

# **Photoactive Derivatives of Main Group Elements**

## **Development of New Type I Photoinitiators and New Macroelectronic**

Materials

# Habilitation

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"Ein Gelehrter in seinem Laboratorium ist nicht nur ein Techniker; er steht auch vor den Naturgesetzen wie ein Kind vor der Märchenwelt."

Marie Curie

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## Abstract

Today, the use of photoinitiators is no longer limited to the production of microelectronics, microlithography and many more, but also gaining importance in the medical field. Consequently, the search for new photoinitiators (PIs) with enhanced properties are of great interest, but also an enormous challenge. Acyl metalloids (mainly germanium-based) are the state-of-the-art photoinitiators in this context. However, all synthetic strategies towards these compounds rely on classical salt metathesis reactions, where only a moderate complexity of the final products can be achieved. During this habilitation we introduced an alternative pathway towards acyl metalloids, which is based on electron transfer reactions. Our innovative pathway involves strong bases and alkali-metal reductions, which will lead to a variety of hitherto unknown enolates, anions and related compounds that are hitherto hardly synthesizable otherwise. In the final step of the synthetic protocol these new species were reacted with a variety of electrophiles to obtain a variety of derivatives with target properties. Additionally, to this new approach we also used the multiple silvl abstraction methodology and the Corey-Seebach approach to synthesize new acyl metalloids. On the basis of sophisticated experiments (i.e.: CIDNP, Photo-DSC, photobleaching etc.) we could determine the activity of our newly formed photoinitiators. Besides the applicability of these compound classes, we also investigated fundamental reactivities of these keto derivatives. Here, we have introduced a synthetic strategy for hitherto unknown geminal bisenolates a new synthon for the synthesis of organometallic reagents. In total this part comprises eleven publications and two review articles published in peer-reviewed journals.

The second part of this habilitation is devoted to the synthesis and characterization of higher silicon hydrides, which serve as a precursor material for liquid phase deposition. Recently, this technique has attracted considerable attention owing to the possibility of low-cost fabrication by printing processes. Moreover, it opens the possibility for large area depositions and patterning materials. Recent studies by us and others have demonstrated the principal feasibility of the liquid phase deposition (LPD) and processing of silicon films of satisfactory quality. In this context silicon-heteroelement thin layer structures produced by solution routes are of great interest. So far literature contains only scattered reports on LPD processed functional silicon layers. In most of these studies, the use of more than one precursor raised considerable problems. Here we were able to isolate the first example of a perydrogenated hypersilanide, which is an important substrate for the synthesis of single source precursors. Moreover, we have developed a new pathway towards higher silicon hydrides based on the synthesis and derivatization of methoxysilanes. Consequently, we were able to synthesize a variety of single source precursors. The first derivatives published, were the single source precursors for Si-C films. In total this part comprises two publications and one submitted manuscript in peer-reviewed journals.

## Kurzfassung

Die Verwendung von Photoinitiatoren ist heute nicht mehr nur auf die Herstellung von Mikroelektronik, und Mikrolithographie beschränkt, sondern findet auch im medizinischen Bereich Anwendung. Daher ist die Suche nach neuen Photoinitiatoren (PIs) mit verbesserten Eigenschaften von großem Interesse, aber auch eine enorme Herausforderung. Acylmetalloide (hauptsächlich auf Germaniumbasis) sind in diesem Zusammenhang die vielversprechendsten Photoinitiatoren. Allerdings beruhen alle Synthesestrategien für diese Verbindungen auf klassischen Salzmetathesereaktionen, bei denen nur eine mäßige Komplexität der Endprodukte erreicht werden kann. Für diese Habilitation haben wir einen alternativen Weg zu Acylmetalloiden entwickelt, der auf Elektronentransferreaktionen beruht. Unser innovativer Syntheseweg beinhaltet starke Basen und Alkalimetallreduktionen, die zu einer Vielzahl von bisher unbekannten Enolaten, Anionen und verwandten Verbindungen führen, die sonst nicht herstellbar sind. Im letzten Schritt des Syntheseprotokolls wurden diese neuen Spezies mit einer Vielzahl von Elektrophilen umgesetzt, um neue Photoinitiatoren mit den gewünschten Eigenschaften zu generieren. Zusätzlich zu diesem neuen Ansatz verwendeten wir auch die Methode der multiplen Silylabstraktion und den Corey-Seebach-Ansatz zur Synthese neuer Acylmetalloide. Anhand von anspruchsvollen Experimenten (z.B. CIDNP, Photo-DSC, Photobleaching etc.) konnten wir die Aktivität unserer neu gebildeten Photoinitiatoren bestimmen. Neben der Anwendbarkeit dieser Verbindungsklassen haben wir auch grundlegende Reaktivitäten dieser Keto-Derivate untersucht. Hier gelang uns die Entwicklung einer Synthesestrategie für bisher unbekannte geminale Bisenolate. Dieser Teil umfasst elf Veröffentlichungen und zwei Übersichtsartikel, die in Fachzeitschriften mit Peer-Review veröffentlicht wurden.

Der zweite Teil dieser Habilitation basiert auf der Synthese und Charakterisierung höherer Siliziumhydride, welche als Vorläufermaterial für die Flüssigphasenabscheidung (LPD) verwendet werden. Diese Technik hat aufgrund der Möglichkeit der kostengünstigen Herstellung durch Druckverfahren große Aufmerksamkeit erregt. Darüber hinaus eröffnet sie die Möglichkeit der großflächigen Abscheidung und Strukturierung von Materialien. Jüngste Studien haben die prinzipielle Durchführbarkeit der LPD und die Verarbeitung von Siliziumschichten mit zufriedenstellender Qualität nachgewiesen. In diesem Zusammenhang sind Silizium-Heteroelement-Dünnschichtstrukturen, die durch Flüssigphasenabscheidung hergestellt werden, von großem Interesse. Bisher gibt es in der Literatur nur vereinzelte Berichte über LPD verarbeitete funktionelle Siliziumschichten. In den meisten dieser Studien warf die Verwendung von mehr als einem Vorläufer erhebliche Probleme auf. Im Zuge dieser Habilitation konnten wir das erste perhydrierte Hypersilanid isolieren, welches ein wichtiges Substrat für neue Single-Source-Vorstufen ist. Außerdem haben wir einen neuen Synthesepfad zu höheren Siliziumhydriden entwickelt, der auf der Synthese und Derivatisierung von Methoxysilanen beruht. Auf der Grundlage dieser beiden Strategien konnten wir eine Reihe von Single-Source-Vorläufern synthetisieren. Als erstes wurden die Single-Source-Precursoren für die Herstellung von SiC-Filme eingereicht. Dieser Teil umfasst zwei Veröffentlichungen und ein eingereichtes Manuskript, die in Fachzeitschriften mit Peer-Review veröffentlicht wurden.

## **Summary**

The main target of this habilitation was the investigation of photo-labile group 14 molecules, with the focus on the development of non-toxic free radical photoinitiators and single source precursors for liquid phase deposition. In detail, we developed a strategy to synthesize group 14 acyl metalloids with tailormade properties, which are high performance non-toxic photoinitiators. Guided by in-depth mechanistic investigations, we enhanced the scope of synthetic procedures and used these compounds as functional precursors, serving as electron-transfer-active agents. Additionally, we performed follow-up reactions and gained access to novel group 14 compounds with non-symmetric substitution patterns, which have not yet been reachable. Importantly, the primary active species emerging from our synthetic routes are radicals and radical ions. To direct the reactivity, it is crucial to understand their electronic features. Consequently, we employed a variety of spectroscopic techniques comprising EPR, NMR, and optical methodology enhanced by theoretical calculations (DFT level of theory). This led to the construction of a rational recursive strategy for unsymmetrically tetra-substituted acyl metalloids displaying orthogonal photo- and electroactivity. The second topic of this work was the synthesis and characterization of novel higher silicon hydrides, which contain one or more heteroatoms covalently linked to silicon. These derivatives were photo-oligomerized and then applied as single source precursors for the deposition of functional silicon films. Additionally, this work provided access to previously unknown processes for the manufacturing of silicon heterostructures of high significance for academic and industrial electronics research.

## Introduction

Photochemistry has recently gained renewed attention in the fields of synthetic and polymer chemistry as light allows a high spatial and temporal control. Moreover, the used wavelength and intensity can be adjusted easily and the performed reactions proceed without producing any waste. It is therefore not surprising that photochemistry is implemented for various applications such as in material science, in synthesis, in photopolymerization, for supramolecular chemistry and in photo-redox chemistry. Consequently, the number of published articles focused on photo-induced chemical reactions or photocatalysis (which often is not used in a strict way) has substantially grown within recent years (Figure 1).



