

# Mixed-Substituted Single-Source Precursors for Si<sub>1-x</sub>Ge<sub>x</sub> Thin Film Deposition

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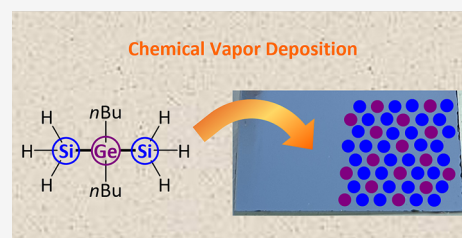
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**ABSTRACT:** A series of new mixed-substituted heteronuclear precursors with preformed Si–Ge bonds has been synthesized via a two-step synthesis protocol. The molecular sources combine convenient handling with sufficient thermal lability to provide access to group IV alloys with low carbon content. Differences in the molecule–material conversion by chemical vapor deposition (CVD) techniques are described and traced back to the molecular design. This study illustrates the possibility of tailoring the physical and chemical properties of single-source precursors for their application in the CVD of Si<sub>1-x</sub>Ge<sub>x</sub> coatings. Moreover, partial crystallization of the Si<sub>1-x</sub>Ge<sub>x</sub> has been achieved by Ga metal-supported CVD growth, which demonstrated the potential of the presented precursor class for the synthesis of crystalline group IV alloys.



## INTRODUCTION

Silicon–germanium Si<sub>1-x</sub>Ge<sub>x</sub> thin films and nanostructures are extensively used in a large portfolio of applications including advanced transistors, quantum devices, photodetectors, electro-optical modulators, photovoltaics, microelectromechanical systems (MEMS), and thermoelectric generators.<sup>1–7</sup> Moreover, Si<sub>1-x</sub>Ge<sub>x</sub> interlayers can be used to control strain and defect densities in Si and Ge layers for electrical applications in CMOS device architectures.<sup>8–10</sup>

The group IV substitutional solid solution Si<sub>1-x</sub>Ge<sub>x</sub> is often described as an alloy with complete solubility over the whole composition range, as illustrated in the binary phase diagram.<sup>11</sup> However, the system has a strong segregation tendency and shows a large regime of coexistence of liquid and solid phases. Therefore, the solidification of a substitutional solid solution of a specific composition from the liquid phase is challenging. Typically, in situ formation of such materials well below the melting temperature is targeted to avoid large compositional variations within the Si<sub>1-x</sub>Ge<sub>x</sub> crystals.

The most popular techniques for the controlled synthesis of thin layers and nanostructures of Si<sub>1-x</sub>Ge<sub>x</sub> include molecular beam epitaxy using the elements as sources<sup>12–14</sup> and the thermal decomposition of SiH<sub>4</sub>/GeH<sub>4</sub> mixtures in chemical vapor deposition (CVD).<sup>15,16</sup> In addition, alternative precursors for CVD synthesis such as higher silanes<sup>17–20</sup> and dichlorosilane<sup>21,22</sup> are reported. Crystal growth of Si<sub>1-x</sub>Ge<sub>x</sub> on Si surfaces also includes the formation of nanodots accompanied by complex bulk and surface diffusion, leading to specific morphologies.<sup>23</sup> This type of Stranski–Krastanov growth typically requires temperatures of ~550–600 °C, and it can result in quite significant Si/Si<sub>1-x</sub>Ge<sub>x</sub> intermixing at the interface. Therefore, lower substrate temperatures are typically

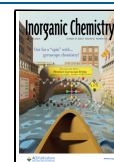
targeted for the deposition of Si<sub>1-x</sub>Ge<sub>x</sub> layers and surface-bound nanostructures on Si.

The electrical properties of the random Si<sub>1-x</sub>Ge<sub>x</sub> alloy with cubic crystal phase have been summarized,<sup>24</sup> but new developments will benefit from molecular precursors providing pre-formed Si–Ge building blocks. For instance, the growth of hexagonal Si<sub>1-x</sub>Ge<sub>x</sub> was reported recently.<sup>25</sup> The direct, tunable bandgap of this hexagonal polymorph should exhibit a narrower emission spectrum when the compositional variation within the Si<sub>1-x</sub>Ge<sub>x</sub> is reduced. Such a very homogeneous atomic intermixing without segregation could be achieved with single-source precursors containing both Si and Ge in one molecule. Moreover, this single-source precursor concept should provide the best chances to enable growth of very recently proposed new polymorphs, providing access to direct bandgap Si<sub>1-x</sub>Ge<sub>x</sub> materials differing in structure and bandgap<sup>26</sup> or other metastable ternary materials with peculiar physical properties based on group IV elements.<sup>27</sup>

Single-source precursors carrying exclusively hydride ligands, such as H<sub>3</sub>SiGeH<sub>3</sub> and Ge(SiH<sub>3</sub>)<sub>4</sub>, have been reported for the CVD of the Si<sub>1-x</sub>Ge<sub>x</sub> layers,<sup>28</sup> but typical scrambling reactions during storage and inefficient synthesis strategies for their controlled formation are the most probable reasons why this strategy has not been further pursued. Moreover, the

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compounds are pyrophoric and require rigorous safety measures similar to the individual  $\text{SiH}_4$  and  $\text{GeH}_4$  sources.<sup>29</sup>

Very recently, a viable alternative to prepare mixed-substituted molecular Si–Ge precursors has been developed by the Wagner group.<sup>30–32</sup> In these studies, the rich chemistry of the  $\text{Si}_2\text{Cl}_6/[\text{nBu}_4\text{N}]\text{Cl}$  system, which releases the powerful nucleophile  $[\text{SiCl}_3]^-$  in situ, has been exploited for the facile formation of  $\text{R}_n\text{E–SiCl}_3$  bonds (E = e.g., B, C, Si, Ge).<sup>33</sup> For the thermal conversion of precursors to  $\text{Si}_{1-x}\text{Ge}_x$ , it should be noted that Si–C-containing silanes typically lead to silicon carbide,<sup>34–37</sup> while Ge–C can be cleaved even at very moderate temperatures, yielding pure Ge material.<sup>38–41</sup> Hence, the molecular design should consider these aforementioned tendencies and stability against inter- or intra-molecular scrambling reactions during storage.

