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Selective Chlorination of Germanium Hydrides

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Abstract. Methods for the selective chlorination of organogermylhydrides are given by the selective functionalization of organogermylhydrides of types R_3GeH , R_2GeH_2 and $RGeH_3$ (R = alkyl, aryl). The use of trichloroisocyanuric acid (TCCA) allows the direct conversion of Ge-H functions into their monochlorinated derivatives $R_2Ge(Cl)H$ and $RGe(Cl)H_2$.

Introduction

Due to increasing energy consumption, the demand of today's world for novel energy storage systems is continuously growing, and the quest for novel materials to enhance their performance has become an extensive task that is without doubt of great importance.^[1] Organohydrido, -chloro and mixed germanium species are possible precursors for the synthesis of oligo- and polygermanes through dehydrogenative or Wurtz-type coupling.^[2] Therefore, these organogermanium derivatives can be considered of interest as potential primary commodities for electronics, energy storage and medical applications.^[3] Regardless of a wealth of possible applications, however, the use of organohydrido, -chloro and mixed germanium species has to date received only little attention, presumably because of a limited range of preparation methods. Since the early 70s, organo(chloro)germylhydrides (RGeCl_nH_{3-n}, R = alkyl, aryl; n = 1-3) have been employed as reagents in the preparation of various organogermanium derivatives, ranging from germylamines,^[4] arylhydridogermyllithiums,^[5] acetylide and silylide germylenes,^[6] transition metal coordinated germane complexes,^[7] germyl esters,^[8] among others.^[2a,9] In addition, organo(chloro)germylhydrides have displayed utility in forming oligo- and polygermanes, therefore providing an avenue for exciting germanium chemistry.^[10] However, the synthesis of alkyl-and aryl(chloro)germylhydrides typically involved the use of toxic or costly reagents. Selective monohalogenation of germyldihydrides was done in the presence of HgX_2 (X = Cl, Br),^[11] AlCl₃,^[12] CuCl₂,^[7b,13] N-halosuccinimide,[11,14] additionally requiring the often tedious to synthesize and isolate organogermylhydride starting materials, R_nGeH_{4-n} $(R = alkyl, aryl; n = 1-3).^{[2,14,15]}$

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/zaac.202000318 or from the author. Since many years, we have been interested in the synthesis of aryl group 14 hydrides R_nEH_{4-n} (E = Si, Sn; n = 1-3) on larger scales as well as their spectroscopic properties as potential precursors for polymers, nano-sized particles or surface modification respectively.^[16] We extended our interest towards convenient synthetic routes for the synthesis of arylgermylhydrides R_nGeH_{4-n} (n = 1-3) and their reaction behavior as well as their spectroscopic properties including ⁷³Ge NMR spectroscopy.^[17] Exploiting the residue steric bulk effect on the preparation of arylgermylhydrides via the well-known Grignard route,^[15f] optimization of reaction stoichiometry, and subsequent reaction with LiAlH₄, allowed for high yield preparation of arylgermylhydrides.^[17]

In case of the arylsilylhydrides, as well as hydridooligosiloxanes, it could be shown that selective monochlorination could be achieved specifically by the use of the cheap, nontoxic, and readily available trichloroisocyanuric acid (TCCA). TCCA as a chlorination agent for silicon hydrides was reported by *Stutts* for full chlorination of all Si–H functions.^[18] The first application of TCCA for the selective monochlorination of siloxanes was in the synthesis of chlorotetramethyldisiloxane ((H)Me₂SiOSiMe₂(Cl)) out of dihydridotetramethyldisiloxane [(H)Me₂SiOSiMe₂(H)], as previously reported by our group and extended to other siloxanes^[19] (Scheme 1).

This selective monochlorination of Si–H functions using TCCA towards silanes with multiple Si–H bonds was later extended towards monosilane derivatives and the chlorination of dihydridotetramethyldisilane ((H)Me₂SiSiMe₂(H)^[19b,20] (see Scheme 2). Selective monochlorination with TCCA was also successful in the preparation of organo(chloro)silylhydrides^[20–21] from corresponding di-^[19b,21a,21c] and organosilyltrihydrides.^[21a] In general, such partial chlorinations require strict control over temperature to avoid over-chlorination independent if $CH_2Cl_2^{[21b]}$ or $THF^{[19c]}$ is used as solvent.

