to cool down to room temperature. After quenching with 10% deaerated HCl at 0 °C, 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 solid Ar_3GeHal was washed several times with pentane.

ii) $LiAlH_4$ Route for Ar_3GeH

A Schlenk tube was charged with $LiAlH_4$ and dry THF. Ar_3GeHal (Hal = Cl, Br) was added as a powder or in solution in small portions at 0 °C. The reaction was stirred at 0 °C for 1 hour and then allowed to warm to room temperature. After additional stirring for 1-2 hours, the mixture was quenched using 3% deaerated H_2SO_4. After extraction with a saturated deaerated sodium tartrate solution, the solution was filtered *via* cannula and dried over Na_2SO_4. After filtration and washing twice with toluene, all solvents were removed under *vacuo*.

B) Synthesis of Ar_2GeH_2 (Triflic Acid Route)

A Schlenk tube was charged with Ar_3GeH and freshly distilled DCM. TfOH was added dropwise at 0 °C, and the mixture was allowed to warm to room temperature. After stirring for 24-48 hours, after which time the ^{19}F NMR spectrum of the solution exhibited a single resonance indicating complete consumption of TfOH and formation of the intermediate triflate, a suspension of LiCl in DME was added at 0 °C and the mixture was stirred for additional 24 hours. Toluene was added, and DCM with DME were evaporated under reduced pressure. After filtration *via* cannula, $LiAlH_4$ was added as a solid in small portions at 0 °C. After stirring for 3 hours at room temperature, the mixture was quenched with 3% degassed H_2SO_4. After extraction with a saturated deaerated sodium tartrate solution, the solution was filtered *via* cannula and dried over Na_2SO_4. After filtration and washing twice with toluene, all solvents were removed under *vacuo*.

C) Synthesis of $Ar_2Ge(Cl)H$ (Triflic Acid Route)

A Schlenk tube was charged with Ar_3GeH and freshly distilled DCM. TfOH was added dropwise at 0 °C, and the mixture was allowed to warm to room temperature. After stirring for 24 hours, after which time the ^{19}F NMR spectrum of the solution exhibited a single resonance indicating complete consumption of TfOH and formation of the intermediate triflate, DCM was exchanged with DME, and LiCl was added as a solid at 0 °C and the mixture was stirred for an additional 24 hours. After removal of solvent, toluene was added, and the solution was purified *via* cannula filtration. After removal of solvent, the resulting product was dried in *vacuo*.

D) Synthesis of $ArGeH_3$ (Triflic Acid Route)

A Schlenk tube was charged with Ar_2GeH_2 and freshly distilled DCM. TfOH was added dropwise at 0 °C, and the mixture was allowed to warm to room temperature. After stirring for 24-48 hours, after which time the ^{19}F NMR spectrum of the solution exhibited a single resonance indicating complete consumption of TfOH and formation of the intermediate triflate, a suspension of LiCl in DME was added at 0 °C and the mixture was stirred for additional 24 hours. Toluene was added, and DCM with DME were evaporated under reduced pressure. After filtration *via* cannula, $LiAlH_4$ was added as a solid in small portions at 0 °C. After stirring for 3 hours at room temperature, the mixture was quenched with 3% deaerated H_2SO_4. The solution was filtered *via* cannula and dried over Na_2SO_4. After filtration, all solvents were removed carefully under *vacuo*. In some cases, the product was further purified *via* condensation.

E) Synthesis of Ar_2GeH_2 (Grignard Route)

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 aryl bromide in THF; about 10% of the solution was added to the reaction vessel. To start the reaction, it was carefully heated or dibromoethane was added. The aryl bromide was subsequently added dropwise at reflux. After complete addition, the mixture was refluxed for approx. 3 hours. 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. After several hours of reflux, the mixture was quenched under acidic conditions. After drying over Na_2SO_4, all solvents were removed under reduced pressure, and unreacted compounds were removed carefully by heating under vacuum. Et_2O was added and freshly ground $LiAlH_4$ was slowly added as a powder or in an Et_2O solution at 0 °C. The mixture was stirred 2 hours at 0 °C and, after letting it warm up to room temperature, for another 30 minutes. After quenching under acidic conditions and extraction with a saturated potassium tartrate solution, the organic layer was dried over Na_2SO_4. Removal of solvents yields a colourless solid, which can be purified by dissolving the dihydride in pentane and filtering of the insoluble triarylgermanium hydride.

F) Synthesis of $ArGeH_3$ (Grignard Route)

A flask equipped with a dropping funnel and a reflux condenser was charged with Mg in Et_2O or THF. The dropping funnel was charged with aryl bromide in THF; about 10% of the solution was added to the reaction vessel. To start the reaction, it was carefully heated or dibromoethane was added. The aryl bromide was subsequently added dropwise at reflux. After complete addition, the reaction was refluxed for approx. 3 hours. Residual Mg was filtered off using a filter cannula or a Schlenk-frit charged with Celite®. The Grignard solution was added dropwise to a solution of $GeCl_4$ in Et_2O at 0 °C. After several hours of reflux, the mixture was quenched under acidic conditions. After drying over Na_2SO_4, all solvents were removed under reduced pressure, and unreacted compounds were removed carefully by heating under vacuum. Et_2O was added and freshly grounded $LiAlH_4$ was slowly added as a powder at 0 °C. The reaction was stirred 2 hours at 0 °C and, after letting it warm up to room temperature, for another 30 minutes. After quenching under acidic conditions and extraction with a saturated potassium tartrate solution, the organic layer was dried over Na_2SO_4. Condensation and subsequent careful removal of solvent yields a colourless liquid. Further purification can be achieved by distillation.