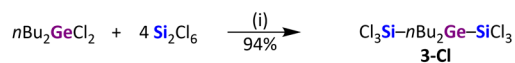
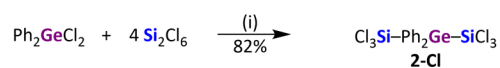
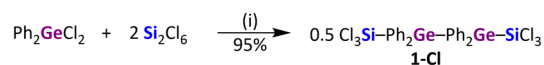
Here, we report on the synthesis and characterization of three mixed-substituted  $(\text{H}_3\text{Si})_2(\text{GeR}_2)_n$  (with  $n = 1$  or  $2$ ; R = Ph or  $n\text{Bu}$ ) molecular sources (**1-H**, **2-H**, and **3-H**) and their applicability as a new class of precursors for  $\text{Si}_{1-x}\text{Ge}_x$  film formation by CVD. Important features are a tamed reactivity against oxidation and scrambling affinity by the introduction of Ge-alkyl/Ge-aryl moieties, while their design allows for an efficient alkyl cleavage by avoiding preformed Si–C bonds. The  $\text{Si}_{1-x}\text{Ge}_x$  layers are characterized by X-ray diffraction (XRD),  $\mu$ -Raman spectroscopy, energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM), and atomic force microscopy (AFM).

## RESULTS AND DISCUSSION

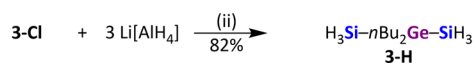
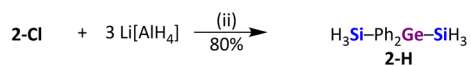
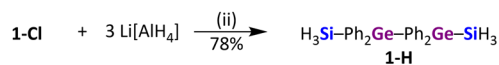
**New Mixed-Substituted Si–Ge Precursors.** The initial experiments targeting  $\text{Cl}_3\text{Si–Ph}_2\text{Ge–SiCl}_3$  (**2-Cl**; Scheme 1)

**Scheme 1. Syntheses of 1-Cl, 2-Cl, and 3-Cl as well as Their Hydrogenation to 1-H, 2-H, and 3-H<sup>a</sup>**

### A) Silylation



### B) Hydrogenation



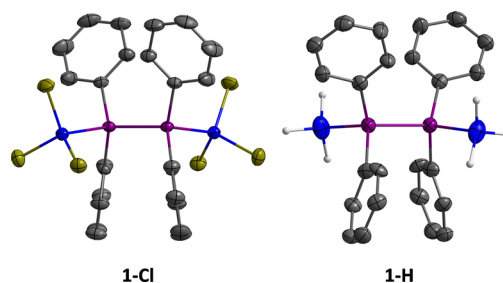
<sup>a</sup>(i) 0.2 equiv of  $[\text{nBu}_4\text{N}]\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ , rt. (ii)  $\text{Et}_2\text{O}$ , rt.

were conducted by treatment of  $\text{Ph}_2\text{GeCl}_2$  with 2 equiv of  $\text{Si}_2\text{Cl}_6$  and 0.2 equiv of  $[\text{nBu}_4\text{N}]\text{Cl}$  as the most obvious stoichiometry for the formation of the desired compound. Surprisingly, the reaction led to the almost-quantitative formation of  $\text{Cl}_3\text{Si–Ph}_2\text{Ge–Ph}_2\text{Ge–SiCl}_3$  (**1-Cl**), which was isolated as a colorless solid (95% yield). In this case,  $[\text{SiCl}_3]^-$  apparently acted not only as a silylating agent but also as a reducing agent to establish the observed Ge–Ge bond.

Subsequent screening of the  $\text{Ph}_2\text{GeCl}_2:\text{Si}_2\text{Cl}_6$  stoichiometry revealed that an excess of  $\text{Si}_2\text{Cl}_6$  (4 equiv) is in fact required to obtain  $\text{Cl}_3\text{Si–Ph}_2\text{Ge–SiCl}_3$  (**2-Cl**) as a colorless liquid in 82% yield. In an analogous reaction, the colorless, liquid alkyl derivative  $\text{Cl}_3\text{Si–}n\text{Bu}_2\text{Ge–SiCl}_3$  (**3-Cl**) was synthesized (94% yield; Scheme 1). A proposal of the formation process, which rationalizes the experimentally found stoichiometries, is detailed in the ESI (Figure S1).

Hydrogenation of **1-Cl**, **2-Cl**, or **3-Cl** with an excess of  $\text{Li}[\text{AlH}_4]$  (3 equiv) resulted in quantitative conversions to **1-H**, **2-H**, and **3-H**. **1-H** was isolated as a colorless solid (78% yield), whereas **2-H** and **3-H** are colorless liquids (80 and 82% yields, respectively).

The solid-state structures of **1-Cl** and **1-H** were determined by single-crystal X-ray diffraction (Figure 1), showing indeed



**Figure 1.** Solid-state structures of **1-Cl** and **1-H**, as determined by single-crystal X-ray diffraction (blue: Si; purple: Ge; yellow-green: Cl; dark gray: C; light gray: H; Ph–H atoms are omitted for clarity). Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths [Å]: **1-Cl**: Ge–Ge = 2.4384(4), Ge–Si = 2.3855(6); **1-H**: Ge–Ge = 2.420(2), Ge–Si = 2.377(4).

individual molecules without any sign of  $\pi$ – $\pi$  interactions and the expected tetrahedral environment of the individual metalloid atoms. Additional information on crystal data and structure refinement are provided in Tables S1 and S2 of the SI. GC–MS data or elemental analyses as well as  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{29}\text{Si}$  NMR spectra are available for all compounds (Figures S2–S24) and described in the Experimental Section below. Particularly important information can be derived from the  $^{29}\text{Si}$  NMR signals of **1-H**, **2-H**, and **3-H**, which have chemical shifts in the range from  $-92.5$  to  $-95.7$  ppm and characteristic quartet multiplicities due to  $^1\text{J}(\text{H},\text{Si})$  coupling (192.3–198.7 Hz).