Figure 1: Number of Hits for "Photocatalysis" According to the Web of Science

Here, photo-active or photo-labile compounds are interesting research objectives.<sup>1,2</sup> In this context, main group element based molecules show intriguing properties.<sup>3</sup> Moreover, the introduction of strong bases as reagents to induce electron transfer reactions opens the way of accessing novel molecules.<sup>4–6</sup> During such reactions paramagnetic compounds are formed, which can be easily characterized by EPR spectroscopy.<sup>7</sup>

In general, photo-induced reactions either permit the synthesis of desirable molecules and/or trigger chemical processes. Such an important process is the photo-polymerization of suitable monomers,<sup>8–10</sup> which allows the manufacturing of tailor-made coatings under temporal and excellent spatial control.<sup>11</sup> The wavelength at which the photoinitiator becomes active is a crucial aspect for the development of new systems. The activating wavelength has to be sufficiently short enough to allow selective triggering, but still long enough to provide a sufficient curing depth.<sup>12–15</sup>

In this respect, molecules that contain an aromatic acyl moiety as photoactive group display the best performance. Here the absorption of light leads to the formation of an  $n-\pi^*$  excited state, which is a prerequisite for an  $\alpha$ -cleavage. The so-obtained radicals initiate the polymerization. The substitution pattern of the initiators and the character of the primary radicals are decisive for the quality of the photoinitiators and have to be adjusted to provide the ideal and custom-made initiator for specific applications.<sup>16</sup>

In the last decade Ge-based photoinitiators have emerged as new class of non-toxic free radical photoinitiators. In their landmark publication Liska, Moszner and co-workers established a variety of mono- and bis-acylgermanes as very active type I photoinitiators.<sup>17,18</sup> Acylgermanes offer the advantages of significantly red-shifted absorption bands and reduced toxicity compared to currently applied phosphorus-based PIs,<sup>19</sup> which restricts their application in biomaterials.<sup>20</sup> Meanwhile a bisacylgermanes is commercial available, which is based on the Corey-Seebach approach (see Scheme 1).



Scheme 1: Synthesis of a Bisacylgermane via the Corey-Seebach Method (Ivocerin®)

However, the synthesis of Ivocerin relies on a multi-step procedure and the final products need to be purified by column chromatography. Moreover, all state-of-the-art free radical photoinitiators suffer from inefficient curing efficiencies at longer wavelength ( $\lambda \ge 420$  nm).

A substantial breakthrough in this research field was the facile synthesis of novel tetraacyl substituted group 14 compounds (Figure 2).<sup>21–23</sup> Moreover, we could demonstrate their superior potential as a novel class of long-wavelength photoinitiators (PIs) for visible-light-induced free-radical polymerization.<sup>24,25</sup> The synthetic protocol is highly group tolerant, easy-to-perform and, therefore, outstrips the methods in the synthesis of state-of-the-art PIs.<sup>26</sup> Intriguingly, a low toxicity for all compounds were found,



Figure 2. Novel Tetraacyl Substituted Group 14 Compounds.

paving the way for the implementation of these compounds in biomedical applications.<sup>27</sup> However, a huge drawback of symmetrical tetraacyl substituted derivatives are their high melting points, which are responsible for low solubility, limiting the field of applications.

To overcome the above-mentioned restrictions, we further studied reactivities of acyl metalloids and developed new pathways towards these compounds classes. Moreover, we discovered that acyl metalloids undergo selective electron transfer (ET) reactions. Furthermore, we found that this pathway delivers novel and innovative precursors for the synthesis of group 14 and 15-based photoinitiators that are hardly accessible *via* other reaction routes. Chapter 1 will focus on this chemistry.

Additionally, this habilitation is also devoted to the chemistry of hydrosilanes, which are also photo labile compounds. Although significant efforts have been directed in recent years at manufacturing new semiconductor materials, silicon (mostly in the form of single-crystal wafer silicon (c-Si)) still accounts for the majority of material used in the industry. The state-of-the-art production technique for c-Si has a high energy consumption and an enormous waste problem, as only 25% of the original single crystal

of silicon are effectively used.<sup>28</sup> Alternatively, thin films of doped or undoped amorphous Si (a-Si), microcrystalline Si ( $\mu$ c-Si) and nanocrystalline Si (nc-Si) have emerged as promising replacements for c-Si, which includes various applications in large-area electronic devices such as solar cells, displays and thin-film transistors.<sup>29–31</sup> Moreover, it opens the possibility for large area depositions and patterning materials.<sup>32–34</sup> Recent studies by us and others have demonstrated the principal feasibility of the liquid phase deposition (LPD) and processing of silicon films of satisfactory quality.<sup>35–39</sup> Open chained and cyclic silicon hydrides such as compounds 1 - 4 (Chart 1) are ideal precursors in this context because they are liquid at room temperature, accessible on a preparative scale in high purity, carbon- and oxygen-free, and decompose to elemental silicon upon heating to T > 300 °C.



Chart 1. Currently used Precursors for LPD Processing of Silicon Films

However, so far the literature contains only scattered reports on LPD processed functional silicon layers including n- or p-doped films. In most of these studies, the use of more than one precursor raised considerable problems. Therefore, it has been suggested to use hydrosilane precursors for the deposition of functional silicon films which contain one or more heteroatoms covalently linked to silicon (single source precursors). In contrast to carbon chemistry, however, the systematic functionalization of higher silicon hydrides necessary for the synthesis of silicon based single-source precursors has not been accomplished on a more general basis so far. Chapter 2 is dedicated to this chemistry.

## Motivation

The modern usage of photoinitiators is no longer limited to the production of microelectronics, microlithography and much more, but also finds application in the medical field. Consequently, the search for new photoinitiators (PIs) with improved properties are of great interest, but also an enormous challenge. Acyl metalloids (mainly germanium-based) are important photoinitiators in this context. However, all synthetic strategies towards these compounds rely on classical salt metathesis reactions, where only a moderate complexity of the final products can be achieved. The goal was to go one step further and investigate their electron transfer reactions. Therefore, we introduced an innovative pathway that involves strong bases and alkali-metal reductions, which will lead to a variety of hitherto unknown enolates, anions and related compounds that are hitherto hardly producible otherwise. In the final step of the synthetic protocol these new species were reacted with a variety of electrophiles to obtain derivatives with a variety of target properties. Additionally, we also used the multiple silyl abstraction methodology and the well-known Corey-Seebach route to synthesize our acyl metalloids. Besides this,

the investigation of fundamental question regarding the chemistry of heavier group 14 enolates was also a major pillar of this habilitation.

Solution processing of silicon based electronic devices has attracted considerable attention owing to the possibility of low-cost fabrication by printing processes. Moreover, it opens the possibility for large area depositions and patterning materials. Recent studies by us and others have demonstrated the principal feasibility of the liquid phase deposition (LPD) and processing of silicon films of satisfactory quality. For future applications LPD processing of silicon based devices must allow continuous manufacturing of all circuit components by successive deposition and printing steps in the same environment. In this context silicon-heteroelement thin layer structures produced by solution routes are of great interest. So far literature contains only scattered reports on LPD processed functional silicon layers. In most of these studies, the use of more than one precursor raised considerable problems. Therefore, we elaborated appropriate pathways for the synthesis of novel heterosubstituted higher silicon hydrides in preparative amounts. After spectroscopic and structural characterization, the resulting materials were investigated with respect to photolytically induced oligomerization processes relevant for the deposition of functional silicon layers. Promising materials, finally, were used as single source precursors for LPD processed silicon heterostructures and important film properties such as thickness, homogeneity, elemental composition and morphology were investigated.

## 1. Chemistry Acyl Group 14 Metalloids

#### 1.1. Introduction

Since their discovery in 1957 by A. G. Brook,<sup>40</sup> acyl group 14 metalloids (AG 14 metalloids) have found numerous applications in organic as well as in main group chemistry.<sup>41–43</sup> In general these compounds are often yellow in color, and early investigations are focused on their spectral properties. These spectroscopic properties are also the reason for the rich chemistry of this compound class. Moreover, the outcome of these light induced reactions is strongly influenced by the central atom. While acylsilanes undergo mainly the Norrish type II reactions, acylgermane and acylstannanes undergo homolytical cleavages of the metal-carbon bond (Norrish type I). In the following section selected synthetic pathways towards this compound class are summarized.

#### 1.2. Literature

#### Synthesis of Acylsilanes

The acylsilane moiety is frequently used in organic as well as in inorganic reaction pathways, a detailed summary on the synthesis and chemistry of this moiety is beyond the scope of this habilitation. Thus, the reader shall be referred to the comprehensive literature existing on this topic including several recent reviews for additional information and bibliography.<sup>42,44,45</sup>



Scheme 2: General Synthetic Strategies towards Acylsilanes.

The most general synthetic strategy for the formation of acylsilanes is the Brook-Corey approach, which involves the formation of a 1,3-dithiane species from the corresponding aldehyde (Scheme 3, Method A).<sup>46,47</sup> Another efficient method is the nucleophilic silylation of carboxylic acid derivatives (Method B).<sup>48,49</sup> The direct approach towards acylsilane by the reaction of silanides and carboxylic acid derivatives is very common; however, the silanides need to be substituted with supplementary silyl-

groups to enable a high yield for this transformation (Method C).<sup>50,51</sup> Alternatively, various acylsilanes can be generated from acid chlorides via palladium-catalyzed reactions (Method D).<sup>52-54</sup>

#### Synthesis of Acylgermanes and Acylstannanes

Historically speaking, the preparation of acylgermanes and acylstannanes was mainly triggered by the need of substrates for spectroscopic studies on acyl-group 14 metal compounds.<sup>55–58</sup> The most common method for acylgermane and acylstannane synthesis is the reaction of anionic derivatives with carboxylic acid derivatives, e.g. acid chlorides,<sup>59–62</sup> amides,<sup>63</sup> and esters (compare Scheme 3, Method C).<sup>64</sup> Again the reader shall be referred to the comprehensive literature existing on the topic including a recent review for additional information and bibliography.<sup>21,46,54,65–73</sup>

#### **Electron Transfer Reactions of Acyl Metalloids**

In contrast to the well-established photochemistry (photo-induced electron transfer) of acyl metalloids (especially acylgermanes), which can be seen as the "bright side" of these molecules, their ground state electron transfer reactions (the "dark side") were not yet extensively investigated. To date, there are only a handful of publications on this topic. Yoshida and co-workers investigated the electrochemical oxidation of acylsilanes in the presence of alcohols, water, and amines.<sup>74,75</sup> They observed the formation of esters, acids, and amides via a selective cleavage of the Si–C bond under very mild reaction conditions (Scheme 3).