(1-Naphthyl)germane 4c was obtained by Route F by treatment of a solution of Mg (2.00 g, 82.3 mmol, 1.22 equiv.) in THF (50 ml) with 1-bromonaphthalene (15.5 g, 74.8 mmol, 1.11 equiv.) in THF (250 ml). After reflux and filtration, a solution of $GeCl_4$ (14.4 g, 67.3 mmol, 1.00 equiv.) in THF (80 ml) was added at 0 °C to the Grignard solution. The (1-naphthyl)$_n$GeHal$_{4-n}$ (Hal = Cl, Br) (67.3 mmol, 1.00 equiv.) mix was suspended in Et_2O (250 ml) at 0 °C. $LiAlH_4$ (4.00 g, 105 mmol, 1.60 equiv.) was added as a solid. Separation by distillation. Colourless liquid. Yield: 88%. B.p.: 102-104 °C at 7 mbar. Elemental analysis (%) for $C_8H_{12}Ge$: C, 59.22; H, 4.97. Found: C, 60.73; H, 4.93. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.54 (s, 3H, Ge-*H*), 7.43 (dd, 1H, 3-Ar*H*, $^{3}J_{\text{H-H}}$ = 7.5 Hz), 7.51; 7.52 (dd, dd, 4H, 6,7-Ar*H*, $^{3}J_{\text{H-H}}$ = 7.6 Hz), 7.72 (2, 4, 5, or 8-Ar*H*, $^{3}J_{\text{H-H}}$ = 7.1 Hz), 7.74 (2, 4, 5, or 8-Ar*H*, $^{3}J_{\text{H-H}}$ = 7.1 Hz), 7.84 (2, 4, 5, or 8-Ar*H*, $^{3}J_{\text{H-H}}$ = 7.1 Hz), 7.89 (2, 4, 5, or 8-Ar*H*, $^{3}J_{\text{H-H}}$ = 7.1 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 137.27 (C1), 135.77 (C8a), 133.44 (C4a), 131.02 (C2), 130.07 (C4), 128.91 (C6), 128.43 (C5), 126.46 (C8), 125.99 (C7), 125.57 (C3) ppm. ATR-IR: 2061.7 cm^{-1} (Ge-H). GCMS: Method 2: t_R = 9.784 min, m/z: 201.0 ($M^{+\bullet}$ - 3H), 128.1 ($M^{+\bullet}$ - GeH_3).

(2,5-Dimethylphenyl)germane 4a was obtained by Route D by treatment of a solution of bis(2,5-dimethylphenyl)germane **3a** (1.00 g, 3.50 mmol, 1.00 equiv.) in CH_2Cl_2 (35 ml) with the solution of TfOH (0.53 g, 3.50 mmol, 1.05 equiv.) in DME (20 ml). LiCl (0.15 g, 3.50 mmol, 1.00 equiv.) was added as a solid to the cooled solution (0 °C). The solution was then treated with $LiAlH_4$ (0.13 g, 3.50 mmol, 1.10 equiv.) added as a solid. The resulting white solid was recrystallized from toluene to yield colourless crystals at room temperature. Colourless liquid. Yield: 21%. **4a** was also obtained by Route F by treatment of a solution of Mg (2.61 g, 107 mmol, 1.22 equiv.) in THF (40 ml) with 2-bromo-*p*-xylene (18.0 g, 97.5 mmol, 1.11 equiv.) in THF (100 ml). After reflux and filtration, a solution of $GeCl_4$ (18.8 g, 87.8 mmol, 1.00 equiv.) in THF (60 ml) was added at 0 °C to the Grignard solution. The (2,5-$Me_2C_6H_3$)$_n$GeHal$_{4-n}$ (Hal = Cl, Br) (87.8 mmol, 1.00 equiv.) mix was suspended in Et_2O (150 ml) at 0 °C. $LiAlH_4$ (5.00 g, 132 mmol, 1.50 equiv.) was added as a solid. Separation by distillation. Colourless liquid. Yield: 72%. B.p.: 45 °C at 5 mbar. Elemental analysis (%) for $C_8H_{12}Ge$: C, 53.14; H, 6.69. Found: C, 52.47; H, 6.25. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.21 (s, 3H, *o*-C*H*$_3$), 2.27 (s, 3H, *m*-C*H*$_3$), 4.14 (s, 3H, Ge-*H*), 7.00 (s, 1H, *o*-ArH), 7.07 (d, 1H, *o*- or *m*-Ar*H*, $^{3}J_{\text{H-H}}$ = 7.3 Hz), 7.15 (d, 1H, *o*- or *m*-Ar*H*, $^{3}J_{\text{H-H}}$ = 8.1 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 140.45 (*m*-C), 137.37 (*o*-C), 134.98 (*o*-C), 131.59 (*m*-C), 130.53 (*p*-C), 129.40 (*i*-C), 22.85 (CH_3), 21.02 (CH_3) ppm. ^{73}Ge NMR (toluene-d_8, 13.96 MHz): δ -200.6 ($^{1}J(^{73}\text{Ge}–^{1}\text{H})$ = 96 Hz; $v_{1/2}$ = 20 Hz) ppm. ATR-IR: 2059.7 cm^{-1} (Ge-H). GCMS: t_R = 6.881 min, m/z: 180.0 ($M^{+\bullet}$), 165.0 ($M^{+\bullet}$ -CH_3), 151.0 ($M^{+\bullet}$ - $(CH_3)_2$), 105.1 ($M^{+\bullet}$ -GeH_3), 91.1 ($M^{+\bullet}$ - $GeH_3(CH_3)$), 77.1 ($M^{+\bullet}$ -($GeH_3(CH_3)_2$).

(2,6-Dimethylphenyl)germane 4b was obtained by Route D by treatment of a solution of bis(2,6-dimethylphenyl)germane **3b** (2.00 g, 7.01 mmol, 1.00 equiv.) in CH_2Cl_2 (35 ml) with the solution of TfOH (1.11 g, 7.37 mmol, 1.05 equiv.) in DME (20 ml). LiCl (0.71 g, 7.72 mmol, 1.10 equiv.) was added as a solid to the cooled solution (0 °C). The solution was then treated with $LiAlH_4$ (0.29, 7.72 mmol, 1.10 equiv.) added as a solid. The resulting white solid was recrystallized from toluene to yield colourless crystals at RT. Colourless liquid. Yield: 24%. **4b** was also obtained by Route F by treatment of a solution of Mg (2.62 g, 108 mmol, 1.23 equiv.) in THF (40 ml) with 2-bromo-*m*-xylene (18.0 g, 97.5 mmol, 1.11 equiv.) in THF (100 ml). After reflux and filtration, a solution of $GeCl_4$ (18.8 g, 87.8 mmol, 1.00 equiv.) in THF (40 ml) was added at 0 °C to the Grignard solution. The (2,6-$Me_2C_6H_3$)$_n$GeHal$_{4-n}$ (Hal = Cl, Br) (87.8 mmol, 1.00 equiv.) mix was suspended in Et_2O (250 ml) at 0 °C. $LiAlH_4$ (5.00 g, 132 mmol, 1.50 equiv.) was added as a solid. Separation by distillation. Colourless liquid. Yield: 70%. B.p.: 39 °C at 4 mbar. Elemental analysis (%) for $C_8H_{12}Ge$: C, 53.14; H, 6.69. Found: C, 52.97; H, 6.51. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.36 (s, 6H, *o*-C*H*$_3$) 4.12 (s, 3H, Ge-*H*), 6.96 (d, 2H, *m*-Ar*H*, $^3J_{H\text{-}H}$ = 7.8 Hz), 7.10 (t, 1H, *p*-Ar*H*, $^3J_{H\text{-}H}$ = 7.8 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 143.96 (*o*-C), 131.37 (*i*-C), 127.12 (*p*-C), 129.21 (*m*-C), 24.34 (*o*-CH_3) ppm. ATR-IR: 2060.1 cm^{-1} (Ge-H). GCMS: t_R = 7.251 min, m/z: 180.0 ($M^{+\bullet}$), 164.9 ($M^{+\bullet}$ -CH_3), 150.9 ($M^{+\bullet}$ - $(CH_3)_2$), 105.1 ($M^{+\bullet}$ - GeH_3), 91.0 ($M^{+\bullet}$ -$GeH_3(CH_3)$), 77.0 ($M^{+\bullet}$ - $GeH_3(CH_3)_2$).