Compounds **1-H**, **2-H**, and **3-H** have the structural arrangement targeted for the CVD of both  $\text{Si}_{0.50}\text{Ge}_{0.50}$  and  $\text{Si}_{0.67}\text{Ge}_{0.33}$  semiconductor layers. In addition, the molecules enable simple handling due to their inertness against oxidation/hydrolysis by introducing the organic ligands at the Ge atom(s) while avoiding Si–C bonding.

**Thin Film Deposition of  $\text{Si}_{1-x}\text{Ge}_x$  by CVD.** The volatilities of the precursors have been determined by heating the precursors under a reduced pressure of  $10^{-3}$  mbar and collecting the volatiles. The  $\text{H}_3\text{Si–Ph}_2\text{Ge–Ph}_2\text{Ge–SiH}_3$  precursor **1-H**, owning the highest molecular mass, is not volatile. The molecular source decomposes when heated up to  $120$  °C ( $10^{-3}$  mbar). Starting from  $\sim 60$  °C, fragments are liberated, and a highly viscous residue remains. Hence, **1-H** is not suitable for gas phase deposition by low-pressure CVD techniques.

In contrast, both **2-H** and **3-H** can be recondensed at moderate temperatures, with the  $n\text{Bu}$  derivative **3-H** being the

most volatile. The most reasonable explanation for the increased volatility is a reduced molecular mass of 40 amu in the case of 3-H and the absence of any intermolecular  $\pi$ - $\pi$  interactions. The physical properties of the new Si-Ge precursors are summarized in Table 1.

**Table 1. Volatility of Precursors Used for Material Synthesis and CVD Parameters Applied for Si<sub>1-x</sub>Ge<sub>x</sub> Thin Film Deposition**

|   | 1-H     | 2-H                                   | 3-H  |
|---|---------|---------------------------------------|--|
| Si:Ge   | 1:1     | 2:1                                   | 2:1  |
| recondensation<br>( $p \approx 10^{-3}$ mbar) | decomp. | $\sim 55$ – $60$ °C                   | $\sim 20$ – $25$ °C                              |
| CVD<br>( $p < 10^{-6}$ mbar)                  |         | $T_S \approx 700$ °C<br>$T_P > 25$ °C | $T_S = 500$ – $700$ °C<br>$T_P > -20$ to $-5$ °C |

Low-pressure CVD was carried out in a home-built cold-wall reactor at a low background pressure of  $\sim 10^{-6}$  mbar and adjusting the precursor temperature to provide sufficient vapor pressure for thin film growth. No carrier gas has been used in these studies, and the deposits' composition will reflect the effectiveness of fragmentation channels in the absence of any reactive gases such as H<sub>2</sub>.

Controlled vaporization of the precursors required adjusting the precursor temperature to 0 to 25 °C for 2-H and  $-20$  to  $-5$  °C for 3-H. A substrate temperature ( $T_S$ ) sweep revealed a decomposition onset of  $T_S \approx 675$  °C for 2-H, while 3-H leads to film formation at  $T_S \approx 500$  °C. The actual film growth was carried out slightly above these onsets in order to achieve reasonable growth rates. Figure 2a shows the composition of Si<sub>1-x</sub>Ge<sub>x</sub> films prepared by CVD on single-crystal sapphire substrates. The coating derived by using precursor 2-H at  $T_S = 700$  °C contains  $\sim 60$  at % C. Moreover, the Si:Ge ratio of

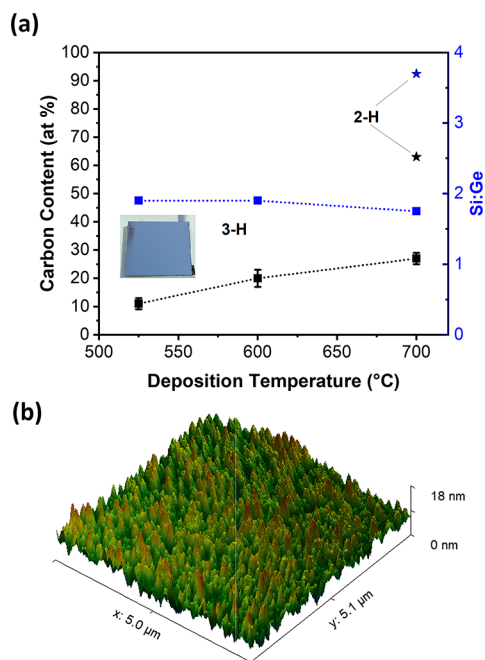
3.7:1 differs significantly from the 2:1 ratio in the precursor. A loss of Ge signifies a fragmentation liberating Ge-containing species from 2-H and inefficiency of complete fragmentation.

In contrast, the decomposition onset of 3-H is much lower at  $T_S = \sim 500$  °C. The lower decomposition temperature during CVD results in significantly reduced carbon contamination levels (11–27 at %) in the whole temperature range of  $T_S = 500$ – $700$  °C investigated for the growth of Si<sub>0.67</sub>Ge<sub>0.33</sub> layers. The lower carbon incorporation illustrates an efficient fragmentation liberating the Ge-bound alkyl ligands even at the lowest temperatures. A likely explanation is  $\beta$ -hydride elimination, widely known in thermal decomposition of organometallic precursors,<sup>42–44</sup> but the homolytic Ge–C bond cleavage or other reaction paths cannot be excluded at this point. This is in line with pure Ge deposition using *n*BuGeH<sub>3</sub> as the precursor.<sup>45</sup> In addition, inter- or intramolecular substituent exchange reaction between the silicon-germanium moieties should be largely diminished in order to achieve a low carbon content in thermal CVD. A preformed Si–C bond is not easily cleaved by thermal processing at moderate temperatures and typically leads to carbide-type deposits with C-contents depending on the fragmentation of the alkyl.<sup>36,37,46</sup>

CVD using 3-H gives access to thin films with shiny silver metallic appearance (inset of Figure 2a). The Si:Ge ratio in the precursor is very close to the ideal 2:1 with values in the range of 1.9–1.7 according to EDX analyses. Representative EDX spectra used for the preparation of Figure 2a are provided in Figure S25. The CVD deposits using 3-H are generally very smooth, and no significant features can be observed in SEM images. AFM provides more information, showing very smooth films with a root mean square (RMS) roughness of  $\sim 2.24$  nm for deposits from 3-H at  $T_S = 525$  °C (Figure 2b). The CVD films deposited at  $T_S = 700$  °C are slightly rougher with an RMS of 14.97 nm (Figure S26).