Scheme 3: Electrochemical Reaction of Acylsilanes in Protic Solvents

Fujiwara has explored the reaction of acylsilanes with lanthanoid reagents such as ytterbium metal and samarium(II) iodide.<sup>76–78</sup> They found that both compounds could reduce aliphatic acylsilanes to  $\alpha$ -silyl alcohols by a single-electron transfer process to the carbonyl group. For aromatic acylsilanes samarium(II) iodide also reduced them to  $\alpha$ -silyl alcohols. Ytterbium metal acted as a double-electron reductant and reacted with acylsilanes to afford nucleophilic Yb-oxametallacycles **5**. The Yb-oxametallacycle reacts with another acylsilane under the formation of symmetrical 1,2-diarylacetylenes (Scheme 4).



Scheme 4: Reactions of Acylsilanes with Ytterbium Metal and Samarium(II) Iodide

Fürstner and co-workers investigated McMurry reactions of simple acylsilanes (R = Aryl). Like aldehydes and ketones, acylsilanes can also undergo titanium-induced reductive coupling reactions leading to the formation of enedisilanes **6** (Scheme 5). The by-product **7** from the corresponding Brook rearrangement was also observed.<sup>79</sup>



Scheme 5: First Titanium Induced Electron Transfer Reaction

However, for other acyl metalloids such electron transfer reactions were unknown until we discovered that tetraacylgermanes undergo their highly selective single electron transfer (SET) reactions. This was also the starting point of my habilitation.

#### **1.3.** Publications

The following section covers the publications on this topic submitted during this habilitation. The starting point of this work was an invited Review article in Chem. Eur. J. about the chemistry of group 14 enolates.<sup>80</sup> The second publication was the introduction of selective single electron transfer (SET) reactions of tetraacylgermanes in Inorg. Chem., which pave the way for the exclusive formation of trisacylgermenolate.<sup>81</sup> The third publication in Chem. Eur. J. illustrates the usage of SET reactions to synthesize hitherto unknown mixed functionalized tetraacylgermanes.<sup>82</sup> followed by a publication about the group tolerance towards trisacylgermenolates published in Eur. J. Inorg. Chem.<sup>83</sup> The fifth paper uses the SET methodology to generate the first isolable geminal bisgermenolates, a new synthon for the synthesis of organometallic reagents, which was published in Angew. Chem. Int. Ed.<sup>84</sup> The SET reactions of tetraacylstannanes are summarized in the sixth publication in ChemPhotoChem.85 The implementation of other counter ion substited trisacylgermenolates was the topic of the seventh publication in *Organometallics*.<sup>86</sup> The synthesis of highly stable diacylgermanes via the Corey-Seebach method, was subject of an investigation, which was published in *Dalton Trans*.<sup>87</sup> The ninth publication in Organometallics was about the synthesis of unknown dianionic cyclic silenolates and germenolates.<sup>88</sup> The tenth publication was the introduction of D-galactose substituted acylsilanes and acylgermanes, which was published in *Organometallics*.<sup>89</sup> Paper number eleven shows the road to bisacyldigermanes, which represent a new class of visible light photoinitiators.<sup>90</sup> Paper twelve is a submitted manusprict about the photochemistry of bishypersilyl-1,2-diones. Finally, the section is rounded off with a Review article in Dalton Trans. about the possibility that Ge-based photoinitiators can substitute the state-ofthe-art P-based photoinitiators.<sup>91</sup>

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### **1.3.1. Recent Advances in the Chemistry of Heavier Group 14 Enolates** Michael Haas

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#### Abstract

HEAVIER GROUP 14 ENOLATES

Recently heavier Group 14 enolates showed their importance and applicability in a broad range of chemical transformations. They were found to be key intermediates during the synthesis of photoinitiators, as well as during the formation of complex silicon frameworks. This Minireview presents general strategies towards the synthesis of heavier Group 14 enolates (HG 14 enolates). Structural properties as well as their spectroscopic behavior are outlined. This study may aid future development in this research area.

#### Introduction

The chemistry of metal enolates is thoroughly investigated and understood to a very high degree.<sup>92</sup> Moreover, the classical aldol reaction is one of the most important biosynthetic tools for life on earth.<sup>93-</sup> <sup>95</sup> Although the first report on the synthesis of heavier Group 14 enolates by Bravo-Zhivotovskii and coworkers was in 1989,<sup>96</sup> the synthesis and characterizations of these derivatives is still a challenging endeavor. In 2003 Ottosson succeeded in isolating a silenolate, which had a high thermal stability, in order to perform a complete structural analysis.<sup>97</sup> Historically speaking the preparation of HG 14 enolates was mainly triggered by the need of substrates for spectroscopic studies on these compounds. Quite recently the Stueger group successfully isolated the first tetraacyl substituted germanes and stannanes, and showed their ability to serve as long-wavelength photoinitiators with superior potential.<sup>21,22</sup> During these reactions key intermediate are HG 14 enolates, which allows a straightforward access to these highly desirable compounds. Another milestone in the chemistry of HG 14 enolates was the report of the first sila-aldol reaction, which emphasizes the tight connection between silicon and carbon chemistry.<sup>98</sup> This new synthetic strategy must be considered as a powerful alternative to standard coupling techniques, such as the Wurtz reaction,<sup>99-102</sup> hydrosilylation,<sup>103-105</sup> as well as transitionmetal-catalyzed silicon-carbon coupling reactions.<sup>106-109</sup> Moreover, this novel synthetic method provides a straightforward access to structurally complex silicon frameworks, in quantitative yield. With these findings, HG 14 enolates demonstrate their importance and applicability in a broad range of chemical transformations.

HG 14 enolates can exist in two possible isomeric structures (Scheme 1). 1-HG 14 enolates are still undiscovered, due to the low stability of a metal-carbon double bond.<sup>110</sup> With regard to 2-HG 14

enolates, numerous reports on this compound class exist. As for metal enolates, two resonance structures for 2-HG 14 enolates are possible: in the enol form (I), where the negative charge is primarily located on the oxygen atom, while in the keto form (II) the negative charge resides predominantly on the heavier Group 14 atom (Scheme 1).<sup>111–113</sup> The dominant structure of metal enolates is generally the enol form and preferably occurs in solid state, as well as in solution.<sup>113</sup> HG 14 enolates show a significantly different resonance behavior. The position of the equilibrium is strongly influenced by the chosen alkali metal, the solvent system, as well as the substituent at the carbonyl-moiety.



Scheme 1. Resonance structures of HG 14 enolates.

In this Minireview, we first present the most important strategies reported towards the synthesis of heavier Group 14 enolates with a particular emphasis on structural assignments and spectroscopic behavior. Then we focus on the recent advances in this field and give a brief outlook.

#### Silenolates

#### Lithium-Silenolates

The first synthesized silenolates were lithium-silenolates by the group of Bravo-Zhivotovskii.<sup>96</sup> They reported on the synthesis of silenolates and introduced the general strategy of reacting a germyl-lithium reagent with an acylsilane in order to generate silenolates (Scheme 2). These silenolates were found to be relatively unstable, with a half-life time of approximately 12h. However, the decomposition products resulting from **1** were not identified.



Scheme 2. Synthesis of lithium-silenolates by Bravo-Zhivotovskii.

In a follow up paper, Apeloig and Bravo-Zhivotovskii succeeded in the identification of a possible degradation process of 1.<sup>114</sup> They found that an excess of the used base (e.g. two fold excess) leads to the formation of a 1:2 mixture of the trisilacyclobutane 2 and of (adamantoyl)adamantylcarbinol 3. (Note: Stirring for 48h at room temperature followed by aqueous work-up) (Scheme 3). The mechanism is rather complex and involves three silenolates moieties as well as a Peterson elimination in order to

obtain compound 2 and 3. For the complete mechanism the reader is referred to the original publication.<sup>114</sup>



Scheme 3. Degradation process of the lithium-silenolate 1.

J. Ohshita and M. Ishikawa expanded this strategy and introduced more precursor molecules as well as the use of different lithium reagents.<sup>115,116</sup> Additionally, they extensively explored the chemistry of their synthesized lithium-silenolates. During the course of their studies concerning the chemical reactivity of acylpolysilanes with organolithium reagents, they found that the reaction of acylpolysilanes with silyllithium reagents resulted in the formation of lithium-silenolates **4a-d** in solution (Scheme 4). These lithium silenolates are thermally instable. **4a** is moderately stable at room temperature. **4b** undergoes a fast degradation even at temperature below  $-80^{\circ}$ C. **4c,d** are more stable than **4b**, but undergo uncharacterized degradation processes at room temperature. Therefore, all chemical manipulations were performed *in situ*.

$$\begin{array}{c} \underset{Me_{3}Si}{\overset{O}{\underset{SiMe_{3}}{He_{3}Si}}}{\overset{O}{\underset{SiMe_{3}}{He_{3}Si}}} R \\ R = \underset{t-Bu \text{ or } 1-Ad}{\overset{O}{\underset{Si}{He_{3}}}} R \\ \end{array} \xrightarrow{\begin{array}{c} R'_{3}Si-Li \\ R'_{3}Si-Li \\ R'_{3}Si-Li \\ R'_{3}Si-Li \\ SiMe_{3})_{3} \text{ or } \\ SiMe_{3})_{3} \text{ or } \\ SiMe_{3} \\ SiMe_{3}$$

Scheme 4. Synthesis of lithium-silenolates by Ohshita and Ishikawa.