With the intent on providing new synthetic routes towards the preparation and characterization of organo(chloro)germylhydrides, we describe here on the selective chlorination of germanium hydrides via electrophilic substitution of an aryl group by a halide through reaction with trifluoromethyl sulfonic acid (TfOH)/LiCl route. While this route had already been emphasized to be very useful in preparing silicon and tin derivatives,^[22] use of TfOH with germanium starting materials had

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Scheme 1. Selective chlorination of dihydridosiloxanes with TCCA.

$$H^{-Si-Si} H^{+1/3} \xrightarrow{CI}_{CI} \stackrel{V}{\longrightarrow}_{CI} \stackrel{V}{\longrightarrow}_{CI} \stackrel{V}{\longrightarrow}_{THF / -20^{\circ}C \text{ to RT}} H^{-Si-Si}_{-55\%}$$

Scheme 2. Selective chlorination of chlorotetramethyldisilane.^[20]

only recently been employed to afford organomono- and organooligogermyltriflate derivatives towards preparation of organooligogermanes,^[23] organogermylhalides,^[23a,23c,24] and silylgermane derivatives.^[22c,23b,24–25] In addition, we describe the use of trichloroisocyanuric acid (TCCA) as a simpler and alternative preparation method, a route that was previously only applied to organosilylhydrides.

Results and Discussion

Two different routes were used for the preparation of diorgano(chloro)germylhydrides, $R_2Ge(Cl)H$, and organo(chloro) germyldihydrides $RGe(Cl)H_2$ within this work (Scheme 3).



Scheme 3. Selective chlorination of germylhydrides with (A) TfOH / LiCl and (B) TCCA.

Reaction of triarylgermylhydrides (R₃GeH) with 1 equiv. of trifluoromethylsulfonic acid (TfOH) and LiCl result in the formation of diaryl(chloro)germylhydrides in yields of >80%.^[17a] The reaction proceeds via the electrophilic substitution of an aryl group by a triflate group.^[22-24] The triflate intermediate, which is typically not isolated, is subsequently reacted with LiCl resulting in the nucleophilic substitution of the triflate group affording the monochlorinated aryl(chloro) germylhydrides. For 2,5-xylyl2Ge(Cl)H and 2,6-xylyl2Ge(Cl)H, it was shown previously that it is important for the reaction temperature to be constantly below 0 °C. This is due to the thermal instability of the organogermyltriflate intermediate which is highly dependent on the ligands used and reaction temperatures, as compared to their silicon and tin counterparts.^[22] In some cases, prolonged storage of organogermyltriflates causes their decomposition with liberation of diphenylgermylene leading to the formation of polymers,^[23a] while higher reaction temperatures resulted in the precipitation of side products including undefined yellow precipitates.^[17a,23a] In the case of 1-naphthyl₂Ge(Cl)H (1), even lower temperatures (-30 °C) were necessary for the desired product to be formed and in order to circumvent formation of side products. After stirring 1-naphthyl₂GeH₂ and TfOH for 24 hours, ¹⁹F NMR spectrum of the solution exhibited a single resonance indicating complete consumption of TfOH and formation of the germanium triflate intermediate (δ –82.1 ppm; TfOH = δ -79.2 ppm). LiCl was added as a solid at 0 °C and the reaction was stirred for an additional 24 hours. In order to isolate the room temperature stable 1-naphthyl₂Ge(Cl)H (1), the solvents were removed and the obtained solid was dissolved in toluene. After filtration via cannula and removal of toluene under vacuo, 1-naphthyl2Ge(Cl)H (1) was obtained as a colorless solid.