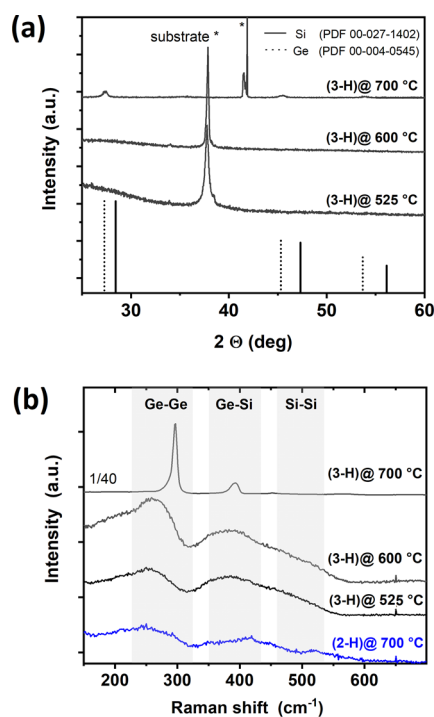
In general, the 3-H-derived CVD films are X-ray-amorphous in the moderate substrate temperature range of up to 600 °C as illustrated in Figure 3a. At the highest temperature of 700 °C, a broad reflection attributed to small nanoparticles of a Ge-rich Si<sub>1-x</sub>Ge<sub>x</sub> phase can be observed. The predominantly amorphous nature of the CVD films could be a result of the carbon contamination delaying any onset of crystallization. Even deposits prepared using 3-H at  $T_S = 525$  °C containing only 11 at % C did not crystallize when post-growth annealing for 2 h at  $T_S = 700$  °C was performed.

However, suitable information on the bonding in Si<sub>1-x</sub>Ge<sub>x</sub> layers can be obtained from Raman analysis. Typically, three ranges of wavenumbers are considered for Ge–Ge, Ge–Si, and Si–Si with increasing values for the individual contributions. Figure 3b shows the typical broad signals for amorphous Si<sub>1-x</sub>Ge<sub>x</sub> with  $x = 0.33$ .<sup>47</sup> All Raman spectra are normalized and shifted vertically for clarity. A significant feature is the missing Si–Si peak in the Raman spectra expected in the range of  $\sim 450$ – $480$  cm<sup>-1</sup>, which is typically weak in amorphous Si<sub>1-x</sub>Ge<sub>x</sub> containing  $\sim 33$  at % Ge. The absence could be related to the carbon content within the samples reducing the Si–Si interactions. The Si–Ge Raman shift of  $\sim 383$  cm<sup>-1</sup> for deposits of 3-H grown at  $T_S = 500$ – $600$  °C is in the expected range according to the literature.<sup>47</sup> The strong Raman signals for Si<sub>1-x</sub>Ge<sub>x</sub> grown using 3-H at 700 °C illustrate an onset of crystallization, but at the same time, the position of the Ge–Ge and Ge–Si signals indicate the formation of Ge-rich clusters. The most intense peak at 296 cm<sup>-1</sup> is close to the pure Ge



**Figure 2.** (a) Carbon content and Si:Ge ratio of CVD deposits determined by EDX analyses using 2-H and 3-H as precursors. The inset shows a silver-metallic deposit prepared using 3-H. (b) The AFM image of a Si<sub>1-x</sub>Ge<sub>x</sub> CVD coating at  $T_S = 525$  °C using 3-H shows the formation of a smooth film.

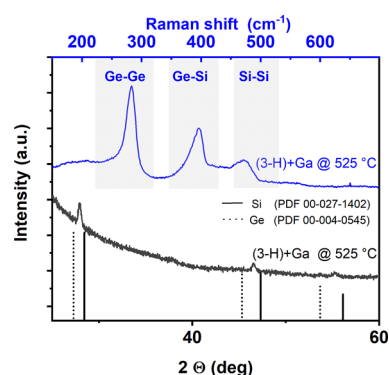




**Figure 3.** (a) XRD pattern of  $\text{Si}_{1-x}\text{Ge}_x$  films prepared using 3-H at substrate temperatures of 525–700 °C. The prominent reflections are assigned to r-cut sapphire (525 and 600 °C) and c-cut sapphire (700 °C). In addition, an unidentified additional reflection in the 700 °C film has been found at 41.5°. (b) Raman analysis reveals typical, broad peaks of amorphous  $\text{Si}_{1-x}\text{Ge}_x$  films using 2-H and 3-H, while the coating using 3-H at 700 °C shows a Ge–Ge signal close to the one expected for pure Ge, illustrating the Ge-rich  $\text{Si}_{1-x}\text{Ge}_x$  phase.

signal at 301  $\text{cm}^{-1}$ ,<sup>48</sup> while the Ge–Si peak is quite low in intensity and its position at  $\sim 393 \text{ cm}^{-1}$  is indicative of  $\text{Si}_{1-x}\text{Ge}_x$  with a high Ge content.<sup>49</sup> Since no information on strain is available, further discussion or calculation/determination of the actual composition of these Ge-rich nanocrystals within the otherwise amorphous matrix is not included.