The reaction of **4a-d** with  $H_2O$  resulted in the formation of bis(trimethylsilyl)acylsilanes **5a-d** in nearly quantitative yields. The reaction of **4a-d** with alkyl halides led to the formation of alkylated acylsilanes in all cases. Additionally, **4a** was also reacted with allyl and benzoyl halides. Again the lithium-silenolate **4a** reacts at the silicon center to give benzylmesitoylbis-(trimethylsilyl)silane (**7**) and allylmesitoylbis(trimethylsilyl)silane (**8**) in good yields (compare Scheme 5).

Metal enolates are known to react with chlorosilanes under the formation of a silyl enol ether.<sup>92,117</sup> Ohshita and Ishikawa further studied the reactivity of **4a-d** towards the reaction with chlorosilanes. Interestingly, the reactions of lithium-silenolates **4a-d** with chlorosilanes underwent two different pathways. The chosen pathway is depending on the substituent at the carbonyl group. **4a,b**, which bear an aryl substituent at the carbonyl group form the Brook-type silenes **9a,b**. On the other hand **4c,d** with alkyl groups at the carbonyl group form the acylsilanes **10a,b** (Scheme 6). The cause for the different reactivity was determined by NMR spectroscopy. The negative charge in **4c,d** is moderately localized

on the central silicon atoms, whereas in **4a**,**b** the negative charge is effectively delocalized over the silicon atoms and carbonyl groups. This reactivity was also found by other groups, which will be discussed in more detail later in this review.



Scheme 5. Reactivity of 4a-d with H<sub>2</sub>O and selected examples of alkyl-, benzyl- and allyl-halides.



Scheme 6. Reactivity of 4a-d with chlorosilanes.

Furthermore, they also demonstrated that oxidative coupling of lithium-silenolates with palladium(II) chloride leads to the formation of bis(acyl)polysilanes **11a**,**c**,**d**.<sup>118,119</sup> This was the first example of polysilanes with two silicon-acyl bonds on the adjacent silicon atoms (Scheme 7). Moreover, they reacted their lithium-silenolates with various acid chlorides and obtained the first examples of di- and tetraacylsilanes **12a-e** and **13a**,**b** (Scheme 7).<sup>120,121</sup>



Scheme 7. Reactivity of 4a,c,d with acid chlorides.

Recently Apeloig and coworkers used a different approach towards the generation of lithium-silenolates. They synthesized them by metal-halogen exchange between silyl-lithium reagents (in excess) and bromo-acylsilanes in hexane. With this methodology they were able to isolate their silenolates and to obtain X-ray molecular structures of the first enol-form silenolates **14a**,**b** (compare Scheme 8).<sup>122</sup> The X-ray structure is depicted in Figure 1 and will be discussed in Section 5 of the review.



Scheme 8. Synthesis of lithium-silenolates.

In a follow up paper this group also investigated the reactivity of their isolated silenolates **14a,b**. Upon addition of a polar solvent such as THF an interesting rearrangement occurred and lithium-silenides were formed.<sup>123</sup> For the complete mechanism the reader is referred to the original publication.

#### **Potassium-Silenolates**

A very important milestone in the chemistry of HG 14 enolates was the introduction of potassium as counterion by Ottosson and co-workers. They reacted tris(trimethylsilyl)acylsilane with potassium *tert*-butoxide (KOtBu) and observed the quantitative formation of a potassium-silenolate (Scheme 9).<sup>97</sup> In contrast to the more difficult preparation of lithium-silenolates, these silenolates are found to be

thermodynamically more stable, and thus could be stored under an inert atmosphere and ambient temperature over a few months without degradation. This stability allowed Ottosson to obtain the first X-ray structure of a silenolate reported in the literature. The molecular structure is depicted in Figure 1 and will be discussed in Section 5 of the review.



Scheme 9. Synthesis of potassium-silenolates.

They also briefly investigated the reactivity of **15**. The trapping of **15** with MeI leads to the formation of the silicon-methylated product **16**. The reaction of **15** with 2,3-dimethyl-1,3-butadiene yields exclusively to the formation of the [4+2] adduct **17** (compare Scheme 10). Ohshita and Ishikawa found the same reactivity for their lithium-silenolates.<sup>115</sup>



Scheme 10. Reactivity of 15 with MeI and 2,3-dimethyl-1,3-butadiene.

Later on, the Stueger group demonstrated the possibility of synthesizing and characterizing cyclic silenolates **18a-c**.<sup>124</sup> **18a-c** were obtained with remarkable selectivity by the addition of 1.05 equiv. of KO*t*Bu to the corresponding acylcyclohexasilanes either in THF or in toluene solution in the presence of 1.05 equiv. of [18]-crown-6 ([18]-cr-6) at -50 °C (Scheme 11). In the absence of air these cyclic potassium-silenolates have the same stability as the acyclic derivatives. However, **18a-c** decompose immediately to uncharacterized material upon exposure to the atmosphere, or the attempted removal of the solvent and other volatile components in vacuum. Nevertheless, they obtained crystal structures for **18b** and **18c**.



Scheme 11. Synthesis of cyclic potassium-silenolates.

Furthermore, they studied the reactivity of **18a-c** towards the reaction with chlorosilanes and MeI. They found the same reactivity as for acyclic lithium silenolates (see Scheme 12). The reaction of **18a,b** with chlorosilanes allowed the formation of exocyclic silenes **19a,b**. The reaction of **18c** with chlorosilanes give rise to the formation of acylcyclohexasilane **19c**. In the reaction of **18a,c** with MeI, same reactivities in terms of reaction sites were found. In both cases, alkylation of the silicon atom was observed in nearly quantitative yields.



Scheme 12. Reactivity of 18a-c with chlorosilanes and MeI.

In a follow up paper they also examined the thermal stability of  $18a,c.^{125}$  A selective rearrangement cascade was found when 18a was stirred for 5h at 60°C leading to the formation of highly interesting carbanion 2-oxahexasilabicyclo[3.2.1]octan-8-ide 21. This observation indicates that 18a was only the kinetic product, which thermodynamically rearranged via a mild, selective silyl-migration cascade to the bicyclic carbanion 21 (Scheme 13). This cascade represents the first example of an intramolecular Sila-Peterson reaction, where the formed silene is trapped by the present oxygen nucleophile intramolecularly (For the complete mechanism the reader is referred to the original publication).<sup>125</sup> Upon the addition of MeI to a freshly prepared toluene solution of 21, the corresponding methylated bicyclic adduct 22 was formed in the diastereomeric ratio of *endo:exo* = 2:1.



Scheme 13. Rearrangement cascade to the substituted carbanion 21 and its subsequent trapping with MeI to 22.

Interestingly the same reaction set-up for **18c** led to complete degradation of **18c** to uncharacterized material. They assumed that, in the case of alkyl-substituted systems, the negative charge could not be distributed in the same way as in compound **21** and the primarily formed carbanion reacted further under the applied reaction conditions.

#### Germenolates

#### Lithium-Germenolates

Again the first synthesized germenolate was a lithium-germenolate by the group of Bravo-Zhivotovskii.<sup>96</sup> They reported briefly on the formation of this lithium-germenolate **23** from the reaction of an acylgermane with  $Et_3GeLi$ . Spectroscopic and structural data of **23** were not given.



Scheme 14. Synthesis of lithium-germenolate.

#### **Potassium-Germenolates**

Potassium-germenolates were found to be crucial intermediates for the synthesis of tetraacylgermanes.<sup>21</sup> To verify this assumption tris(trimethylsilyl)acylgermane **24** was reacted with 1.05 eq. of KO*t*Bu (see Scheme 15). A quantitative formation of the corresponding germenolate was observed. The molecular structure of **24** as determined by single-crystal X-ray crystallography and the complete set of consistent NMR data can be found in Section 5 of this review.



Scheme 15. Synthesis of potassium-germenolate 24.

Our group also succeeded in the isolation and characterization of the first cyclic germenolates. Therefore, the corresponding acyl-1,4-digermacyclohexasilanes were reacted with 1.05 eq. of KO*t*Bu at  $-70^{\circ}$ C (see Scheme 16).<sup>126</sup> The stability of these cyclic germenolates is comparable to their silicon homologs. After addition of [18]-cr-6 in toluene we were able to grow crystals of the 1:1 [18]-cr-6 adducts of **25b** and **25c**, which were suitable for single-crystal X-ray crystallography (see Section 5).



Scheme 16. Synthesis of cyclic potassium-germenolates.

The reactivity of 25a-c versus chlorosilanes parallels that observed earlier for silenolates. Thus, 25c, with an alkyl group attached to the carbonyl moiety, reacted with Me<sub>3</sub>SiCl at 0°C under formation of the corresponding cyclic acylgermane **26c**, while the aryl-substituted compounds **25a**,**b**, under the same conditions, exclusively afforded the O-silylated germenes **26a**,**b** (compare Scheme 17).

Furthermore our group demonstrated the possibility to generate the first examples of dianionic germenolates **27a,b**, which were synthesized by the reaction of the corresponding cyclic acylgermanes with 2.1 eq. of KO*t*Bu (see Scheme 18). After addition of [18]-cr-6 in toluene we were able to grow crystals of the 1:2 [18]-cr-6 adducts of **27a** and **27b**, which were suitable for single-crystal X-ray crystallography (see Section 5).<sup>127</sup>



Scheme 17. Reactivity of 25a-c with chlorosilanes.



Scheme 18. Synthesis of cyclic dianionic potassium-germenolates.