(3,5-Dimethylphenyl)germane 4e was obtained by Route F by treatment of a solution of Mg (1.36 g, 56.0 mmol, 1.23 equiv.) in THF (30 ml) with 5-bromo-*m*-xylene (9.00 g, 49.0 mmol, 1.11 equiv.) in THF (90 ml). After reflux and filtration, a solution of $GeCl_4$ (9.40 g, 43.9 mmol, 1.00 equiv.) in THF (30 ml) was added at 0 °C to the Grignard solution. The $(3{,}5\text{-}Me_2C_6H_3)_nGeHal_{4-n}$ (Hal = Cl, Br) (43.9 mmol, 1.00 equiv.) mix was suspended in Et_2O (150 ml) at 0 °C. $LiAlH_4$ (3.48 g, 101 mmol, 2.3 equiv.) was added as a solid. Separation by distillation. Colourless liquid. Yield: 72%. Elemental analysis (%) for $C_8H_{12}Ge$: C, 53.14; H, 6.69. Found: C, 52.47; H, 6.25. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.33 (s, 6H, *m*-C*H*$_3$), 4.24 (s, 3H, Ge−*H*), 7.02 (s, 1H, p-Ar*H*), 7.17 (s, 2H, o-Ar*H*) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): *δ* 137.87 (*m*-C), 133.22 (*p*-C), 130.94 (*i*-C), 130.77 (*o*-C), 21.37 (*m*-CH_3) ppm. ATR-IR: 2064.3 cm^{-1} (Ge−H). GCMS (Method 2): tR = 6.506 min, m/z: 180.0 (M+•), 165.0 (M+• - CH_3), 150.9 (M+• - $(CH_3)_2$), 107.1 (M+• - GeH_3), 91.1 (M+• - GeH_3, - CH_3), 77.1 (M+• - GeH_3, - $(CH_3)_2$).

(4-*n*-Butylphenyl)germane 4d was obtained by Route F by treatment of a solution of Mg (1.00 g, 41.3 mmol, 1.22 equiv.) in THF (25 ml) with 1-bromo-4-*n*-butylbenzene (8.00 g, 37.5 mmol, 1.11 equiv.) in THF (55 ml). After reflux and filtration, a solution of $GeCl_4$ (7.23 g, 33.8 mmol, 1.00 equiv.) in THF (40 ml) was added at 0 °C to the Grignard solution. The $(4{-}^nBuC_6H_4)_nGeHal_{4-n}$ (Hal = Cl, Br) (33.8 mmol, 1.00 equiv.) mix was suspended in Et_2O (150 ml) at 0 °C. $LiAlH_4$ (3.0 g, 79.1 mmol, 2.30 equiv.) was added as a solid. Separation by distillation. Colourless liquid. Yield: 61%. Elemental analysis (%) for $C_{10}H_{16}Ge$: C, 57.51; H, 7.72. Found: C, 56.78; H, 7.23. ^1H NMR ($CDCl_3$, 300 MHz): δ 0.93 (t, 3H, C_dH_3, $^3J_{H\text{-}H}$ = 7.3 Hz), 1.36 (h, 2H, C_cH_2, $^3J_{H\text{-}H}$ = 7.5 Hz), 1.60 (q, 2H, C_bH_2, $^3J_{H\text{-}H}$ = 7.4 Hz), 2.61 (t, 2H, C_aH_2, $^3J_{H\text{-}H}$ = 7.8 Hz), 4.25 (s, 3H, Ge−H), 7.18 (d, 2H, *m*-Ar*H*, $^3J_{H\text{-}H}$ = 7.8 Hz), 7.45 (d, 2H, *o*-Ar*H*, $^3J_{H\text{-}H}$ = 7.8 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 143.99 (*p*-C), 135.52 (*o*-C), 128.68 (*m*-C), 127.84 (*i*-C), 35.72 (C_a), 33.73 (C_b), 22.50 (C_c), 14.10 (C_d) ppm. ATR-IR: 2066.7 cm^{-1} (Ge−H). GCMS (Method 2): tR = 8.093 min, m/z: 208.0 (M+•), 165.0 (M+• - H_3, - C_3H_7), 150.9 (M+• - H_3, - C_4H_9), 133.1 (M+• - GeH_3), 105.1 (M+• - GeH_3, - C_3H_5), 91.1 (M+• - GeH_3, - C_3H_7).

Di(1-naphthyl)germane 3c was obtained by Route B by treatment of a solution of tri(1-naphthyl)germane **1c** (2.11 g, 4.60 mmol, 1.00 equiv.) in CH_2Cl_2 (70 ml) with the solution of TfOH (0.83 g, 5.60 mmol, 1.20 equiv.) in DME (20 ml). LiCl (0.29 g, 6.90 mmol, 1.50 equiv.) was added as a solid to the cooled solution (-30 °C). The solution was then treated with $LiAlH_4$ (0.26 g, 6.90 mmol, 1.50 equiv.) added as a solid. A white solid was obtained. Yield: 24%. **3c** was also obtained by Route E by treatment of a solution of Mg (2.00 g, 82.3 mmol, 1.22 equiv.) in THF (50 ml) with 1-bromo-naphthalene (15.5 g, 74.8 mmol, 1.11 equiv.) in THF (250 ml). After reflux and filtration, a solution of $GeCl_4$ (14.4 g, 67.3 mmol, 1.00 equiv.) in THF (80 ml) was added at 0 °C to the Grignard solution. The $(1\text{-naphthyl})_nGeHal_{4-n}$ (Hal = Cl, Br) (67.3