Crystallization at lower temperatures for the CVD of 3-H has been attempted by the aid of an additional metal. No complete transformation is attempted but, rather, a partial crystallization of the deposit grown at  $T_S = \sim 525 \text{ °C}$  with  $\sim 90$  at % metalloid. For this purpose, tris-(dimethylamino)-gallium(III) has been used for CVD of metallic Ga as a crystallization enhancer. We do not detail whether the Ga metal will support (i) the growth of the semiconductor by in situ metal-induced crystallization (MIC) of the amorphous  $\text{Si}_{1-x}\text{Ge}_x$  deposit,<sup>50,51</sup> (ii) a combined deposition of an amorphous  $\text{Si}_{1-x}\text{Ge}_x$  layer forming simultaneously to a vapor–liquid–solid growth mode of the group IV alloy,<sup>52,53</sup> or (iii) a combination of all the effects described in (i) and (ii). For these experiments, Ga has been pulsed in the CVD chamber prior to 3-H or also three times in between the actual  $\text{Si}_{1-x}\text{Ge}_x$  growth. Indeed, partial crystallization can be achieved at substrate temperatures of  $T_S = 525 \text{ °C}$  as shown in Figure 4. According to calculations of the composition using Vegard's law, the Si:Ge ratio in several deposits was between 1.1 and 1.7, while the overall Si:Ge ratio determined by EDX remained close to 2. Typical control samples for crystalline deposits are illustrated in Figure S27, showing the XRD pattern of a partially crystallized deposit with and without a Au/AuGa reference, which was sputtered on top of the  $\text{Si}_{0.67}\text{Ge}_{0.33}$  film



**Figure 4.** XRD pattern of  $\text{Si}_{1-x}\text{Ge}_x$  films prepared using 3-H at  $T_S = 525 \text{ °C}$  using Ga as a crystallization enhancer. Clearly, a  $\text{Si}_{1-x}\text{Ge}_x$  alloy with significant Si content has been obtained as indicated in the lower part of the graph. The Raman analysis in the upper section reveals all expected signals for  $\text{Si}_{1-x}\text{Ge}_x$  obtained from the same sample used for XRD.

post-growth. Similarly, Raman spectroscopy in Figure 4 shows the three expected major peaks at  $\sim 284$ , 396, and 496  $\text{cm}^{-1}$ , corresponding to first-order Ge–Ge, Si–Ge, and Si–Si optical phonon modes for crystalline  $\text{Si}_{1-x}\text{Ge}_x$ .<sup>54</sup> A distinct difference to the phase-separated Ge-rich material obtained in CVD experiments at 700 °C is observed. Strong variations with predominantly crystalline and otherwise mostly amorphous material are recorded depending on the positioning in the  $\mu$ -Raman measurement.

## CONCLUSIONS

A series of new Si–Ge-based precursors have been synthesized and tested in thermal conversion studies using CVD. Compounds 1-Cl, 2-Cl, and 3-Cl were selectively synthesized from  $\text{R}_2\text{GeCl}_2$ ,  $\text{Si}_2\text{Cl}_6$ , and  $\text{Cl}^-$  in good yields ( $\text{R} = \text{Ph}$  or  $n\text{Bu}$ ). Subsequent hydrogenation of the  $\text{SiCl}_3$  groups with  $\text{Li}[\text{AlH}_4]$  led to the quantitative formation of 1-H, 2-H, and 3-H. Remarkably, these hydrogenated Si–Ge species are stable against exposure to air and moisture, which renders them safe for handling, storage, and transport.

This paper illustrates that alkyl-substituted  $\text{H}_3\text{Si}-\text{R}_2\text{Ge}-\text{SiH}_3$  such as 3-H ( $\text{R} = n\text{Bu}$ ) are suitable precursors for the CVD of inorganic coatings with predefined Si:Ge ratios. This reduces the parameters for the controlled synthesis of  $\text{Si}_{1-x}\text{Ge}_x$  materials and, at the same time, should be key for the synthesis of highly homogeneous cubic  $\text{Si}_{1-x}\text{Ge}_x$  alloys. The predominantly amorphous coatings retain the Si:Ge ratio reasonably well, and the contamination level of 10 at % C is low for CVD deposition without any carrier gas or complex procedures. Moreover, the  $\text{Si}_{0.67}\text{Ge}_{0.33}$  material can be partially crystallized by the presence of metallic Ga, showing Si:Ge ratios in the crystals up to a value of 1.7. Hence, this report illustrates the first successful conversion of alkyl-modified single-source precursors to group IV alloys. A large variety of potential predefined compositions, including Si–Ge connectivities and modified ligand design, can be prepared by this precursor/synthesis strategy, providing a toolbox to be exploited for the synthesis of  $\text{Si}_{1-x}\text{Ge}_x$  materials.

## EXPERIMENTAL SECTION

**General Considerations.** All reactions were carried out under an inert-gas atmosphere (dry argon or nitrogen) using standard Schlenk or glove-box techniques. Commercially available starting materials

were used as received:  $[n\text{Bu}_4\text{N}]\text{Cl}$  (Sigma Aldrich),  $\text{Li}[\text{AlH}_4]$  (Sigma Aldrich),  $n\text{Bu}_2\text{GeCl}_2$  (Alfa Aesar), and  $\text{Si}_2\text{Cl}_6$  (Evonik, see Acknowledgements).  $\text{Ph}_2\text{GeCl}_2$  was prepared according to the literature.<sup>55</sup> *n*-Hexane,  $\text{C}_6\text{H}_6$ , and  $\text{Et}_2\text{O}$  were dried over Na metal;  $\text{CH}_2\text{Cl}_2$  was dried over  $\text{CaH}_2$ . All solvents were freshly distilled prior to use.  $\text{C}_6\text{D}_6$ ,  $[\text{D}_8]\text{THF}$ , and  $\text{CD}_2\text{Cl}_2$  were stored over molecular sieves (3 Å). NMR spectra were recorded at 298 K on a Bruker Avance III HD 500 spectrometer equipped with a Prodigy BBO 500 S1 probe.  $^1\text{H}/^{13}\text{C}$  NMR spectra were referenced against (residual) solvent signals<sup>56</sup> ( $\text{C}_6\text{D}_6$ : 7.16 ppm/128.06 ppm;  $[\text{D}_8]\text{THF}$ : 1.72 ppm/25.31 ppm;  $\text{CD}_2\text{Cl}_2$ : 5.32 ppm/53.84 ppm).  $^{29}\text{Si}$  NMR spectra were calibrated against external  $\text{Si}(\text{CH}_3)_4$  ( $\delta(^{29}\text{Si}) = 0$ ). Abbreviations: s = singlet, t = triplet, q = quartet, m = multiplet. Resonance assignments were supported by two-dimensional NMR measurements ( $^1\text{H}/^{13}\text{C}$ -HSQC,  $^1\text{H}/^{13}\text{C}$ -HMBC,  $^1\text{H}/^{29}\text{Si}$ -HSQC, and  $^1\text{H}/^{29}\text{Si}$ -HMBC). For the carbon atoms of the phenyl moieties, the resonance intensities were also considered. **Note:** The corresponding NMR spectra are shown in Figures S2–S24, together with numbering schemes for the specific C and H atom positions of each compound. For simplicity, only chemically inequivalent positions are labeled in these structural formulas.