#### Stannenolates

No stable stannenolates are reported so far. Recently our group published a paper on previously unknown tetraacylstannanes. During their formation, stannenolates were found to be crucial intermediates.<sup>22</sup>

#### **Characterization and Bonding in Group 14 Enolates (Section 5)**

In the following section, the spectroscopic behavior, as well as important structural features of HG 14 enolates will be discussed. Moreover, a short summary of theoretical studies concerning HG 14 enolates will be given.

#### NMR Spectroscopy

The chemical shift of the central metal atom for HG 14 enolates is strongly influenced by the dominant resonance structure, the solvent as well as the used counter ion. The <sup>29</sup>Si NMR chemical shifts of the central silicon atom of silenolates, which adopt the keto resonance structure, were found in the region from  $\delta = -59$  ppm to  $\delta = -93$  ppm. The measured <sup>29</sup>Si NMR shifts are in the typical range for silyl anions.<sup>128</sup> The use of crown ethers leads to an even stronger high field shift of the central silicon atoms (<sup>29</sup>Si chemical shifts of the Si atom of **15** are  $\delta = -78.7$  ppm in THF and  $\delta = -93.8$  ppm when [18]-cr-6 is present). The measured <sup>13</sup>C-NMR shifts of the carbonyl C atoms of HG 14 enolates adopting the keto resonance structure were found in the region of  $\delta = 262$  to  $\delta = 274$  ppm, which are typical for sp<sup>2</sup> hybridization, and close to the ones measured for the corresponding acyl-derivatives. The measured <sup>29</sup>Si

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NMR shifts for the central silicon atom of the silenolate, which adopts the enol form is  $\delta$ = 8.4 ppm. This is significantly downfield shifted compared to keto derivatives and in the region for <sup>29</sup>Si shifts of silicon atoms of a Si=C double bond. No <sup>13</sup>C NMR spectrum for this compound is reported. The exact values for the reported HG 14 enolates are depicted in Table 1.

<b>Table 1.</b> <sup>29</sup> Si NMR shifts of the central silicon atoms and <sup>13</sup> C NMR shifts of the carbonyl atoms.					
Com.	<sup>29</sup> Si NMR (ppm)	<sup>13</sup> C NMR (ppm)	Com.	<sup>29</sup> Si NMR (ppm)	<sup>13</sup> C NMR (ppm)
<b>4</b> a	-55.9 <sup>[a]</sup>	262.7 <sup>[a]</sup>	18c	-70.0 <sup>[e]</sup>	265.1 <sup>[e]</sup>
<b>4</b> b	-70.5 <sup>[a]</sup>	274.1 <sup>[a]</sup>	24	-	280.9 <sup>[e]</sup>
4d	-70.3 <sup>[a]</sup>	274.3 <sup>[a]</sup>	25a	-	281. <sup>6[f]</sup>
14b	8.4 <sup>[b]</sup>	-	25b	-	279.5 <sup>[f]</sup>
15	$-78.7^{[c]}$	271.1 <sup>[c]</sup>	25c	-	281.9 <sup>[f]</sup>
	-93.0 <sup>(1)</sup>		25		10
18a	-/3.16	264.76	27a	-	282.45 <sup>[1]</sup>
18b	$-73.1^{[e]}$	264.7 <sup>[e]</sup>	27b	-	282.78 <sup>[f]</sup>

<sup>a</sup> measured in 70% THF + 30% THF-d<sub>8</sub> at -40°C; <sup>b</sup> solid state isotropic NMR; <sup>c</sup> measured in THF-d<sub>8</sub> at RT;

 $^d$  measured in THF-d\_8 with (18)-cr-6 at RT;  $^e$  measured in C\_6D\_6 with (18)-cr-6 at RT;  $^f$  measured in THF with D\_2O capillary at RT

#### **UV-Vis Spectroscopy**

To gain more insight into the electronic nature of silenolates, as well as of germenolates, our group recorded the absorption spectra of **18a,c** and **25a-c** and assigned the longest wavelength absorption through time-dependent functional in combination with the polarizable continuum model (TDDFT-PCM) calculations at the B3LYP/6-31+G(d,p) level. All HG 14 enolates exhibit an intense absorption maximum between 400 and 500 nm. According to calculations, these bands are unequivocally assigned to a HOMO  $\rightarrow$  LUMO or a HOMO  $\rightarrow$  LUMO+1 transition. The HOMOs mainly correspond to the p<sub>z</sub> orbital of the metal atom with little variation in shape and energy. Upon excitation, electron density is displaced into the  $\pi^*$  orbital of the carbonyl moiety (LUMO or LUMO+1). The LUMOs of the aryl-substituted species showed additionally conjugation of the carbonyl and the aromatic  $\pi$  systems, which results in the observed bathochromic shifts of the corresponding absorption bands. The obtained experimental and computational data are summarized in Table 2. Therefore, silenolates **18a,c** and **25a-c** are best described as acyl metal anions (keto form in Scheme 1) in solution irrespective of the nature

of the R group attached to the carbonyl moiety. In contrast to that, Apeloig also calculated the HOMO orbitals for their silenolates with enol character and found that they have pronounced  $\pi$ -character.<sup>122</sup>

	$\lambda_{\max,\exp}$ (nm)	$\lambda_{\max, calc}$ (nm)	assignment			
18a/Si	448	429	$p_z \rightarrow \pi^* (\text{CO/aryl})$	HOMO→LUMO		
18c/Si	438	418	$p_z \rightarrow \pi^* (CO)$	HOMO→LUMO		
25a/Ge	442	426	$p_z \rightarrow \pi^* (\text{CO/aryl})$	HOMO→LUMO		
25b/Ge	463	496	$p_z \rightarrow \pi^* (\text{CO/aryl})$	HOMO→LUMO		
25c/Ge	422	412	$p_z \rightarrow \pi^* (CO)$	HOMO→LUMO+1		

**Table 2.** Experimental and TDDFT-PCM B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) calculated absorption bands  $\lambda$  in THF for the potassium-HG 14 enolates **18a,c** and **24a-c**.

#### **Structural Assignments**

All silenolates adopting the keto resonance structure, which were characterized by single X-ray crystallography, have potassium as counter ion. Generally, they have a strong pyramidal central silicon atom with an elongated Si-C single bond. Two examples of these compounds are depicted in Figure 1. Selected bond lengths d[Å] and selected sum of valence angles  $\Sigma \alpha Si_1$  and  $\Sigma \alpha C_1$  [deg] for the silenolates are illustrated in Table 3.



**Figure 1.** Selected examples of single X-ray structures of HG 14 metal enolates. (Top Left: potassium-silenolate **15**; Top Right: lithium-silenolate **14a**; Bottom Left: cyclic potassium-silenolate **18c**; Bottom Right: cyclic potassium-germenolate **25b**).

All silenolates adopting the enol resonance structure, which were characterized by single X-ray crystallography, have lithium as counter ion. Generally, they have a planar central silicon atom and the central Si-C bond shows double bond character. One example is depicted in Figure 1.

**Table 3.** Selected bond lengths d [Å] and sum of valence angles  $\Sigma\alpha(Si1)$  and  $\Sigma\alpha(C1)$  [deg] for silenolates.

	14b	14b	15	18b	18c
d C <sub>1</sub> -Si <sub>1</sub>	1.822(7)	1.811(2)	1.926(3)	1.966(2)	1.874(2)
d C <sub>1</sub> -O <sub>1</sub>	1.315(7)	1.367(2)	1.245(3)	1.244(2)	1.260(2)
$d\;M_1\text{-}O_1{}^{[a]}$	1.858(12)	1.858(2)	2.846(2)	2.743(1)	2.701(1)
$d\;M_1\text{-}Si_1{}^{[a]}$	2.795(2)	2.871(4)	3.714(1)	3.603(2)	4.935(1)
$\Sigma \alpha(Si_1)$	360.0	359.9	317.8	316.7	326.8
$\Sigma \alpha(C_1)$	360.0	360.0	359.7	359.9	359.7

[a] **14b**: M = Li; **15** and **18b**,c: M = K.

All germenolates, which were characterized by single X-ray crystallography, have potassium as counter ion and adopt the keto resonance structure. Generally, they have a strong pyramidal central germanium atom with an elongated Ge-C single bond. One example of these compounds is depicted in Figure 1. Selected bond lenghts d[Å] and selected sum of valence angles  $\Sigma \alpha Ge1$  and  $\Sigma \alpha C1$  [deg] for the germenolates are depicted in Table 4.

**Table 4.** Selected bond lengths d [Å] and sum of valence angles  $\Sigma\alpha(Ge1)$  and  $\Sigma\alpha(C1)$  [deg] for germenolates.