mmol, 1.00 equiv.) mix was suspended in Et_2O (200 ml) at 0 °C. $LiAlH_4$ (4.00 g, 105 mmol, 1.60 equiv.) was added as a solid. A white solid was obtained. Yield: 88% M.p.: 94.3 °C. Elemental analysis (%) for $C_{20}H_{16}Ge$: C, 73.02; H, 4.90. Found: C, 74.21; H, 4.92. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.64 (s, 2H, Ge-*H*), 7.43 (dd, 2H, 3-Ar*H*, $^3J_{H\text{-}H}$ = 7.1 Hz), 7.49; 7.51 (dd, dd, 4H, 6,7-Ar*H*, $^3J_{H\text{-}H}$ = 7.9 Hz), 7.69 (d, 2H, 2, 4, 5, or 8-Ar*H*, $^3J_{H\text{-}H}$ = 7.9 Hz), 7.89 (d, 2H, 2, 4,5, or 8-Ar*H*, $^3J_{H\text{-}H}$ = 7.4 Hz), 8.00 (d, 2H, 2, 4, 5, or 8-Ar*H*, $^3J_{H\text{-}H}$ = 7.9 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 137.14 (C1), 135.56 (C8a), 133.47 (C4a), 132.90 (C2), 130.04 (4), 128.84 (C6), 128.30 (C5), 126.36 (C8), 125.85 (C7), 125.56 (C3) ppm. ATR-IR: 2049.5 (Ge-H) cm^{-1}. GCMS: Methode2: t_R = 18.99 min, m/z: 330.1 ($M^{+\bullet}$), 252.1 ($M^{+\bullet}$ - GeH_2), 201.0 ($M^{+\bullet}$ - 1-naphthylH_2), 128.0 ($M^{+\bullet}$ - 1-naphthylGeH_2).

Bis(2,5-dimethylphenyl)germane 3a was obtained by Route B by treatment of a solution of tris(2,5-dimethylphenyl)germane **1a** (5.03 g, 12.9 mmol, 1.00 equiv.) in CH_2Cl_2 (70 ml) with the solution of TfOH (2.13 g, 14.2 mmol, 1.10 equiv.) in DME (30 ml). LiCl (0.66 g, 15.5 mmol, 1.20 equiv.) was added as a solid to the cooled solution (0 °C). The solution was then treated with $LiAlH_4$ (0.59 g, 15.5 mmol, 1.20 equiv.) added as a solid. The resulting white solid was recrystallized from toluene to yield colourless crystals at room temperature. Yield: 69%. **3a** was also obtained by Route E by treatment of a solution of Mg (3.00 g, 125 mmol, 2 equiv.) in Et_2O (40 ml) with 2-bromo-*p*-xylene (19.3 g, 104 mmol, 1.67 equiv.) in Et_2O (100 ml). After reflux and filtration, a solution of $GeCl_4$ (13.4 g, 62.5 mmol, 1.00 equiv.) in Et_2O (60 ml) was added at 0 °C to the Grignard solution. The $(2,5\text{-}Me_2C_6H_3)_nGeHal_{4\text{-}n}$ (Hal = Cl, Br) (62.5 mmol, 1.00 equiv.) mix was suspended in Et_2O (150 ml) at 0 °C. $LiAlH_4$ (4.28 g, 112.5 mmol, 1.8 equiv.) in Et_2O (150 ml) was added. A white solid was obtained. Yield: 81%. M.p.: 61 °C. Elemental analysis (%) for $C_{16}H_{20}Ge$: C, 67.44; H, 7.07. Found: C, 67.52; H, 6.91. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.26 (s, 6H, *o*-C*H*$_3$), 2.31 (s, 6H, *m*-C*H*$_3$), 5.03 (s, 2H, Ge-*H*), 7.08 (s, 4H, *m*-, *p*-Ar*H*), 7.21 (s, 2H, *o*-Ar*H*) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 140.60 (*m*-C), 136.91 (*o*-C), 134.96 (*o-C*), 133.85 (*m*-C), 130.40 (*p*-C), 129.53 (*i*-C), 22.48 (*C*H$_3$), 20.90 (*C*H$_3$) ppm. ^{73}Ge NMR (toluene-d_8, 13.96): δ -125.6 ($^1J(^{73}Ge{-}^1H)$ = 107(5) Hz; $\nu_{1/2}$ = 41 Hz) ppm. ATR-IR: 2055.2 (Ge-H) cm^{-1}. GCMS: Methode2: t_R = 13.53 min, m/z: 286.1 ($M^{+\bullet}$), 180.0 ($M^{+\bullet}$ - $(2,5\text{-}Me_2C_6H_3)H_2$), 165.0 ($M^{+\bullet}$ - $(2,5\text{-}Me_2C_6H_3)H_2(CH_3)$), 151.0 ($M^{+\bullet}$ - $(2,5\text{-}Me_2C_6H_3)H_2(CH_3)_2$), 105.1 ($M^{+\bullet}$ - $2,5\text{-}Me_2C_6H_3GeH_2$), 91.1 ($M^{+\bullet}$ - $2,5\text{-}Me_2C_6H_3GeH_2(CH_3)$), 77.1 ($M^{+\bullet}$ -$2,5\text{-}Me_2C_6H_3GeH_2(CH_3)_2$).

Bis(2,6-dimethylphenyl)germane 3b was obtained by Route B by treatment of a solution of tris(2,6-dimethylphenyl)germane **1b** (4.00 g, 10.3 mmol, 1.00 equiv.) in CH_2Cl_2 (100 ml) with the solution of TfOH (2.01 g, 13.4 mmol, 1.20 equiv.) in DME (30 ml). LiCl (0.71 g, 16.8 mmol, 1.50 equiv.) was added as a solid to the cooled solution (0 °C). The solution was then treated with $LiAlH_4$ (0.44 g, 11.5 mmol, 1.20 equiv.) added as a solid. A white solid was obtained**.** Yield: 82%. **3b** was also obtained by Route E by treatment of a solution of Mg (2.95 g, 123 mmol, 2.00 equiv.) in Et_2O (40 ml) with 2-bromo-*m*-xylene (18.96 g, 102 mmol, 1.67 equiv.) in Et_2O (100 ml). After reflux and filtration, a solution of $GeCl_4$ (13.2 g, 61.5 mmol, 1.00 equiv.) in Et_2O (60 ml) was added at 0 °C to the Grignard solution. The $(2,6\text{-}Me_2C_6H_3)_nGeHal_{4\text{-}n}$ (Hal = Cl, Br) (37 mmol, 1.00 equiv.) mix was suspended in Et_2O (150 ml) at 0 °C. $LiAlH_4$ (4.20 g, 111 mmol, 3.00 equiv.) in Et_2O (150 ml) was added. A white solid was obtained. Yield: 84%. M.p.: 50.7 °C. Elemental analysis (%) for $C_{16}H_{20}Ge$: C, 74.08; H, 7.25. Found: C, 72.48; H, 6.99. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.36 (s, 12H, *o*-C*H*$_3$), 5.13 (s, 2H, Ge-*H*), 6.99 (d, 4H, *m*-H, $^3J_{H\text{-}H}$ = 7.8 Hz), 7.13 (t, 2H, *p*-Ar*H*, $^3J_{H\text{-}H}$ = 7.8 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 143.85 (*m*-C), 134.90 (*i*-C), 129.06 (*p*-C), 127.62 (*o*-C), 24.00 (*o*-CH_3) ppm. ATR-IR: 2056.2 (Ge-H) cm^{-1}. GCMS: Methode2: t_R = 14.18 min, m/z: 286.1 ($M^{+\bullet}$), 180.0 ($M^{+\bullet}$ - 2,6-$Me_2C_6H_3H_2$), 165.0 ($M^{+\bullet}$ - (2,6-$Me_2C_6H_3$)H_2(CH_3)), 151.0 ($M^{+\bullet}$ - (2,6-$Me_2C_6H_3$)H_2(CH_3)$_2$), 105.1 ($M^{+\bullet}$ - 2,6-$Me_2C_6H_3GeH_2$), 91.1 ($M^{+\bullet}$ - 2,6-$Me_2C_6H_3GeH_2$(CH_3)), 77.1 ($M^{+\bullet}$ -2,6-$Me_2C_6H_3GeH_2$(CH_3)$_2$).