GC–MS (gas chromatography–mass spectrometry) data were recorded using a Shimadzu GCMS-QP 2010SE. The stationary phase (Restek) had a length of 60 m with an inner diameter of 0.32 mm. The analyte was diluted with  $\text{CH}_2\text{Cl}_2$  prior to the measurement. To avoid overloading the MS, a solvent cut was used. Samples were injected at 230 °C, and 1/10 thereof was transferred onto the column with a flow rate of 1.86 mL/min, carried by He gas. The oven was heated to 50 °C for 1 min; the temperature was subsequently elevated at a rate of 10 °C/min up to 250 °C and held for 40 min (60 min in the case of compound 1-H). Finally, the oven temperature was elevated again at a rate of 25 °C/min up to 270 °C and held for 5 min. After a certain retention time  $\tau$ , the substances exited the column and were ionized with 70 eV, and cationic fragments were measured within a range of  $m/z = 30$ –800 (mass per charges). Elemental analyses were performed at the Institute of Organic Chemistry and Chemical Biology, Goethe University Frankfurt, Germany.

**Synthesis of  $\text{Cl}_3\text{Si}-\text{Ph}_2\text{Ge}-\text{Ph}_2\text{Ge}-\text{SiCl}_3$  (1-Cl).** A solution of  $[n\text{Bu}_4\text{N}]\text{Cl}$  (0.933 g, 3.36 mmol) and  $\text{Ph}_2\text{GeCl}_2$  (5.000 g, 16.79 mmol) in  $\text{CH}_2\text{Cl}_2$  (40 mL) was prepared in a Schlenk tube. After addition of neat  $\text{Si}_2\text{Cl}_6$  (9.030 g, 33.59 mmol) at room temperature, the reaction solution was stirred for 24 h. All volatiles were removed under reduced pressure to obtain a colorless solid, which was washed with  $\text{CH}_2\text{Cl}_2$  (10 mL) to isolate 1-Cl as a colorless solid. Yield: 5.810 g (8.041 mmol, 95%). Single crystals of 1-Cl suitable for X-ray analysis were grown by slow evaporation of a solution in  $\text{CH}_2\text{Cl}_2$ :*n*-hexane (4:1).

$^1\text{H}$  NMR (500.2 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 7.54$ –7.51 (m, 8H; H-2), 7.46–7.42 (m, 4H; H-4), 7.39–7.35 (m, 8H; H-3);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 136.4$  (C-2), 132.2 (C-1), 130.5 (C-4), 129.4 (C-3);  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99.4 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 12.4$ ; Elemental analysis: Calculated for  $\text{C}_{24}\text{H}_{20}\text{Cl}_6\text{Ge}_2\text{Si}_2$  (722.55): C 39.90; H 2.79. Found: C 40.64; H 3.02.

**Synthesis of  $\text{Cl}_3\text{Si}-\text{Ph}_2\text{Ge}-\text{SiCl}_3$  (2-Cl).** A solution of  $[n\text{Bu}_4\text{N}]\text{Cl}$  (0.933 g, 3.36 mmol) and  $\text{Ph}_2\text{GeCl}_2$  (5.000 g, 16.79 mmol) in  $\text{CH}_2\text{Cl}_2$  (40 mL) was prepared in a Schlenk tube. After addition of neat  $\text{Si}_2\text{Cl}_6$  (18.06 g, 67.18 mmol) at room temperature, the reaction solution was stirred for 1 h. All volatiles were removed under reduced pressure, and the highly viscous, colorless residue was extracted with *n*-hexane (50 mL). All volatiles were removed from the extract under reduced pressure to obtain 2-Cl as a colorless liquid. Yield: 6.802 g (13.72 mmol, 82%).

$^1\text{H}$  NMR (500.2 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 7.65$ –7.62 (m, 4H; H-2), 7.53–7.46 (m, 6H; H-3 and H-4);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 136.0$  (C-2), 131.1 (C-4), 129.9 (C-3), 129.4 (C-1);  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99.4 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 9.7$ ; Elemental analysis: Calculated for  $\text{C}_{12}\text{H}_{10}\text{Cl}_6\text{GeSi}_2$  (495.71): C 29.08; H 2.03. Found: C 29.51; H 2.07.

**Synthesis of  $\text{Cl}_3\text{Si}-n\text{Bu}_2\text{Ge}-\text{SiCl}_3$  (3-Cl).** A solution of  $[n\text{Bu}_4\text{N}]\text{Cl}$  (1.078 g, 3.879 mmol) and  $n\text{Bu}_2\text{GeCl}_2$  (5.000 g, 19.40

mmol) in  $\text{CH}_2\text{Cl}_2$  (60 mL) was prepared in a Schlenk tube. After addition of neat  $\text{Si}_2\text{Cl}_6$  (20.86 g, 77.60 mmol) at room temperature, the reaction solution was stirred for 1 h. All volatiles were removed under reduced pressure, and the highly viscous, colorless residue was extracted with *n*-hexane (40 mL). All volatiles were removed from the extract under reduced pressure to obtain 3-Cl as a colorless liquid. Yield: 8.280 g (18.17 mmol, 94%).

$^1\text{H}$  NMR (500.2 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 1.65$ –1.57 (m, 4H; H-2), 1.50–1.35 (m, 8H; H-1 and H-3), 0.93 (t,  $^3J(\text{H,H}) = 7.3$  Hz, 6H; H-4);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 28.7$  (C-2), 26.6 (C-3), 13.6 (C-1 and C-4);  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99.4 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 13.5$ ; GC–MS (EI):  $\tau = 22.43$  min,  $m/z = 399$  ( $[\text{M} - n\text{Bu}]^+$ ), 343 ( $[\text{M} - 2 \times n\text{Bu}]^+$ ), 321 ( $[\text{M} - \text{SiCl}_3]^+$ ). All signals show the correct isotope pattern.