In efforts to provide a faster, alternative route to the electrophilic substitution of aryl substituents by a combination TfOH/ LiCl towards organo(chloro)germylhydrides, the potential for selective chlorination of organogermylhydrides via the use of the cheaper trichloroisocyanuric acid (TCCA) was also investigated. In contrast to replacing aryl substituents from triarylgermylhydrides with TfOH, the mono- and diorganogermylhydrides: butyl2GeH2,^[26] phenyl2GeH2^[27] and 1-naphthylGeH₃^[17a] were selectively converted into their monochlorinated species: butyl2Ge(Cl)H (2), phenyl2Ge(Cl)H (3) and 1naphthyl(Cl)H₂ (4), (Scheme 3B). In previous work, it was shown that 1-naphthyl₂SiH₂ was selectively chlorinated to give 1-naphthyl₂Si(Cl)H in CH₂Cl₂ at cold temperatures when an excess of chlorinating agent was provided.[19a,19b,21a,21c] However, when the chlorination of silanes was performed in THF, a solution of TCCA, cooled down to -80 °C, was slowly transferred into another solution of starting material (dissolved in THF at -80 °C) to perform the selective chlorination reaction. The colder temperatures when employing THF were necessary to circumvent the chlorination of THF due to the exothermic nature of the reaction.[18]

While monosilanes required 1 equiv. TCCA per Si–H function and therefore an excess of chlorinating agent for selective chlorination in THF at -80 °C,^[19a,19b,21a,21c] the same excess applied on organogermylhydrides led only to the formation of fully or higher chlorinated species (butyl₂GeCl₂, phenyl₂GeCl₂ and 1-naphthylGe(H)Cl₂). In addition, remaining starting materials were found. To circumvent this problem, we used stoichiometric amounts of TCCA (1 /₃ eq for each hydrogen atom allaemeine Chemie

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of the starting material). In each case, the starting material was cooled down in a solution of THF at -80 °C, in order to prevent the aforementioned possible chlorination of the solvent and prevent decomposition of the organogermylhydride. These were then subsequently reacted with TCCA. By keeping low reaction temperatures and careful consideration of stoichiometry, the formation of higher chlorinated species or remaining of starting materials was not observed. Yield reduction was only caused by product loss during workup procedure as product conversion was found to be quantitative by NMR spectroscopy.

During the chlorination process, TCCA is converted into TCCH, which is highly insoluble in pentane and can be removed by filtration. Selective chlorination of 1-naphthylGeH₃ towards 1-naphthylGe(Cl)H₂ (**4**) was confirmed by comparing NMR shifts of Ge-H signals from the starting material to those of the product (Figure 1). No remaining starting material was found. In addition, GC/MS analysis showed quantitative conversion towards the monochlorinated species without formation of higher chlorinated species. For the known compounds butyl₂Ge(Cl)H (**2**)^[26] and phenyl₂Ge(Cl)H (**3**),^[27] the NMR spectroscopic data was consistent with literature reported shifts (see Experimental Section).



Figure 1. ¹H-NMR spectra (C_6D_6) of 1-naphthylGeH₃ (above) and 1-naphthylGe(Cl)H₂ (4) (below).



Compounds 1-naphthyl2Ge(Cl)H (1) and 1-naphthylGe(Cl)H2 (4) were recrystallized from toluene and THF respectively at below room temperature. This allowed for their structural analysis using single-crystal X-ray diffraction (Figure 2), joining a list of only four other structurally characterized aryl(halo) germylhydrides.^[17a,28] Both compounds crystallize in the space group $P2_1/c$. In the presented aryl(chloro)organogermylhydrides, averaged Ge-C bond lengths fall within a narrow range of 1.9267(13)-1.9412(17) Å and do not seem to be influenced by the number of naphthyl substituents on the germanium atom (Table 1). All hydrogen atoms bound to the central germanium atom were found in the electron density map. The Ge-H bonds fall in a range of 1.33(3)-1.48(2) Å but any bulk substituent effects on the Ge-H bond cannot be considered. These bond lengths are also comparable in length as compared to germylmono- and dihydrides (1.30-1.71 Å) presented by our working group and based on a Cambridge Structural Database (CSD) search.^[17,29]

Conclusions

Two effective methods for the selective chlorination of organogermylhydrides to form organo(chloro)germylhydrides is presented. It was shown that the selective chlorination potential of trichloroisocyanuric acid (TCCA) could be extended from hydrido- silanes and siloxanes also towards germylhydrides. The target compounds were monochlorinated, without the formation of higher chlorinated species or remaining starting materials. The variation of residues on the germanium atoms from alkyl to phenyl to naphthyl group did not change the selectivity of chlorination. TCCA provides a faster, alternative route towards organo(chloro)germylhydrides in comparison to the electrophilic substitution of aryl-substituted germanes by a combination of TfOH/LiCl.