	24	25b	25c	27a
d C <sub>1</sub> -Si <sub>1</sub>	2.004(7)	2.007(5)	2.063(2)	2.055(3)
d C <sub>1</sub> -O <sub>1</sub>	1.249(2)	1.236(6)	1.231(3)	1.252(4)
d K <sub>1</sub> -O <sub>1</sub>	2.782(10)	2.733(4)	2.740(2)	2.758(8)
d K <sub>1</sub> -Ge <sub>1</sub>	3.947(4)	3.855(6)	3.613(9)	3.423(2)
$\Sigma \alpha(Ge_1)$	310.5	304.6	310.7	314.0
$\Sigma \alpha(C_1)$	359.8	359.9	359.9	359.6

#### **Theoretical Studies**

The keto–enol equilibrium in metal silenolates has also been investigated computationally. Apeloig et al. found that in non-solvating media the enol-form of the silenolate dominates. The effective solvation of the cation, e.g., by crown ethers, results in the formation of the keto-form.<sup>122</sup> Additionally, Ottosson et al. revealed in a related study that coordination of a solvated metal ion to the oxygen atom in silenolates results in shorter Si-C bond lengths, a smaller degree of pyramidalization around the central silicon atom, and a lower charge difference at the carbon and at the silicon atom ( $\Delta q(SiC)$ ) compared to the naked silenolate.<sup>129,130</sup>

#### **Recent Advances**

The synthesis and characterization of HG 14 enolates was mainly triggered by fundamental investigations in the field of main group chemistry. This changed drastically when the Stueger group found an elegant synthetic protocol towards the synthesis of the first tetraacyl substituted germanes and stannanes. Moreover, these compounds showed their ability to serve as long-wavelength photoinitiators with superior potential.<sup>21,22,131</sup> During these reactions, key intermediates are HG 14 enolates, which allows a straightforward access to these highly desirable compounds. Another important discovery in the chemistry of HG 14 enolates was the report of the first sila-aldol reaction.<sup>98</sup> In the following section of this review this recent advances will be summarized.

#### **Tetraacylgermanes and --stannanes as Photoinitiators**

Photoinitiators (PIs) play a very important role in a wide range of industrial processes (coatings, adhesives, dental filling materials, and the manufacture of 3D objects). Among the promising PI systems, tetraacylgermanes and tetraacylstannanes can act as suitable radical precursors generating acyland metal-centered radicals upon irradiation, which add very rapidly to double bonds of various monomers.<sup>24,132–134</sup> Moreover, they offer the advantages of significantly red-shifted absorption bands and reduced toxicity compared to the frequently applied phosphorus-based PIs.<sup>135–138</sup> Furthermore, the synthetic protocol is very robust, one-pot, and outperforms the methods in the synthesis of state-of-theart photoinitiators.<sup>18</sup> The Stueger group discovered that the reaction of a potassium germanide and stannide with 4.1 equiv. of acid fluorides leads to the exclusive formation of tetraacylgermanes or tetraacylstannanes in high yields. The mechanism is outlined in Scheme 19. HG 14 enolates were determined as crucial intermediates of this reaction.



Scheme 19. Mechanism for the synthesis of tetraacylgermanes and -stannanes.

#### Sila-Aldol Chemistry

The classical aldol reaction with its power in the reversible formation of carbon-carbon bonds, is one of the most important organic reaction types.<sup>93,139</sup> The aldol reaction for silicon-based compounds, were unknown until our group reported on the first sila-aldol reaction. This reaction provides a straightforward access to structurally complex silicon frameworks. The starting point for the development of this transformation was the reaction of 1,4-bis-(acyl)cyclo-hexasilane **28** with KO*t*Bu. As expected, the base abstracted one SiMe<sub>3</sub> group to give monosilenolate **29**, which immediately reacted further in the proposed sila-aldol reaction. Interestingly, the silicon–carbon addition product **30** was not directly observed by NMR spectroscopy, as this reaction selectively led to the formation of the bicyclic carbanion **31** in an ensuing anionic rearrangement cascade (compare Scheme 20). This transformation introduces a pioneering strategy for the formation of silicon–carbon bonds by establishing a further link between the two related fields of silicon and carbon chemistry. The sila-aldol reaction provides a significant addition to the synthetic methods available for the formation of a new class of silicon-based compounds.



Scheme 20. Sila-aldol chemistry with the formation of complex silicon frameworks.

#### **Conclusions and Outlook**

Given that the chemistry of HG 14 enolates is relatively young, we have summarized in a concise and a complete way, the most important synthetic strategies towards this compound class. We have also shown their reactivity towards selected examples of electrophiles and trapping agents. Furthermore, we have summarized the spectroscopic behavior and the structural data for HG 14 enolates. Inspired by the promising potential of tetraacylgermanes and -stannanes acting as long-wavelength photoinitiators, we have highlighted their synthesis, where HG 14 enolates are crucial intermediates during their formation. More research towards the chemistry of this new photoinitiator class is likely to emerge soon. The sila-aldol chemistry has been shown to be highly efficient in the formation of complex silicon framework. This new synthetic strategy can be a powerful alternative to standard coupling techniques, such as the Wurtz reaction, hydrosilylation, as well as transitionmetal-catalyzed silicon-carbon coupling reactions.

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Keywords: metal enolates • silenolates • germenolates • stannenolates • sila-aldol chemistry

# **1.3.2.** The Chemistry of Acylgermanes: Triacylgermenolates Represent Valuable Building Blocks for the Synthesis of a Variety of Germanium-based Photoinitiators

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#### Abstract

The formation of a stable triacylgermenolate **2** as a decisive intermediate was achieved by using three pathways. The first two methods involve the reaction of KO*t*Bu or alternatively potassium with tetraacylgermane **1** yielded **2** via one electron transfer. The mechanism involves





the formation of radical anions (shown by EPR). This reaction is highly efficient and selective. The third method is a classical salt metathesis reaction toward 2 in nearly quantitative yields. The formation of 2 was confirmed by NMR spectroscopy, UV-vis measurements and X-ray crystallography. Germenolate 2 serves as a starting point for a wide variety of organo-germanium compounds. We demonstrate the potential of this intermediate by introducing new types of Ge-based photoinitiators 4b-f. The UV-vis absorption spectra of 4b-f show considerably increased band intensities due to the presence of eight or more chromophores. Moreover, compounds 4d-f show absorption tailing up to 525 nm. The performance of these photoinitiators is demonstrated by spectroscopy (time-resolved EPR, laser flash photolysis (LFP), photobleaching (UV-vis)) and photopolymerisation experiments.

#### Introduction

In organic as well as in inorganic chemistry, alkoxides of alkali metals are widely used as powerful bases. Recently, these alkoxides were also found to be involved in a wide variety of reactions where single electron transfer reactions take place.<sup>6,140–188</sup> In his landmark work, Murphy et al.<sup>5</sup> explained the controversial electron transfer from KOtBu to benzophenone (compare Scheme 1). They showed that KOtBu and benzophenone form a metastable complex, which absorbs light above 400 nm. The light-induced activation results in an electron transfer from the alkoxide to benzophenone, which leads to the

formation of a radical anion. Subsequently, the *tert*-butoxyl radicals undergo a fragmentation to form acetone and methyl radicals, which were trapped by unreacted benzophenone.<sup>5</sup>



Scheme 1. Photochemical induced SET of benzophenone with KOtBu.

Benzophenone and related derivatives are frequently applied as photoinitiators for UV-curing of inks and coatings.<sup>189</sup> In this context, the keto-derivatives of main group IV organometalloids (mainly germanium-based) have also attracted considerable attention as visible light induced photoinitiators.<sup>17,18,21,22,190,191</sup> To date, di- and tetraacylgermanes are well established (see Chart 1), although both compounds classes have significant drawbacks.



Chart 1. The state-of-the-art germanium-based photoinitiators

The synthetic pathway for all commercially available diacylgermanes (e.g., Ivocerin) relies on a multistep synthesis (based on the Corey-Seebach reactions), which results in a complex purification process. Tetraacylgermanes, on the other hand, have a low solubility in various monomers, which excludes them from several applications. Therefore, these systems cannot fully meet the requirements for photoinitiators in high-throughput polymer synthesis. To overcome the above mentioned restrictions, we further studied reactivities of acylgermanes to develop new pathways towards oligoacylgermanes.

Recently, we investigated the redox chemistry of acylgermanes and discovered their "dark side". Upon reduction with metallic potassium under inert conditions, the corresponding acylgermane radical anions are formed (see Scheme 2), which were characterized by EPR spectroscopy in combination with DFT calculations.<sup>192</sup> While monoacylgermanes display similar reduction potentials as benzaldehyde derivatives, the di- and tetraacylgermanes can be reduced at less negative potentials due to the presence of more electron-withdrawing acyl groups.<sup>192</sup>



Scheme 2. Alkali metal reduction of acylgermanes to the corresponding radical anions.

On the basis of the accessibility of acylgermanium based radical anions and taking into account the seminal work of Murphy and coworkers, merging the chemistry of strong bases and electron transfer, we now explore whether the reduction of acylgermanes provides synthetically attractive reaction pathways.

Our results show a novel aspect of acylgermane chemistry. The aim of this work is to demonstrate that triacylgermenolates can serve as new building blocks for the formation of high performance group-14-based photoinitiators. Additionally, this pathway significantly expands the number of available acylgermanes. Finally, the performance of these photoinitiators was evaluated by spectroscopy (time-resolved EPR), laser flash photolysis (LFP), photobleaching (UV-vis)) and photopolymerisation experiments (photo-DSC measurements).

#### **Results and Discussion**

**Reaction of 1 with K<sup>0</sup> (method 1)**. Our first task was to explore the reactivity of **1** with potassium. Therefore, **1** was dissolved in THF, and solid freshly cleaned potassium was added. The surface of the potassium became immediately reddish, which indicates the beginning of the reaction. After approximately 5 min, the yellow reaction solution became orange. The full consumption of the potassium marks the end of the reaction, which results in the formation of hitherto unknown triacylgermenolate **2**. This germenolate was obtained with remarkable selectivity. The obtained THF solution could be stored for prolonged periods (usually days). Analytical and spectroscopic data that strongly support the structural assignment are given in the Experimental Section, together with experimental details.

