

Figure 1 Solid-state structures of compounds (a) (2,5-Me₂C₆H₃)₃GeH **1a**, (b) (2,5-Me₂C₆H₃)₂GeH₂ **3a** and (c) (2,5-Me₂C₆H₃)₂Ge(Cl)H **2a**. Ellipsoids are shown at the 30% probability level. All hydrogen atoms removed for clarity, except those bonded to germanium. For selected bond lengths and angles, see Online Supplementary Materials.

However, the development of straightforward preparation of the corresponding arylgermanium dihydrides (Ar₂GeH₂) and trihydrides (ArGeH₃) is more challenging as the separation of undesired side products is tedious, which reduces the product yields.^{21–26} Therefore, a synthetic route employing triflic acid (TfOH) with lithium chloride resulting in chemoselective chlorodearylation was explored.^{27–36} Treatment of preceding triarylgermanium hydrides Ar₃GeH **1a–c** with 1 equiv. of triflic acid and LiCl, as previously described,³⁷ caused dearylation and afforded the corresponding diaryl(chloro)germanium hydrides (2,5-Me₂C₆H₃)₂Ge(Cl)H **2a** and (2,6-Me₂C₆H₃)₂Ge(Cl)H **2b**. Subsequently, diaryl(chloro)germanium hydride derivatives were converted into the corresponding diarylgermanium dihydrides **3a–c** by simply reacting them with LiAlH₄ (see Scheme 1). X-ray quality crystals of (2,5-Me₂C₆H₃)₂GeH₂ **3a** and (2,5-Me₂C₆H₃)₂Ge(Cl)H **2a** were obtained by crystallization from toluene at room temperature (see Figure 1).[†] The triflic acid route was further employed with the resulting diarylgermanium dihydrides (Ar₂GeH₂) **3a,b** to afford the corresponding arylgermanium trihydrides (ArGeH₃) **4a,b** which appeared as colourless liquids (see Scheme 1). However, this method was found to be not only time consuming and laborious for arylgermanium trihydrides, their yields (20–24%) were not satisfactory. Therefore, an alternative Grignard route was explored.

It was reported that the application of Grignard reagents towards GeCl₄ to form Ar₂GeHal₂ or ArGeHal₃ (Hal = Cl, Br) directly leads to mixtures of products,^{38–40} especially, as employed in our work, when more reactive aryl bromides are used for the preparation of the Grignard reagent. These mixtures are difficult for the separation into individual diarylgermanium dichlorides Ar₂GeCl₂ and/or arylgermanium trichlorides ArGeCl₃, in particular, in large scale preparations. In addition, it is crucial that unreacted magnesium metal must be removed before further reaction with GeCl₄, in order to avoid the formation of digermanes or higher oligogermanes.⁴¹

However, employment of precise stoichiometry to favor the formation of chloro/bromogermane mixtures of the types Ar₂GeHal₂ or ArGeHal₃ (Hal = Cl, Br) is possible. Careful adjustment of parameters and reaction procedures allowed for control over the product mixtures and shift to the main product. Choosing the correct stoichiometry between GeCl₄ and the Grignard reagent enabled the preferential formation of either Ar₄Ge, Ar₃GeHal, Ar₂GeHal₂ or ArGeHal₃, respectively. Table 1 displays the different stoichiometric ratios used for the selective synthesis of mono-, di- and triarylated germanium halides (for their characterization, see Online Supplementary Materials).

Due to the fact that arylbromide and GeCl₄ were used, halide exchange between bromide and chloride occurred. Thus,

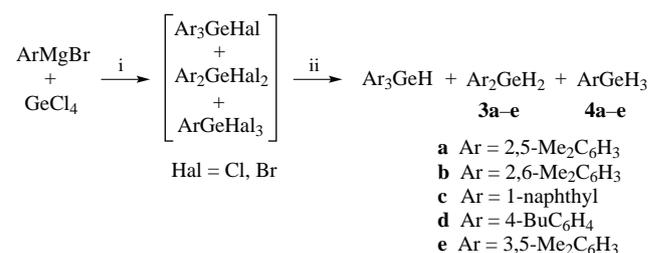
Table 1 Optimized product mixtures obtained by the conversion of GeCl₄ with Grignard reagent; semi-quantitative determination using GC-MS.