Experimental Section

All moisture and air sensitive reactions were carried out under inert atmosphere using Schlenk-techniques unless otherwise stated. Nitro-



Figure 2. Crystal structures of (a) 1-naphthyl₂Ge(Cl)H (1) and (b) 1-naphthylGe(Cl)H₂ (4). All non-carbon atoms shown as 30% shaded ellipsoids. All hydrogen atoms except those bonded to germanium are omitted for clarity.

a)

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Table 1. Selected bond lengths /Å and angles /° in presented compounds.											
	Ge–C	Ge–H	Ge–Cl	C–Ge–C	H–Ge–H	C-Ge-H	C-Ge-Cl	Cl-Ge-H			
1-naphthyl2Ge(Cl)H (1)	1.9344(18), 1.9412(17)	1.44(2)	2.1855(5)	113.59(7)	_	114.7(8), 112.0(7)	106.03(5), 106.03(5)	103.4(7)			
1-naphthylGe(Cl)H ₂ (4)	1.9267(13)	1.33(3), 1.48(2)	2.1843(4)	-	107.8(16)	117.5(13), 114.0(9)	107.49(4)	102.7(12), 106.1(9)			

gen was used as inert gas and passed through molecular-sieves 4 Å and P_4O_{10} with moisture indicator (Sicapent[®] by Merck) to remove trace water. Solvents were stored over a drying agent (LiAlH₄ in case of THF) under N₂ and distilled prior to use or taken directly form an Innovative Technology[®] solvent drying system. C_6D_6 was refluxed with P_4O_{10} for 3 days, distilled and stored under N₂ over molecular sieves. TCCA was supplied from Sigma Aldrich and used as received. DCM was dried with P_2O_5 and distilled prior to usage. LiCl was purchased from ABCR and stored under inert gas prior to use. All other chemicals from commercial sources were utilized without further purification. Celite[®] with a median particle size of 16.4 µm was used (Celite[®] 512). H₂SO₄ (95%) and HCl (32%) were diluted with degassed, deionized water. Starting materials 1-naphthyl₃GeH₂,^[17a] butyl₂GeH₂,^[26] phenyl₂GeH₂,^[27] and 1-naphthylGeH₃^[17a] were synthesized according to literature.

¹H (300.22 MHz), ¹³C{¹H} (75.5 MHz) and ¹⁹F (282.46 MHz) NMR spectra were recorded on a Mercury 300 MHz spectrometer from Varian at 25 °C. Chemical shifts regarding ¹H and ¹³C{¹H} are given in part per million (ppm) relative to TMS ($\delta = 0.00$ ppm). NMR spectra were taken in CDCl₃ or C₆D₆.The letters s, d, t, q and m are used to indicate singlet, doublet, triplet, quadruplet and multiplet. Coupling constants (*J*) are reported in Hertz (Hz). Processing of the data was carried out using MestReNova7 (Mestrelab research).

GC/MS measurements were carried out on an Agilent Technologies 7890A GC system coupled to an Agilent Technologies 5975 VLMSD mass spectrometer using HP5 column (30 m × 0.250 mm × 0.025 µm) and a carrier helium gas flow of 0.92726 mL·min⁻¹. An injection at a temperature of 280 °C was performed. The MS conditions included positive EI ionization at ionization energy of 70 eV and a full scan mode (50–500 *m/z*). Siloxanes are a viable part of the column used in the GC/MS device (see experimental section), common impurities of the GC/MS measurement device were similar to those of the products that were characterized, so that only a few characteristic MS fragments are given. In some cases, EI-DI measurements up to 500 °C were performed on a Waters GCT Premier with EI ionization at ionization energy of 70 eV and an ion source temperature of 200 °C. Samples were prepared in either THF or toluene with a concentration of 1 mg·mL⁻¹. All data was interpreted using Masslynx software.