Bis(3,5-dimethylphenyl)germane 3e was obtained by Route E by treatment of a solution of Mg (1.36 g, 56.0 mmol, 1.23 equiv.) in THF (30 ml) with 5-bromo-*m*-xylene (9.0 g, 49 mmol, 1.11 equiv.) in THF (90 ml). After reflux and filtration, a solution of $GeCl_4$ (9.4 g, 43.9 mmol, 1.00 equiv.) in THF (30 ml) was added at 0 °C to the Grignard solution. The (3,5-$Me_2C_6H_3$)$_n$$GeHal_{4-n}$ (Hal = Cl, Br) (43.9 mmol, 1.00 equiv.) mix was suspended in Et_2O (150 ml) at 0 °C. $LiAlH_4$ (3.48 g, 101 mmol, 2.30 equiv.) was added as a solid. Separation by dissolving in pentane. Colourless liquid. Yield 21%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.33 (s, 12H, *m*-C*H*$_3$), 5.02 (s, 2H, Ge−*H*), 7.04 (s, 4H, *o*-Ar*H*), 7.19 (s, 2H, *p*-Ar*H*) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): *δ* 137.81 (*m*-C), 134.01 (*p*-C), 132.94 (*i*-C), 130.89 (*o*-C), 21.41 (*o*-CH_3) ppm. ATR-IR: 2044.2 cm^{-1} (Ge−H). GCMS (Method 2): tR = 11.765 min, m/z: 286.0 (M+•), 180.0 (M+• - 3,5−xylyl), 105.1 (M+• - GeH_2, - 3,5-$Me_2C_6H_3$).

Bis(4-*n*-butylphenyl)germane 3d was obtained by Route E by treatment of a solution of Mg (1.00 g, 41.3 mmol, 1.22 equiv.) in THF (25 ml) with 1-bromo-4-*n*-butylbenzene (8.00 g, 37.5 mmol, 1.11 equiv.) in THF (55 ml). After reflux and filtration, a solution of $GeCl_4$ (7.23 g, 33.8 mmol, 1.00 equiv.) in THF (40 ml) was added at 0 °C to the Grignard solution. The (4-$Bu^nC_6H_4$)$_n$$GeHal_{4-n}$ (Hal = Cl, Br) (33.8 mmol, 1.00 equiv.) mixture was suspended in Et_2O (150 ml) at 0 °C. $LiAlH_4$ (3.00 g, 79.1 mmol, 2.30 equiv.) was added as a solid. Separation by dissolving in pentane. Colourless liquid. Yield 24%. Elemental analysis (%) for $C_{20}H_{28}Ge$: C, 70.43; H, 8.28. Found: C, 68.93; H, 7.97. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.93 (t, 6H, C_dH_3, $^3J_{H\text{-}H}$ = 7.3 Hz), 1.36 (h, 4H, C_cH_2, $^3J_{H\text{-}H}$ = 7.4 Hz), 1.60 (q, 4H, C_bH_2, $^3J_{H\text{-}H}$ = 7.2 Hz), 2.61 (t, 4H, C_aH_2, $^3J_{H\text{-}H}$ = 7.8 Hz), 5.04 (s, 2H, Ge−*H*), 7.19 (d, 4H, *m*-Ar*H*, $^3J_{H\text{-}H}$ = 7.6 Hz), 7.45 (d, 4H, *o*-Ar*H*, $^3J_{H\text{-}H}$ = 7.6 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): *δ* 144.02 (*p*-C), 135.25 (*o*-C), 130.90 (*m*-C), 128.66 (*i*-C), 35.76 (C_a), 33.72 (C_b), 22.53 (C_c), 14.10 (C_d) ppm. ATR-IR: 2044.2 cm^{-1} (Ge−H). GCMS (Method 2): tR = 13.937 min, m/z: 341.2 (M+•), 208.0 (M+• - 4-$Bu^nC_6H_4$, 180.1 (M+• - 4-$Bu^nC_6H_4$, - C_2H_5), 133.1 (M+• - GeH_2, - 4-$Bu^nC_6H_4$, 91.0 (M+• - GeH_2, - 4-$Bu^nC_6H_4$, - C_3H_7).

Chloro[bis(2,5-dimethylphenyl)]germane 2a was obtained by Route C by treatment of solution of tris(2,5-dimethylphenyl)germane **1a** (3.40 g, 8.74 mmol, 1.00 equiv.) in CH_2Cl_2 (70 ml) with the solution of TfOH (1.31 g, 8.74 mmol, 1.00 equiv.) in DME (50 ml). LiCl (0.37 g, 8.74 mmol, 1.00 equiv.) was added as a solid to the cooled solution (0 °C). A white solid was obtained and recrystallized in toluene to yield colourless crystals at room temperature. Yield: 85%. M.p.: 61 °C. Elemental analysis (%) for $C_{16}H_{19}GeCl$: C, 60.17; H, 6.00. Found: C, 58.52; H, 5.58. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.38 (s, 2H, 6-H, ArH), 7.13 (dd, 4H, 3,4-H, ArH), 6.61 (s, 1H, Ge-H), 2.34 (s, 6H, *m*-CH_3), 2.31 (s, 6H, *o*-CH_3) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 139.85, 135.57, 134.97, 131.78, 130.20, 21.95 (CH_3), 21.20 (CH_3) ppm. ATR-IR: 2090.0 (Ge-H) cm^{-1}. GCMS: Methode2: t_R = 14.99 min, m/z: 320.1 ($M^{+\bullet}$), 283.1 ($M^{+\bullet}$ - HCl), 269.0 ($M^{+\bullet}$ - HCl(CH_3)), 214.0 ($M^{+\bullet}$ - (2,5-$Me_2C_6H_3$)H), 178.0 ($M^{+\bullet}$ - (2,5-$Me_2C_6H_3$)HCl), 165.0 ($M^{+\bullet}$ - (2,5-$Me_2C_6H_3$)HCl(CH_3)), 106.0 ($M^{+\bullet}$ - 2,5-$Me_2C_6H_3GeHCl$), 91.1 ($M^{+\bullet}$ - 2,5-$Me_2C_6H_3GeHCl$(CH_3)), 77.1 ($M^{+\bullet}$ - 2,5-$Me_2C_6H_3GeHCl$(CH_3)$_2$).