The reduction potential of **1** (-1.57 V vs SCE in DMF <sup>192</sup>) falls well in line with the reduction potentials observed for other tetraacylgermanes, for which radical anions could be detected by EPR spectroscopy.<sup>192</sup> Therefore, we investigated a THF solution of **1** after exposure to metallic potassium by EPR spectroscopy and could obtain an EPR spectrum (SI, Figure S14). The unresolved EPR signal (g = 2.0039) is likely caused by the formation of tight ion pairs between the ketyl-type radical anions and the magnetically active <sup>39</sup>K nuclei (I = 3/2; natural abundance 93.3 %) in ethereal solvents (like THF).<sup>193</sup> Generally, the interaction of a <sup>39</sup>K nucleus in an ion pair between a radical anion and a K<sup>+</sup> counterion leads to four equidistant lines (1:1:1:1) with a very small hyperfine coupling constant. Accordingly, these lines only rarely appear resolved in the EPR spectra and, in most cases, lead to line broadening. This is in accordance with observations on the related radical anions of TPO ((2,4,6-trimethylbenzoyl)diphenylphosphane oxide) and BAPO (2,4,6-bis(trimethylbenzoyl)phenylphosphane oxide). Whereas electrochemically (in CH<sub>3</sub>CN with Bu<sub>4</sub>NClO<sub>4</sub> as supporting electrolyte) generated radical anions where the Bu<sub>4</sub>N<sup>+</sup> counterions have no close interaction with the radical anion revealed well-resolved spectra, reduction with K metal in THF leads to severely broadened lines caused by tight ion-pair formation with K<sup>+</sup>.<sup>194</sup>
**Electron transfer reaction mechanism.** On the basis of the above-mentioned observations, Scheme 3 presents a plausible single electron transfer (SET) mechanism for the formation of **2** with the use of potassium as reduction agent. In the initial reaction step, the radical anion is formed via an SET reaction. This radical anion undergoes an acyloin condensation and after elimination of the diketone, the germenolate **2** is formed. A second SET reaction probably leads to the formation of a diradical, which undergoes a complex und uncharacterized degradation sequence.



Scheme 3. SET reaction of 1 with K<sup>0</sup> (method 1)

In order to prove our mechanism a trapping experiment with MeI was performed. The reaction solution was quenched with an excess of MeI. The expected triacylgermane **3** was obtained in a very selective fashion alongside with uncharacterisable degradation products deriving from the diketone intermediate (Scheme 4).



Scheme 4. Reaction of 2 with MeI

**Reaction of 1 with KOtBu (method 2).** Following the work of Murphy et al., we explored the reactivity of **1** with KOtBu. On the one hand KOtBu is, in comparison to potassium, significantly easier to handle and on the other hand a more selective reducing reagent than potassium. Therefore, **1** was dissolved in  $C_6D_6$  in the presence of [18]-crown-6 and solid KOtBu was added. The reaction solution became immediately reddish, which indicates the beginning of the reaction. After approximately 60 min, the mixture became clear, which indicates the full consumption of the KOtBu. This marks the end of the reaction and again the selective formation of **2** alongside with the corresponding ester. Also, this obtained solution could be stored for prolonged periods (usually days). Analytical and spectroscopic data that strongly support the structural assignment are given in the Experimental Section, together with experimental details.

We also obtained a well-resolved EPR spectrum for the mixture of **1**, [18]-crown-6 and KOtBu in C<sub>6</sub>D<sub>6</sub> at room temperature (g = 2.0047), which corroborates the formation of *t*BuO<sup>•</sup> radicals (see SI, Figure S15 and the corresponding discussion below the caption). On the basis of the results from the EPR

investigation, we propose a single electron transfer reaction, which allows the straight forward access to a radical anion and a *tert*-butoxy radical. Subsequently, these two radials undergo a hemiketal formation. After elimination of the *tert*-butyl-2,4,6-trimethylbenzoate, the germenolate 2 is formed in excellent yields (see Scheme 5).



Scheme 5. SET Reaction of 1 with KOtBu (method 2)

**Direct Approach toward 2 (method 3)**. As published previously, KOtBu is also of central importance for the formation of tetraacylgermane 1.<sup>21</sup> During the synthesis of 1, this strong base cleaves all silicongermanium bonds in order to form the desired product 1. On the basis of our new observations that KOtBu also reacts with 1 to form 2 we reinvestigated the formation of 1. Indeed, we found that during the synthetic protocol towards 1 (reaction of 4K with 4 molar equiv. of mesitoylfluoride)<sup>54</sup> and prolonged stirring of this mixture (more than 2 days at room temperature), the formation of small amounts of 2 was observed. A complete conversion of 1 to 2 was not detected. Therefore, we set out and reacted the potassium germanide 4K with 3.0 molar equiv. of the mesitoylfluoride, which gave rise to the quantitative formation of 2 within 60 min (see Scheme 6). This direct approach presents a facile synthesis towards 2. Due to the quantitative formation of 2, the reaction solution can be directly derivatized with electrophiles.



Scheme 6. Direct approach toward 2 (method 3)

**X-ray Crystallography of 2.** The structure of **2** was confirmed by single-crystal X-ray diffraction analysis (compare Figure 1 and 2). Figure 1 depicts the standard structure of a heavier group 14 enolate as a 1:1 adduct of [18]-crown-6. Compound **2-18-c-6** crystallized in the triclinic space group  $P^-1$  and the unit cell contains two molecules. Figure 2 shows the first undistorted structure of a heavier group 14 enolate. Compound **2** crystallized in the monoclinic space group C2/c and the unit cell contains eight molecules. As for all other structural characterized germenolates,<sup>80,126,127</sup> the central Ge atoms of **2-18-c-6** and **2** are pyramidal and have elongated Ge-C single bonds. Particularly striking are two interesting

structural features in the structures of **2** with respect to the relative orientation of the three carbonyl groups as well as the distance between anionic and cationic center in the molecule. In the case of the **2-18-c-6** derivative, the crown ether is successfully saturating the metal coordination site of the potassium in the equatorial plane, forcing two carbonyl groups to approach the metal centre form the axial position. However, in the case of the smaller dimethoxyethane, which is bidentate and considerably less sterically encumbering than the crown ether, the potassium metal is less coordinative saturated and essentially all the carbonyl groups orient themselves in order to satisfy the coordination sphere of potassium. While the distance between the central germanium atom and the potassium atom in **2-18-c-6** is well in line with all other structural characterized germenolates,<sup>126,127</sup> the distance of the coordination sphere described above.



**Figure 1**. ORTEP representation for compound **2-18-c-6** (1:1 adducts with [18]crown-6). Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations:  $\sum \alpha Ge(1)$  310.34, Ge(1)-C(1) 2.0137 (12), Ge(1)-C(2) 2.0161 (12), Ge(1)-C(3) 2.0279 (12), C(1)-O(1) 1.2311 (15), C(2)-O(2) 1.2298 (15), C(3)-O(3) 1.2259 (15), K(1)-O(1) 2.7562 (10), K(1)-O(2) 2.7052 (10), K(1)-O(3) 6.289 (10), K(1)-Ge(1) 3.615 (4).



**Figure 2**. ORTEP representation for compound **2**. Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations:  $\sum \alpha Ge(1)$  309.13, Ge(1)-C(1) 2.017 (3), Ge(1)-C(11) 2.016 (3), Ge(1)-C(21) 2.011 (3), C(1)-O(1) 1.234 (3), C(11)-O(2) 1.229 (4), C(21)-O(3) 1.232 (3), K(1)-O(1) 2.605 (2), K(1)-O(2) 2.616 (2), K(1)-O(3) 2.648 (2), K(1)-Ge(1) 4.397 (7).

**Stability of 2**. Compound **2** can be stored in the absence of air at room temperature for several months without detection of any degradation products. Furthermore, **2** can be completely vacuum-dried. This is in stark contrast to the vacuum instability of all other known heavier group 14 enolates,<sup>80</sup> which undergo degradation reactions during this process. We assume that the remaining acyl groups significantly stabilize the negative charge due to hyperconjugation.

**UV-Vis Spectroscopy of 2.** THF was used as a solvent to determine the charge transfer behavior for the longest wavelength absorption bands.<sup>195</sup> Figure 3 depicts the measured and calculated UV-vis spectra in THF together with their calculated frontier Kohn-Sham orbitals for the HOMO and LUMO orbitals. The germenolate **2** exhibits two intense absorption bands with  $\lambda_{max} = 427$  nm (band I) and 353 nm (band II). Qualitative agreement between calculated and experimental absorption maxima could be achieved for both bands. In band I, consisting of the first two excitations, the S1 transition is assigned mainly to the HOMO-LUMO excitation. The HOMO mainly correspond to the p<sub>z</sub> orbital of the germanium atom with little variation in shape and energy. Upon excitation, electron density is displaced into the  $\pi^*$  orbital of the carbonyl moieties (LUMO). The next transitions (S2-S5) consist of carbonyl  $\pi$ - $\pi^*$  excitations from HOMO-2, HOMO-1, HOMO into LUMO, LUMO+1, LUMO+2 orbitals with different mixing (see the transition density, the detailed orbital pictures and the interpretation of the spectrum in the *Supporting Information*).



Figure 3. Measured UV-vis spectra of 2 in THF ( $5 \times 10^{-4}$  mol/L) (top left) and calculated absorption spectrum for compound 2 with two K<sup>+</sup> as counterions (top right). The vertical transitions are marked as vertical lines with their respective oscillator strengths (right axis). The orbitals involved in the first bands are presented (bottom).