All 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 N₂ stream provided by an Oxford Cryosystems cryostream. XRD data collection was performed for compounds **1** and **4**, on a Bruker APEX II diffractometer with use of an Incoatec microfocus sealed tube of Mo- K_a radiation ($\lambda =$ 0.71073 Å) and a CCD area detector. Empirical absorption corrections were applied using SADABS or TWINABS.^[30] The structures were solved with use of the intrinsic phasing option in SHELXT and refined by the full-matrix least-squares procedures in SHELXL.^[31] The space group assignments and structural solutions were evaluated using PLA-TON.^[32] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to germanium for all compounds were located in a difference map. All other hydrogen atoms were located in calculated positions corresponding to standard bond lengths and angles and refined using a riding model. Compound 1-naphthylGe(Cl)H₂ (**4**) was refined as a 2-component inversion twin (BASF 0.53). All crystal structures representations were made with the program Diamond.^[33] All CIF files were edited, validated and formatted with the program publCIF.^[34] Table 2 contains crystallographic data and details of measurements and refinement for compounds **1** and **4**.

Table 2. Crystallographic data and details of measurements for compounds 1 and 4. $^{\rm a)}$

	1-naphthyl2Ge(Cl)H (1)	1-naphthylGe(Cl)H ₂ (4)
Formula	C ₂₀ H ₁₅ ClGe	C ₁₀ H ₉ ClGe
Fw /g·mol ⁻¹	363.36	237.21
a /Å	12.6919(5)	8.4286(3)
b /Å	10.6746(4)	10.6009(4)
c /Å	11.7011(5)	10.7651(4)
a /°	90	90
β /°	115.295(2)	99.511(2)
γ /°	90	90
V /Å ³	1584.35(11)	948.65(6)
Z	4	4
Crystal size /mm	$0.34 \times 0.33 \times 0.30$	$0.10 \times 0.04 \times 0.04$
Crystal habit	block, colorless	block, colorless
Crystal system	monoclinic	monoclinic
Space group	$P2_{1}/c$	$P2_1/c$
d_{calc} /mg·m ⁻³	1.523	1.661
μ /mm ⁻¹	2.10	3.45
Т /К	100(2)	100(2)
2θ range /°	2.5-29.7	2.5-33.1
F(000)	736	472
R _{int}	0.079	0.067
Independent reflns	4600	3623
No. of params	203	118
R_1, wR_2 (all data)	$R_1 = 0.0518$	$R_1 = 0.0311$
/	$wR_2 = 0.0758$	$wR_2 = 0.0658$
$R_1, wR_2 (> 2\sigma)$	R1 = 0.0356	$R_1 = 0.0264$
	$wR_2 = 0.0727$	$wR_2 = 0.0634$

a) Mo- K_{α} ($\lambda = 0.71073$ Å). $R_1 = \Sigma / |F_0| - |F_c| / |\Sigma|F_d$; $wR_2 = [\Sigma w (F_o^2 - F_2^2)^2 / \Sigma_w (F_o^2)^2]^{1/2}$.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1975283 and CCDC-1975284 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Synthesis using TfOH

1-naphthyl₂Ge(Cl)H (1): 3.05 g (6.70 mmol, 1.00 equiv.) 1-naphthyl₃GeH was dissolved in 100 mL freshly distilled DCM. 2.01 g TfOH was added dropwise at 0 °C (13.4 mmol, 2.0 equiv.), and the