Chloro[bis(2,6-dimethylphenyl)]germane 2b was obtained by Route C by treatment of solution of tris(2,6-dimethylphenyl)germane **1b (**6.00 g, 15.4 mmol, 1.00 equiv.) in CH_2Cl_2 (70 ml) with a solution of TfOH (2.77 g, 18.5 mmol, 1.20 equiv.) in DME (50 ml). LiCl (0.98 g, 23.1 mmol, 1.50 equiv.) was added as a solid to the cooled solution (0 °C). A white solid was obtained. Yield: 75% M.p.: 82 °C. Elemental analysis (%) for $C_{16}H_{19}GeCl$: C, 60.17; H, 6.00. Found: C, 58.52; H, 5.58. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.46 (s, 12H, *o*-C*H*$_3$), 6.89 (s, 1H, Ge-*H*), 7.02 (d, 4H, *m*-Ar*H*, $^{3}J_{H\text{-}H}$ = 7.3 Hz), 7.20 (d, 1H, *p*-Ar*H*, $^{3}J_{H\text{-}H}$ = 7.2 Hz), 7.24 (d, 1H, *p*-Ar*H*, $^{3}J_{H\text{-}H}$ = 7.1 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 143.35 (*m*-C), 135.36 (*o*-C), 130.50 (*i*-C), 128.74 (*p*-C), 23.37 (*o*-CH_3) ppm. ATR-IR: 2103.2 (Ge-H) cm^{-1}. GCMS: Methode2: t_R = 15.63 min, m/z: 320.1 ($M^{+\bullet}$), 283.1 ($M^{+\bullet}$ - HCl), 214.0 ($M^{+\bullet}$ - (2,6-$Me_2C_6H_3$)H), 178.0 ($M^{+\bullet}$ - (2,6-$Me_2C_6H_3$)HCl), 165.1 ($M^{+\bullet}$ - (2,6-$Me_2C_6H_3$)HCl(CH_3)), 106.1 ($M^{+\bullet}$ - 2,6-$Me_2C_6H_3GeHCl$), 91.1 ($M^{+\bullet}$ - 2,6-$Me_2C_6H_3GeHCl(CH_3)$), 77.1 ($M^{+\bullet}$ - 2,6-$Me_2C_6H_3GeHCl(CH_3)_2$).

Chloro[tris(3,5-dimethylphenyl)]germane was obtained by Route C by treatment of solution of tetrakis(3,5-dimethylphenyl)germane[S1] (3.00 g, 6.08 mmol, 1.00 equiv.) in CH_2Cl_2 (100 ml) with the solution of TfOH (1.00 g, 6.69 mmol, 1.10 equiv.) in DME (50 ml). LiCl (0.26 g, 6.08 mmol, 1.00 equiv.) was added as a solid to the cooled solution (0 °C). A white solid was obtained and recrystallized in toluene to yield colourless crystals at RT. A white solid was obtained. Yield: 43%. M.p.: 159 °C. Elemental analysis (%) for $C_{24}H_{27}GeCl$: C, 68.06; H, 6.43. Found: C, 67.77; H, 6.23. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.31 (s, 18H, *o*-, *m*-C*H*$_3$), 7.08 (s, 3H, *p*-Ar*H*), 7.22 (s, 6H, *o*-Ar*H*) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 138.19 (*m*-C), 134.96 (*p*-C), 132.35 (*i*-C) 131.79 (*o*-C), 21.53 (*m*-CH_3) ppm. GCMS: Method 2: t_R = 18.94 min, m/z: 424.2 ($M^{+\bullet}$), 319.1 ($M^{+\bullet}$ - Cl), 210.2 ($M^{+\bullet}$ - 3,5-$Me_2C_6H_3GeCl$), 179.1 ($M^{+\bullet}$ - (3,5-$Me_2C_6H_3)_2Cl$), 105.0 ($M^{+\bullet}$ - 3,5-$Me_2C_6H_3GeCl$), 77.1 ($M^{+\bullet}$ - (3,5-$Me_2C_6H_3)_2GeCl(CH_3)_2$).

Tri(1-naphthyl)germane 1c was obtained by Route A by treatment of a solution of bromo/chloro[tris(1-naphthyl)]germane (12.7 g, 24.0 mmol, 1.00 equiv.) in THF (150 ml) with $LiAlH_4$ (1.00 g, 26.4 mmol, 1.00 equiv.) added as a solid. The resulting colourless solid was washed several times with toluene and pentane. A white solid was obtained. Yield: 81%. M.p.: 244 °C. Elemental analysis (%) for $C_{30}H_{22}Ge$: C, 79.17; H, 4.87. Found: C, 79.50; H, 4.92. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.84 (s, 1H, Ge-*H*), 7.25 (d, 3H, 3-Ar*H*, $^{3}J_{H\text{-}H}$ = 7.1 Hz), 7.34 (d, 3H, 5-Ar*H*, $^{3}J_{H\text{-}H}$ = 8.9 Hz), 7.32; 7.40; (dd, dd, 6H, 6,7-Ar*H*, $^{3}J_{H\text{-}H}$ = 7.9 Hz), 7.83 (d, 3H, 2 or 4-Ar*H*, $^{3}J_{H\text{-}H}$ = 8.1 Hz), 7.85 (d, 3H, 2 or 4-Ar*H*, $^{3}J_{H\text{-}H}$ = 8.1 Hz), 7.99 (d, 3H, 8-Ar*H*, $^{3}J_{H\text{-}H}$ = 8.2 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 137.34 (C1), 135.86 (C8a), 133.79 (C4a), 133.72 (C2), 130.19 (C4), 128.93 (C6), 128.76 (C5), 126.36 (C8), 125.89 (C7), 125.72 (C3) ppm. ATR-IR: 2062.9 (Ge-H) cm^{-1}. GCMS: Methode2: t_R = 26.92 min, m/z: 456.1 ($M^{+\bullet}$), 327.0 ($M^{+\bullet}$ - 1-naphthylH), 252.1 ($M^{+\bullet}$ - 2-naphthylGeH), 201.0 ($M^{+\bullet}$ - 1-naphthyl$_2$H), 128.0 ($M^{+\bullet}$ - 1-naphthyl$_2$GeH).