**Synthesis of  $\text{Cl}-\text{Ph}_2\text{Ge}-\text{Ph}_2\text{Ge}-\text{Cl}$ .** A solution of  $[n\text{Bu}_4\text{N}]\text{Cl}$  (0.093 g, 0.34 mmol) and  $\text{Ph}_2\text{GeCl}_2$  (1.000 g, 3.359 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) was prepared in a Schlenk tube. After addition of neat  $\text{Si}_2\text{Cl}_6$  (0.455 g, 1.69 mmol) at room temperature, the reaction solution was stirred for 3 h. All volatiles were removed under reduced pressure to obtain a colorless solid (920 mg).  $\text{Cl}-\text{Ph}_2\text{Ge}-\text{Ph}_2\text{Ge}-\text{Cl}$  was identified as the main product by means of  $^{13}\text{C}$  NMR spectroscopy. We detected only minor Ph-containing impurities (plus  $[n\text{Bu}_4\text{N}]\text{Cl}$ ). No resonances were found in the  $^{29}\text{Si}$  NMR spectrum. The crude product was washed with  $\text{CH}_2\text{Cl}_2$  (3 mL) to obtain  $\text{Cl}-\text{Ph}_2\text{Ge}-\text{Ph}_2\text{Ge}-\text{Cl}$  as a colorless solid. Yield: 0.379 g (0.722 mmol, 43%). Single crystals of  $\text{Cl}-\text{Ph}_2\text{Ge}-\text{Ph}_2\text{Ge}-\text{Cl}$  suitable for X-ray analysis were grown by slow evaporation of a solution in  $\text{CH}_2\text{Cl}_2$ :*n*-hexane (4:1).

The formation of  $\text{Cl}-\text{Ph}_2\text{Ge}-\text{Ph}_2\text{Ge}-\text{Cl}$  was unambiguously demonstrated by comparing the dimensions of its unit cell with those of the published solid state structure.<sup>57</sup>  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts were also identical to the reference values ( $\text{C}_6\text{D}_6$ ).<sup>58</sup>

$^1\text{H}$  NMR (500.2 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 7.77$ –7.73 (m, 8H; H-2), 7.02–7.05 (m, 12H; H-3 and H-4);  $^1\text{H}$  NMR (500.2 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 7.64$ –7.59 (m, 8H; H-2), 7.49–7.39 (m, 12H; H-3 and H-4);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 136.1$  (C-1), 134.2 (C-2), 130.8 (C-4), 129.2 (C-3);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 135.7$  (C-1), 134.1 (C-2), 131.2 (C-4), 129.3 (C-3).

**Synthesis of  $\text{H}_3\text{Si}-\text{Ph}_2\text{Ge}-\text{Ph}_2\text{Ge}-\text{SiH}_3$  (1-H).** A Schlenk tube was charged with 1-Cl (2.100 g, 2.906 mmol) and  $\text{Et}_2\text{O}$  (45 mL).  $\text{Li}[\text{AlH}_4]$  (0.330 g, 8.70 mmol) was slowly added in portions of 50 mg at room temperature, and the reaction mixture was stirred for 2 h. All volatiles were removed under reduced pressure, and the residue was extracted with  $\text{C}_6\text{H}_6$  (40 mL).  $\text{H}_2\text{O}$  (1.0 mL) was carefully added to the extract at room temperature (moderate  $\text{H}_2$  evolution and precipitation of a colorless solid). The mixture was dried over  $\text{Na}_2\text{SO}_4$  and filtered. All volatiles were removed from the filtrate under reduced pressure to obtain 1-H as a colorless solid. Yield: 1.162 g (2.252 mmol, 78%). Single crystals of 1-H suitable for X-ray analysis were grown by slow evaporation of a solution in  $\text{CH}_2\text{Cl}_2$ :*n*-hexane (4:1).

$^1\text{H}$  NMR (500.2 MHz,  $[\text{D}_8]\text{THF}$ ):  $\delta = 7.42$ –7.36 (m, 8H; H-2), 7.31–7.22 (m, 12H; H-3 and H-4), 3.55 (s with satellites,  $^1J(\text{H,Si}) = 198.5$  Hz, 6H;  $\text{SiH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz,  $[\text{D}_8]\text{THF}$ ):  $\delta = 137.4$  (C-1), 136.2 (C-2), 129.5 (C-4), 129.2 (C-3);  $^{29}\text{Si}$  NMR (99.4 MHz,  $[\text{D}_8]\text{THF}$ ):  $\delta = -93.8$  (q,  $^1J(\text{H,Si}) = 198.5$  Hz); GC–MS (EI):  $\tau = 53.00$  min,  $m/z = 516$  ( $[\text{M}]^+$ ), 485 ( $[\text{M} - \text{SiH}_3]^+$ ), 408 ( $[\text{M} - \text{SiH}_3 - \text{Ph}]^+$ ), 259 ( $[\text{Ph}_2\text{Ge}-\text{SiH}_3]^+$ ). All signals show the correct isotope pattern.

**Synthesis of  $\text{H}_3\text{Si}-\text{Ph}_2\text{Ge}-\text{SiH}_3$  (2-H).** A Schlenk tube was charged with 2-Cl (6.800 g, 13.72 mmol) and  $\text{Et}_2\text{O}$  (70 mL).  $\text{Li}[\text{AlH}_4]$  (1.562 g, 41.16 mmol) was slowly added in portions of 50 mg at room temperature, and the reaction mixture was stirred for 2 h. All volatiles were removed under reduced pressure, and the residue was extracted with *n*-hexane (40 mL).  $\text{H}_2\text{O}$  (1.0 mL) was added to the extract at room temperature (moderate  $\text{H}_2$  evolution and precipitation of a colorless solid). The mixture was dried over  $\text{Na}_2\text{SO}_4$  and filtered. All volatiles were removed from the filtrate under reduced pressure to obtain 2-H as a colorless liquid. Yield: 3.160 g (10.93 mmol, 80%).