reaction mixture was stirred overnight and allowed to warm to room temperature. After stirring for 24 h, after which time the ¹⁹F NMR spectrum of the solution exhibited a single resonance indicating complete consumption of TfOH and formation of the desired product (δ -82.1 ppm). DCM was exchanged with 50 mL DME and 0.71 g (16.8 mmol, 2.51 equiv.) LiCl was added as a solid at 0 °C and the reaction was stirred for an additional 24 h. After removal of solvent, toluene was added and the solution was filtered via cannula filtration. After removal of solvent, the resulting product was dried in vacuo. 1naphthyl₂Ge(Cl)H (1) was obtained as a colorless solid and recrystallized from toluene below room temperature (7 °C). Yield: 82 %. T_d: 225 °C. C₂₀H₁₅GeCl: found 64.12% C (calcd. 66.10), found: 4.05% H (calcd. 4.16%). ¹H NMR (CDCl₃, 300.22 MHz): $\delta = 7.21$ (s, 1H, Ge-*H*), 7.48 (dd, 2H, 3-Ar*H*, ${}^{3}J_{H-H} = 8.1$ Hz), 7.46; 7.50 (dd, dd, 4H, 6,7-ArH, ${}^{3}J_{H-H} = 8.1$ Hz), 7.85 (d, 2H, 2, 4, 5, or 8-ArH, ${}^{3}J_{H-H} =$ 7.1 Hz), 7.89 (d, 2H, 2, 4, 5, or 8-ArH, ${}^{3}J_{H-H} = 7.1$ Hz), 7.96 (d, 2H, 2, 4, 5, or 8-ArH, ${}^{3}J_{H-H}$ = 8.2 Hz), 8.05 (d, 2H, 2, 4, 5, or 8-ArH, ${}^{3}J_{H-H}$ _H = 7.6 Hz) ppm. ¹³C{¹H} NMR (CDCl₃, 75.5 MHz): δ = 125.7 (C3), 126.5 (C7), 127.1 (C9), 127.5 (C9), 129.3 (C6), 131.8 (C4), 132.6 (C2), 133.9 (C5), 134.5 (C10), 136.1 (C1) ppm. **IR** (ATR): $\tilde{v} = 2104.6$ (Ge–H) cm⁻¹. **GCMS**: $t_R = 20.17 \text{ min}, m/z$: 364.0 (M^{+•}), 327.0 (M^{+•·} – HCl), 252.1 (M^{+•} – GeHCl), 235.9 (M^{+•} – 1-naphthylH), 201.0 (M^{+•} - 1-naphthylHCl), 128.0 (M^{+•} - 1-naphthylGeHCl), 77.0 (M^{+•} naphthylGeHCl(C_4H_4)).

Synthesis using TCCA

butyl₂Ge(Cl)H (2): 0.388 g (2.05 mmol) of butyl₂GeH₂ were dissolved in 10 mL of THF and cooled down to -80 °C and kept under constant stirring. 0.16 g (0.683 mmol) TCCA was added in small portions, under intensive stirring. New TCCA portions were added only, if the last portions already went into solution. After TCCA addition was completed, stirring was continued for 15 minutes, afterwards, the cooling bath was removed and the solution was allowed to reach room temperature overnight. THF was removed via membrane pump vacuum (8 mbar). Afterwards, 30 mL of pentane was added to the TCCH, which is insoluble in pentane. The reaction mixture was filtered under inert conditions via syringe filters (200 nm), followed by removal of pentane under vacuum. 0.39 g (1.75 mmol) of butyl₂Ge(Cl)H (2) was isolated as a colorless liquid. Yield: 85%. ¹H NMR (C₆D₆, 300.22 MHz): $\delta = 0.80$ (t, ${}^{3}J_{H-H} = 7.5$ Hz, 6H, -CH₂CH₃), 0.97 (m, 4H, -GeCH₂CH₂), 1.19 (tq, 4H, -CH₂CH₃, J_{H-H} = 16.9, 9.5 Hz), 1.38 (tt, 4H, -CH₂CH₂, J_{H-H} = 15.8, 7.9 Hz), 5.47 (dt, 1H, J_{H-H} = 2.7 Hz, 1.8 Hz, Ge-*H*) ppm. ¹³C{¹H} **NMR** (C₆D₆, 75.50 MHz): δ = 13.8 (-CH₃), 18.7 (-CH₂-), 25.6 (-CH₂-), 26.8 (-CH₂-) ppm. NMR spectroscopic data is consistent with literature.[26]