Tris(2,4-dimethylphenyl)germane 1e was obtained by Route A by treatment of a solution of bromo/chloro[tris(2,4-dimethylphenyl)]germane (27.88 g, 62.3 mmol, 1.00 equiv.) in THF (200 ml) with $LiAlH_4$ (2.84 g, 74.8 mmol, 1.20 equiv.) added as a solid. A white solid was obtained. Yield: 75%. M.p.: 138 °C. Elemental analysis (%) for $C_{24}H_{28}Ge$: C, 74.08; H, 7.25. Found: C, 72.48; H, 6.99. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.26 (s, 9H, *o*-C*H*$_3$), 2.30 (s, 9H, *p*-C*H*$_3$), 5.84 (s, 1H, Ge-*H*), 6.91 (d, 3H, *o*- or *m*-Ar*H*, $^{3}J_{H\text{-}H}$ = 7.5 Hz), 7.04 (d, 3H, *o*- or *m*-Ar*H*, $^{3}J_{H\text{-}H}$ = 7.5 Hz), 7.06 (s, 3H, *m*-Ar*H*) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 143.89 (*p*-C), 139.26 (*o*-C), 135.83

(*m*-C), 131.46 (*o*-C), 130.74 (*i*-C), 126.40 (*m*-C), 23.03 (*o*-CH$_3$), 21.51 (*p*-CH$_3$) ppm. ATR-IR: 2050.4 (Ge-H) cm^{-1}. GCMS: Methode2: t$_R$ = 18.63 min, m/z: 389.2 (M$^{+\bullet}$ -H), 284.1 (M$^{+\bullet}$ - (2,4-Me$_2$C$_6$H$_3$)H), 269.1 (M$^{+\bullet}$ - (2,4-Me$_2$C$_6$H$_3$)H(CH$_3$)), 179.1 (M$^{+\bullet}$ - (2,4-Me$_2$C$_6$H$_3$)$_2$), 105.1 (M$^{+\bullet}$ - (2,4-Me$_2$C$_6$H$_3$)$_2$GeH), 91.1 (M$^{+\bullet}$ - (2,4-Me$_2$C$_6$H$_3$)$_2$GeH(CH$_3$)), 77.1 (M$^{+\bullet}$ - (2,4-Me$_2$C$_6$H$_3$)$_2$GeH(CH$_3$)$_2$).

Tris(2,5-dimethylphenyl)germane 1a was obtained by Route A by treatment of a solution of bromo/chloro[tris(2,5-dimethylphenyl)]germane (10.0 g, 22.3 mmol, 1.00 equiv.) in THF (70 ml) with LiAlH$_4$ (0.88 g, 22.3 mmol, 1.00 equiv.) added as a solid. The resulting white solid was recrystallized from toluene to yield colourless crystals at RT. Yield: 82%. M.p.: 177 °C. Elemental analysis (%) for C$_{24}$H$_{28}$Ge: C, 74.08; H, 7.25. Found: C, 74.12; H, 7.20. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 2.20 (s, 9H, *o*-C*H*$_3$), 2.24 (s, 9H, *m*-C*H*$_3$), 5.82 (s, 1H, Ge-*H*), 6.98 (s, 3H, *p*-Ar*H*), 7.09 (s, 6H, *o*- or *m*-Ar*H*) ppm. ^{13}C NMR (CDCl$_3$, 75.5 MHz): δ 140.83 (*m*-C), 136.39 (*o*-C), 134.89 (*o*-C), 134.82 (*m*-C), 130.29 (*i*-C), 129.66 (*p*-C), 22.70 (*o*-CH$_3$), 21.23 (*m*-CH$_3$) ppm. ^{73}Ge NMR (toluene-d$_8$, 13.96 MHz): δ -80.2 ($\nu_{1/2}$ = 52 Hz) ppm. ATR-IR: 2036.9 (Ge-H) cm^{-1}. GCMS: Methode2: t$_R$ = 17.42 min, m/z: 389.2 (M$^{+\bullet}$ -H), 284.1 (M$^{+\bullet}$ - (2,5-Me$_2$C$_6$H$_3$)H), 269.0 (M$^{+\bullet}$ - (2,5-Me$_2$C$_6$H$_3$)H(CH$_3$)), 209.2 (M$^{+\bullet}$ - 2,5-Me$_2$C$_6$H$_3$GeH), 179.0 (M$^{+\bullet}$ - (2,5-Me$_2$C$_6$H$_3$)$_2$), 105.1 (M$^{+\bullet}$ - (2,5-Me$_2$C$_6$H$_3$)$_2$GeH), 91.0 (M$^{+\bullet}$ - (2,5-Me$_2$C$_6$H$_3$)$_2$GeH(CH$_3$)), 77.0 (M$^{+\bullet}$ - (2,5-Me$_2$C$_6$H$_3$)$_2$GeH(CH$_3$)$_2$).

Tris(2,6-dimethylphenyl)germane 1b was obtained by Route A by treatment of a solution of bromo/chloro[tris(2,6-dimethylphenyl)]germane (16.3 g, 34.8 mmol, 1.00 equiv.) in THF (200 ml) with LiAlH$_4$ (1.45 g, 38.3 mmol, 1.10 equiv.) added as a solid. A white solid was obtained. Yield: 86%. M.p.: 147 °C. Elemental analysis (%) for C$_{24}$H$_{28}$Ge: C, 74.08; H, 7.25. Found: C, 73.93; H, 7.09. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 2.17 (s, 18H, *o*-C*H*$_3$), 5.90 (s, 1H, Ge-*H*), 6.95 (d, 6H, m-Ar*H*, $^3J_{\text{H-H}}$ = 7.9 Hz), 7.13 (t, 3H, *p*-Ar*H*, $^3J_{\text{H-H}}$ = 7.4 Hz) ppm. ^{13}C NMR (CDCl$_3$, 75.5 MHz): δ 143.90 (*m*-C), 134.90 (*i*-C), 128.92 (*p*-C), 128.08 (*o*-C), 23.93 (o-CH$_3$) ppm. ATR-IR: 2072.1 (Ge-H) cm^{-1}. GCMS: Methode2: t$_R$ = 18.33 min, m/z: 389.2 (M$^{+\bullet}$ -H), 284.1 (M$^{+\bullet}$ - (2,6-Me$_2$C$_6$H$_3$)H), 269.1 (M$^{+\bullet}$ - (2,6-Me$_2$C$_6$H$_3$)H(CH$_3$)), 209.1 (M$^{+\bullet}$ - 2,6-Me$_2$C$_6$H$_3$GeH), 178.0 (M$^{+\bullet}$ - 2,6-Me$_2$C$_6$H$_{32}$), 105.1 (M$^{+\bullet}$ - (2,6-Me$_2$C$_6$H$_3$)$_2$GeH), 91.1 (M$^{+\bullet}$ - (2,6-Me$_2$C$_6$H$_3$)$_2$GeH(CH$_3$)), 77.1 (M$^{+\bullet}$ - (2,6-Me$_2$C$_6$H$_3$)$_2$GeH(CH$_3$)$_2$).