Entry	ArMgBr/GeCl ₄ ratio	Conditions	Product composition ^a (%)		
			Ar ₃ GeHal	Ar ₂ GeHal ₂	ArGeHal ₃
1	5 : 1	reflux	100	0	0
2	1.67 : 1	stirring, ~20 °C	11	85	4
3	1.11 : 1	stirring, ~20 °C	traces	8	92

^aAr = 2,5-Me₂C₆H₃; Hal = Cl, Br. Percentage of product based on the stoichiometry.

all possible halide species were present in the product (ArGeHal₃ = ArGeCl₃, ArGeCl₂Br, ArGeClBr₂, ArGeBr₃; Ar₂GeHal₂ = Ar₂GeCl₂, Ar₂GeClBr, Ar₂GeBr₂; Ar₃GeHal = Ar₃GeCl, Ar₃GeBr), which was observed in the GC-MS spectra (see Online Supplementary Materials). While separation of the halogenide derivatives could not be achieved, the direct treatment of the chloride/bromide mixtures with LiAlH₄ (Scheme 2), in order to prepare the hydride derivatives, made separation of the desired product based on solubility and volatility possible. In all cases, colourless solids were obtained which were further purified by extraction with solvents and/or crystallization. Reports on earlier attempts to separate these mixtures are normally referring to distillation.^{39,42,43} Since minor amounts of side products were normally abundant, work up procedures differed depending on the desired product. In the case of diarylgermanium dihydrides, all solvents were first removed. Afterwards, due to the advantageous insolubility of triarylgermanium hydrides in pentane, the diarylgermanium dihydrides **3a–e** were extracted several times with pentane and obtained as white solids in better yields as compared to the triflic acid route (see Scheme 2). In the event of arylgermanium trihydrides being the desired compounds, the product was distilled from the reaction solution in the course of the total removal of solvent, with triarylgermanium hydrides and diarylgermanium dihydrides remaining as solids. In all cases, colourless liquid arylgermanium trihydrides **4a–e** were obtained.

All presented compounds were characterized by ¹H NMR spectroscopy. The chemical shifts of the ‘hydride’ [δ ¹H (Ge)–H (ppm)] resonances (see Online Supplementary Materials) fall into a range of 4 to 7 ppm which is typical of these species. The down-field chemical shifts for hydrides increase with the number of aryl substituents [δ ¹H (Ge)–H = 4.1–4.5 ppm for ArGeH₃ **4a–e**, 5.0–5.6 ppm for Ar₂GeH₂ **3a–e**, 5.5–6.5 ppm for Ar₃GeH **1a–e**], which reflects a trend that has previously been observed for a subset of germanium hydrides^{44,45} also common for silanes⁴⁶ and hydrocarbons. As expected, the hydride resonances in diaryl(chloro)germanium hydrides, Ar₂Ge(Cl)H, are even further deshielded [δ ¹H (Ge)–H = 6.6 ppm in **2a** and 6.9 ppm in **2b**]. Solution ⁷³Ge NMR chemical shifts were also determined: (2,5-Me₂C₆H₃)₃GeH **1a** (δ ⁷³Ge = –80.2 ppm), (2,5-Me₂C₆H₃)₂GeH₂ **3a** (δ ⁷³Ge = –125.6 ppm), and the 2,5-Me₂C₆H₃GeH₃ **4a** (δ ⁷³Ge = –200.6 ppm) in toluene-*d*₈. The chemical shifts of 2,5-Me₂C₆H₃-substituted germanes **1a**, **3a**, **4a**



Scheme 2 Reagents and conditions: i, THF, Et₂O, reflux; ii, LiAlH₄, THF, 0 °C.

are somewhat more negative than those of the analogous phenylgermanes ($\delta^{73}\text{Ge}$, $\text{Ph}_n\text{GeH}_{4-n}$, $n = 3$, -56.0 ppm; $n = 2$, -108.5 ppm; $n = 1$, -187.5 ppm)⁴⁷ and exhibit a similar second order dependence on the number of hydride substituents.

In conclusion, the synthetic procedures herein developed may provide more use of arylgermanium hydrides in synthetic and materials applications.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.01.006.

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