phenyl₂Ge(Cl)H (3): The complete procedure was performed in an analogous manner to the chlorination of butyl₂GeH₂. 0.4 g (1.75 mmol) of phenyl₂GeH₂ were used in 10 mL of THF with 0.136 g (0.58 mmol) TCCA. 0.41 g (1.56 mmol) of compound phenyl₂Ge(Cl)H (**3**) was isolated as colorless oil. Yield: 89%. ¹H NMR (C₆D₆, 300.22 MHz): $\delta = 6.37$ (s, 1H, Ge-H), 7.04–7.12 (m, 6H, *o-/p*-ArH), 7.44–7.57 (m, 4H, *m*-ArH) ppm. ¹³C{¹H} NMR (C₆D₆, 75.50 MHz): $\delta = 129.0$ (*meta*), 130.8 (*para*), 134.0 (*ortho*), 134.6 (*ipso*) ppm. NMR spectroscopic data is consistent with literature.^[27]

1-naphthylGe(Cl)H₂ (4): 0.41 g (2.01 mmol) of 1-naphthyl₂GeH₂ were dissolved in 20 mL of THF and cooled down to -80 °C and kept under constant stirring. 0.16 g (0.67 mmol) TCCA was added in small portions, under intensive stirring. New TCCA portions were added only, if the last portions already went into solution. After TCCA addition was completed, stirring was continued for 15 min, afterwards,

the cooling bath was removed and the solution was allowed to reach room temperature overnight. THF was removed via membrane pump vacuum (8 mbar). Afterwards, 30 mL of pentane was added to the TCCH, which is insoluble in pentane. The reaction mixture was filtered under inert conditions via syringe filters (20 nm), followed by removal of pentane under vacuum. After workup, 0.42 g (1.77 mmol) of compound 1-naphthylGe(Cl)H₂ (4) was isolated was obtained as a colorless solid and recrystallized from THF below room temperature (7 °C). Yield: 88 %. T_d: 42 °C. C₁₀H₉ClGe: found 50.51 % C (calcd. 50.62), found: 3.73% H (calcd. 3.82%). ¹H NMR (C₆D₆, 300.22 MHz): δ = 5.84 (s, 2H, Ge-*H*), 7.07 (dd, 1H, 3-Ar*H*, ${}^{3}J_{H-H}$ = 7.33 Hz), 7.19; 7.22 (dd,dd, 2H, 6,7-Ar*H*, ${}^{3}J_{H-H}$ = 7.5 Hz), 7.46 (d, 1H, 2, 4, 5, or 8-Ar*H*, ${}^{3}J_{H-H} = 6.7$ Hz), 7.54 (d, 1H, 2, 4, 5, or 8-Ar*H*, ${}^{3}J_{\text{H-H}} = 7.1 \text{ Hz}$, 7.56 (d, 1H, 2, 4, 5, or 8-Ar*H*, ${}^{3}J_{\text{H-H}} = 8.1 \text{ Hz}$), 7.89 (d, 1H, 2, 4, 5, or 8-ArH, ${}^{3}J_{H-H} = 8.2 \text{ Hz}$) ppm. ${}^{13}C{^{1}H} NMR$ (C₆D₆, 75.50 MHz): δ = 125.5 (C3), 126.5 (C7), 127.2 (C8), 127.4 (C9), 129.2 (C6), 131.8 (C4), 132.0 (C5), 133.9 (C2), 134.6 (C10), 136.0 (C1) ppm. GC/MS: 238 (M), 202 (M-Cl-H).

Supporting Information (see footnote on the first page of this article): NMR spectra for compounds (1) and (4) can be found in the Supporting Information.

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Keywords: Selective chlorination; Monochlorination; Trifluoromethylsulfonic acid; Trichloroisocyanuric acid (TCCA); Organo(chloro)germylhydrides

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T. Hafner, A. Torvisco, M. Traxler, M. Wolf, F. Uhlig*	1–7	R _n Ge H ₄₋n	A)	TfOH, LiCI THF / -30 °C to RT -LiOTf, -RH	R _n Ge H ₃₋nCI
Selective Chlorination of Germanium Hydrides		R = alkyl, aryl	B)	18 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	n = 2; R = 1-naphthyl (1), butyl (2), phenyl (3) n = 1; R = 1-naphthyl (4)