Tris(3,5-dimethylphenyl)germane 1d was obtained by Route A by treatment of a solution of chloro[tris(3,5-dimethylphenyl)]germane (3.53 g, 7.20 mmol, 1.00 equiv.) in THF (100 ml) with LiAlH$_4$ (0.33 g, 8.64 mmol, 1.50 equiv.) added as a solid. A white solid was obtained. Yield: 82%. M.p.: 124 °C. Elemental analysis (%) for C$_{24}$H$_{28}$Ge: C, 74.08; H, 7.25. Found: C, 73.93; H, 7.09. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 2.28 (s, 18H, *o*-, *m*-C*H*$_3$) 5.52 (s, 1H, Ge-*H*), 7.00 (s, 3H, *p*-Ar*H*), 7.13 (s, 6H, *o*-Ar*H*) ppm. ^{13}C NMR (CDCl$_3$, 75.5 MHz): δ 137.78 (*m*-C), 135.83 (*p*-C), 132.98 (*i*-C), 131.01 (*o*-C), 21.55 (*m*-CH$_3$) ppm. ATR-IR: 2034.6 (Ge-H) cm^{-1}. GCMS: Methode2: t$_R$ = 17.83 min, m/z: 389.2 (M$^{+\bullet}$ -H), 284.1 (M$^{+\bullet}$ - (3,5-Me$_2$C$_6$H$_3$)H), 269.1 (M$^{+\bullet}$ - (3,5-Me$_2$C$_6$H$_3$)H(CH$_3$)), 179.1 (M$^{+\bullet}$ - (3,5-Me$_2$C$_6$H$_3$)$_2$), 105.1 (M$^{+\bullet}$ - (3,5-Me$_2$C$_6$H$_3$)$_2$GeH), 91.1 (M$^{+\bullet}$ - (3,5-Me$_2$C$_6$H$_3$)$_2$GeH(CH$_3$)), 77.1 (M$^{+\bullet}$ - (3,5-Me$_2$C$_6$H$_3$)$_2$GeH(CH$_3$)$_2$).

Table S3: Optimized product mixtures gained by the conversion of $GeCl_4$ with Grignard reagent; semi-quantitative determination using GCMS.[S24]

Ar	ArMgBr/$GeCl_4$	Ar_3GeHal (%)	Ar_2GeHal_2 (%)	$ArGeHal_3$ (%)
2,5-$Me_2C_6H_3$	5 : 1, reflux	100	0	0
2,6-$Me_2C_6H_3$	6 : 1, stir, 0 °C	100	0	0
1-naphthyl	6.23 :1, stir, ~20 °C	100	0	0
2,5-$Me_2C_6H_3$	1.67 : 1, stir, 0 °C	11	85	4
2,6-$Me_2C_6H_3$	Not optimized	Not optimized	Not optimized	Not optimized
1-naphthyl	Not optimized	Not optimized	Not optimized	Not optimized
4-$Bu^nC_6H_4$	1.11 : 1, stir, 0 °C	6	26	62
3,5-$Me_2C_6H_3$	1.11 : 1, stir, 0 °C	3	23	74
2,5-$Me_2C_6H_3$	1.11 : 1, stir, 0 °C	traces	8	92
2,6-$Me_2C_6H_3$	1.11 : 1, stir, 0 °C	traces	23	76
1-naphthyl	1.11 : 1, stir, 0 °C	traces	7	93

Percentage of product based on stoichiometry

References

S1 M. Wolf, A. Falk, M. Flock, A. Torvisco and F. Uhlig, *J. Organomet. Chem.*, 2017, **851**, 143.

S2 K. Harris Robin, D. Becker Edwin, M. Cabral de Menezes Sonia, R. Goodfellow and P. Granger, *Pure Appl. Chem.*, 2001, **73**, 1795.

S3 *APEX2 and SAINT*, Bruker AXS Inc., Madison, Wisconsin, USA, 2012.

S4 R. H. Blessing, *Acta Crystallogr., Sect. A: Found. Adv.*, 1995, **51**, 33.

S5 *SADABS, Version 2.10, Siemens Area Detector Correction*, Universität Göttingen, Germany, 2003.

S6 *CELL_NOW*, Universität Göttingen, Germany, 2008.

S7 *TWINABS*, Bruker AXS Inc., Madison, Wisconsin, USA, 2001.

S8 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, **71**, 3.

S9 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.*, 1990, **46**, 467.

S10 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.*, 2008, **64**, 112.

S11 G. M. Sheldrick, *Acta Crystallographica, Section C: Structural Chemistry*, 2015, **71**, 3.

S12 *SHELXS97*, Univ. Göttingen, Germany, 1997.

S13 C. B. Huebschle, G. M. Sheldrick and B. Dittrich, *J. Appl. Crystallogr.*, 2011, **44**, 1281.

S14 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.

S15 A. L. Spek, *Acta Crystallogr., Sect. D: Biol. Crystallogr.*, 2009, **65**, 148.

S16 *Diamond - Crystal and Molecular Structure Visualization*, Crystal Impact, Bonn, Germany.

S17 F. H. Allen, O. Johnson, G. P. Shields, B. R. Smith and M. Towler, *J. Appl. Crystallogr.*, 2004, **37**, 335.

S18 S. Westrip, *J. Appl. Crystallogr.*, 2010, **43**, 920.

S19 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.

S20 G. S. McGrady, M. Odlyha, P. D. Prince and J. W. Steed, *CrystEngComm*, 2002, **4**, 271.

S21 T. S. Cameron, K. M. Mannan and S. R. Stobart, *Cryst. Struct. Commun.*, 1975, **4**, 601.

S22 J. B. Lambert, C. L. Stern, Y. Zhao, W. C. Tse, C. E. Shawl, K. T. Lentz and L. Kania, *J. Organomet. Chem.*, 1998, **568**, 21.

S23 C. R. Samanamu, C. R. Anderson, J. A. Golen, C. E. Moore, A. L. Rheingold and C. S. Weinert, *J. Organomet. Chem.*, 2011, **696**, 2993.

S24 M. Traxler, Master Thesis, Graz University of Technology, Graz, Austria, 2019.