$^1\text{H}$  NMR (500.2 MHz,  $[\text{D}_8]\text{THF}$ ):  $\delta = 7.50\text{--}7.46$  (m, 4H; H-2), 7.34–7.30 (m, 6H; H-3 and H-4), 3.57 (s with satellites,  $^1\text{J}(\text{H},\text{Si}) = 198.7$  Hz, 6H;  $\text{SiH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz,  $[\text{D}_8]\text{THF}$ ):  $\delta = 137.0$  (C-1), 135.8 (C-2), 129.5 (C-4), 129.4 (C-3);  $^{29}\text{Si}$  NMR (99.4 MHz,  $[\text{D}_8]\text{THF}$ ):  $\delta = -92.5$  (qq,  $^1\text{J}(\text{H},\text{Si}) = 198.7$  Hz,  $^3\text{J}(\text{H},\text{Si}) = 2.9$  Hz); GC–MS (EI):  $\tau = 20.12$  min,  $m/z = 258$  ( $[\text{M} - \text{SiH}_3]^+$ ), 213 ( $[\text{M} - \text{Ph}]^+$ ), 183 ( $[\text{M} - \text{SiH}_3 - \text{Ph}]^+$ ). All signals show the correct isotope pattern.

**Synthesis of  $\text{H}_3\text{Si}-n\text{Bu}_2\text{Ge}-\text{SiH}_3$  (3-H).** A Schlenk tube was charged with 3-Cl (8.000 g, 17.55 mmol) and  $\text{Et}_2\text{O}$  (100 mL).  $\text{Li}[\text{AlH}_4]$  (2.000 g, 52.70 mmol) was slowly added in portions of 50 mg at room temperature, and the reaction mixture was stirred for 24 h. All volatiles were removed under reduced pressure, and the residue was extracted with *n*-hexane (40 mL).  $\text{H}_2\text{O}$  (1.0 mL) was added to the extract at room temperature (moderate  $\text{H}_2$  evolution and precipitation of a colorless solid). The mixture was dried over  $\text{Na}_2\text{SO}_4$  and filtered. All volatiles were removed from the filtrate under reduced pressure to obtain 3-H as a colorless liquid. Yield: 3.568 g (14.32 mmol, 82%).

$^1\text{H}$  NMR (500.2 MHz,  $[\text{D}_8]\text{THF}$ ):  $\delta = 3.26$  (s with satellites  $^1\text{J}(\text{H},\text{Si}) = 192.3$  Hz, 6H;  $\text{SiH}_3$ ), 1.50–1.43 (m, 4H; H-2), 1.40–1.31 (m, 4H; H-3), 1.18–1.12 (m, 4H; H-1), 0.90 (t,  $^3\text{J}(\text{H},\text{H}) = 7.3$  Hz, 6H; H-4);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz,  $[\text{D}_8]\text{THF}$ ):  $\delta = 30.7$  (C-2), 27.0 (C-3), 14.3 (C-1), 13.9 (C-4);  $^{29}\text{Si}$  NMR (99.4 MHz,  $[\text{D}_8]\text{THF}$ ):  $\delta = -95.7$  (qm,  $^1\text{J}(\text{H},\text{Si}) = 192.3$  Hz); GC–MS (EI):  $\tau = 12.96$  min,  $m/z = 250$  ( $[\text{M}]^+$ ), 219 ( $[\text{M} - \text{SiH}_3]^+$ ), 163 ( $[\text{M} - \text{SiH}_3 - n\text{Bu}]^+$ ). All signals show the correct isotope pattern.

**CVD Process and Thin Film Characterization.** CVD has been carried out in a home-built cold-wall reactor using high-frequency heating of a graphite or steel susceptor for indirect heating of sapphire (0001) or (11–20) (Crystal GmbH, Germany) and surface-oxidized Si (911) substrates with approx. 50 nm oxide (Crystec GmbH, Germany). The substrates are attached to the susceptor by silver paste to ensure efficient thermal contact. Substrate temperatures have been limited to  $T_s = 400\text{--}700$  °C. The precursors were introduced in the reactor through a glass flange applying dynamic vacuum ( $\sim 10^{-6}$  mbar) while keeping the precursor temperatures in the range of  $-20$  to  $0$  °C. Temperatures below  $0$  °C are maintained using a cooling bath based on chilled isopropyl alcohol as coolant. Typically, 40–80 mg of the precursors were used as source for the CVD experiments, and growth was carried out for 60–150 min. CVD based on tris-(dimethylamino)gallium(III) was carried out at  $T_s = 500$  °C and a precursor temperature of  $80$  °C for 2 s per pulse using approx. 100 mg of the precursor to deposit metallic Ga. A similar CVD setup has been described in the literature for the growth of thin films and nanostructures using molecular sources.<sup>59,60</sup>

The sample composition was characterized by energy dispersive X-ray analysis (EDX) at a beam energy of 10 kV. Error bars represent variations between several EDX spectra recorded for at least three individual deposits using a defined set of parameters and several spots on the substrates. In addition, the standard-less quantification provides an estimate on the actual composition and will not be as accurate as EDX using defined material compositions for calibration. A slight overestimation of carbon content could be caused by additional carbon deposition during EDX associated to residual carbon sources in the background gas. Higher beam energies of 10 kV and thick deposits were used to limit the potential error determining the content of lighter elements. The topographical features of the deposits were determined by atomic force microscopy (AFM) operated in tapping mode (Nanosurf, Easyscan 2). For the sample characterization by X-ray diffraction, a Bruker D8 Discover was used in a Bragg–Brentano geometry. Match! software (Crystal Impact) was used for data analysis.  $\mu$ -Raman measurements were performed on a WITec Alpha300 Raman system with a frequency-doubled Nd:YAG laser ( $\lambda = 532$  nm) in a backscattering geometry. The power of the incident laser was adjusted to 250  $\mu\text{W}$ . The laser was focused through an achromatic Nikon EPI Eplan 100 $\times$  objective (NA = 0.9, WD = 0.23 mm), enabling a diffraction-limited spot size of  $\sim 720$  nm. The integration time was set to 300 s.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c02835>.

NMR spectra of the intermediates and hydrogenated precursors; important single crystal data of 1-Cl and 1-H; proposal of the formation process; additional EDX spectra; XRD, SEM, and AFM images of the CVD deposits (PDF)

### Accession Codes

CCDC 2182827–2182828 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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The authors declare the following competing financial interest(s): BK, HWL, and MW are inventors on patent application WO2021244705A1 submitted by the Goethe



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