**Reactivity of 2 with selected electrophiles.** In order to test our new precursor system, we reacted **2** with selected examples of electrophiles. As suitable electrophiles we choose aryl- as well as alkyl-substituted di- and triacyl chlorides and two bromo-alkanes. All these reactions resulted in the clean

formation of a variety of new oligoacylgermanes in good to excellent yields (compare Scheme 7). These new compounds represent promising high performance photoinitiators. Analytical and spectroscopic data obtained for **4a-f** are consistent with the proposed structures. NMR spectra and detailed assignments are provided in the Experimental Section and in the *Supporting Information*. All derivatives show very similar <sup>13</sup>C chemical shifts for the carbonyl C-atom between  $\delta = 219.5$  and 237.6 ppm, which is characteristic for carbonyl groups directly linked to a germanium atom. As method 3 circumvents the usage of [18]-crown-6 and furthermore gives higher yields, this method was used for our reactions with electrophiles.



Scheme 7. Reaction of 2 with selected electrophiles

Crystals suitable for single-crystal X-ray diffraction analysis were obtained for compounds **4b**, **4d** and **4e**. As a representative example, the molecular structure of **4d** is depicted in Figures 4. All other structures are included in the *Supporting Information*. Structural data are in accordance with literature values of other acyl germanium compounds.<sup>21,24,126,127</sup> A structural feature, which significantly influences the optical properties is the torsion angle between the C=O groups and the aromatic ring planes. As a representative example we discuss the structure of **4d**, which has two substituted carbonyl

groups. The six mesityl substituted carbonyl groups have a torsion angle of 57.70°. The two 1,4-phenyl substituted carbonyl groups adopt an angle of 20.94°. The smaller the angle the more pronounced conjugation between the aromatic ring and the carbonyl group is possible and this results in a bathochromic shift of  $\lambda_{max}$ .



**Figure 4** ORTEP representation for compound **4d.** Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å):  $d_{Ge-C}$  (mean) = 2.028,  $d_{C-O}$  (mean) = 1.211.

**UV/vis Spectroscopy of 4a-f.** To further elucidate substituent effects on the absorption behavior of these new oligoacylgermanes, UV-vis absorption spectra of **4a-f** were recorded (compare Figure 5). As previously shown for this compound class, the absorption behavior is strongly influenced by the substitution pattern at the aromatic ring system. In comparison to the tetraacylgermane  $1^{21}$  and the triacylgermane **4a**, all oligoacylgermanes **4b-f** showed a significant higher extinction coefficient, which can be attributed to the higher number of chromophores in the molecule. Moreover, the oligoacylgermanes **4d-f**, where the two triacylgermyl moieties are connected *via* a dicarbonyl-phenyl bridge display a substantial red-shift of the absorption edge. The *para*-substitution of compound **4d** induces the bathochromic shifted absorption edge, which shows absorption up to 525 nm (see Table 1). In contrast, the traditional phosphorus-based photoinitiators TPO and BAPO do not absorb above 420 and 440 nm, respectively.<sup>24</sup>



**Figure 5**. a) UV/vis absorption spectra of **4a-f**; dichloromethane solution,  $c = 5 \ge 10^{-4} \mod/L$  and b) expanded tails of  $n/\sigma - \pi^*$  transition bands.

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	$\lambda_{\max,\exp}$ [nm] (n/ $\sigma$ - $\pi$ *(CO/Aryl))	$\varepsilon [L \cdot mol^{-1} \cdot cm^{-1}]$
1	375, 408	1485, 938
<b>4</b> a	382, 402	1303, 938
4b	382, 400	2628, 1982
<b>4</b> c	363, 400	3464, 1960
4d	377, 434sh	5252, 1645
<b>4</b> e	379, 394sh	4328, 3642
<b>4</b> f	381, 434sh	5142, 1776

**Table 1.** Experimental Wavelength Absorption Maxima  $\lambda$  [nm], Extinction Coefficients  $\varepsilon$  [L·mol<sup>-1</sup>·cm<sup>-1</sup>] for 1 and **4a-f** (Dichloromethane).

**Characterization of oligoacylgermane photoinitiators**. In the following paragraphs, the photochemical performance of the newly synthesized oligoacylgermanes is investigated. Compound **4a** has been already characterized in a previous publication,<sup>24</sup> and the low solubility of compound **4c** prevents the further characterization of this compound.

**Detection of primary radicals**. Laser-flash photolysis ( $\lambda = 355$  nm) of the compounds **4b** and **4d-f** (4 mM in toluene) yields TR-EPR (time-resolved electron paramagnetic resonance) spectra, which are compared to the TR-EPR spectrum of tetramesitoylgermane **1**. In all five spectra, the typical unresolved signal from the mesitoyl radical **M**· (g = 2.000) is present (see Figure 6 and *Supporting Information*). The TR-EPR spectrum of **4b** shows additional peaks, which can be attributed to the germyl radical featuring a CH<sub>2</sub> group adjacent to the Ge center (triplet (1 : 2 : 1), a = 0.53 mT, g = 2.003) as shown in Figure 6. This value is in good agreement with the hyperfine coupling constants observed for the related germyl radicals originating from **4a** (triplet, a = 0.44 mT) and bis(*p*-methoxybenzoyl)diethylgermane (BMDG, Ivocerin), which shows a quintet (two CH<sub>2</sub> groups, a = 0.5 mT).<sup>24</sup> Most of the spin density in the germyl radical **Ge(4b)**· is found at the Ge center, as DFT calculations show (see Figure S32 and the corresponding discussion in *Supporting Information*).



**Figure 6.** a) TR-EPR spectrum of **4b** (4 mM in toluene) in the time span of 500 to 1300 ns (black). Red: simulation of the spectrum. The black bars indicate the splitting due to the protons marked in red. b) Full time profile of the spectrum.

In case of **1** and **4d-f** with no protons adjacent to the germanium center, relatively narrow and unresolved peaks are expected for the germyl radicals. Accordingly, the intensive EPR signal detected upon photolysis of **1** and **4d-f** represents a superposition of the benzoyl and germyl radical.

Kinetics of the Addition to Double Bonds. Laser-flash photolysis<sup>196</sup> ( $\lambda = 355$  nm) was used for observing the short-lived germyl radicals and determining the kinetics of their addition to double bonds (of styrene and butyl acrylate) using a pseudo-first-order analysis. At first, the transient optical absorption spectra were acquired for **4b**, and **4d-f** (see *Supporting Information*). The spectra show absorption bands in the area around 350 nm and also between 400 and 500 nm. This latter absorption is characteristic for germyl radicals.<sup>24,190,197</sup> Absorptions of the mesitoyl radical are centered in the UV range and therefore do not interfere with the germyl radicals.<sup>198,199</sup>

Following an exponential fitting to the decay curves of the transient optical absorptions (at the maxima), the pseudo-first-order rate constants  $k_{exp}$  were obtained. The second-order addition rate constant  $k_{monomer}$  was then determined by using the following relation, where  $k_0$  is the rate constant for the decay in absence of monomer<sup>190,200</sup>:

$$k_{exp} = k_0 + k_{monomer} \cdot c_{monomer} \tag{1}$$

The linear fits are displayed in the *Supporting Information* and the obtained values for  $k_{monomer}$  are shown in a bar chart in Figure 7. The numerical values are listed in Table S2 (*Supporting Information*). For **1**, which serves as reference, the obtained value in this work (in toluene) is lower than the value in acetonitrile<sup>24</sup>. This is in agreement with observations made by Neshchadin et al.<sup>190</sup> who found that the addition rate for Et<sub>2</sub>BzGe• to butyl acrylate is slightly higher in acetonitrile than in toluene.



**Figure 7**. Bar graph of the second-order addition rate constants for the germyl radicals **Ge(1)**, **Ge(4b)** and **Ge(4d-f)** to the monomers styrene (green bars) and butyl acrylate (red bars) and their respective structures.

The rate constants for the addition of the germyl radicals to the electron-poor double bond of butyl acrylate decrease in the following order:  $Ge(4b) \approx Ge(4d) > Ge(4e) > Ge(1) > Ge(4f)$ . This is in agreement with observations made in a previous publication by our groups.<sup>24</sup> The more sterically congested the Ge center the lower is the reactivity toward double bonds (e.g., in Table S2 in the *Supporting Information*, compare Ge(1) bearing three mesitoyl groups with Ge(4a) featuring two mesitoyl groups and one ethyl group). Ge(4b) comprises an alkyl substituent (or bridge) at the Ge center (comparable to Ge(4a)) resulting in an increased reactivity compared to Ge(1). Replacing one of the mesitoyl groups with a *para*-dicarbonyl benzene bridge (Ge(4d)) also leads to a higher addition rate constant, since the bridge is sterically less demanding than a mesitoyl group. This effect is only slightly pronounced in Ge(4e), where the carbonyl groups in the bridge are in *meta* position to each other. The lowest rate is seen for Ge(4f), which is the heaviest and bulkiest germyl radical in this row.

Previous investigations<sup>24</sup> indicate that germyl radicals derived from mono- to tetraacylgermanes prefer electron-rich double bonds (e.g., higher rate constants for addition to methyl methacrylate compared to butyl acrylate). To inspect whether this trend is also evident for the oligoacylgermanes, we choose the electron-rich double bond of styrene as second reaction partner. Indeed, the addition rate constants increase for all investigated germyl radicals. In the case of **Ge(4d)**, a multiplication by the factor of 7 is observed, compared to the other germyl radicals, where the factor is between 3.5 and 4. The higher addition rate constant toward styrene suggests that the germyl radicals show electrophilic behavior – a feature which they share with phosphanoyl radicals derived from bis(acyl)phosphane oxide

photoinitiators.<sup>201</sup> Accordingly, their addition rate constants towards butyl acrylate are in the same order of magnitude as those of TPO and BAPO (see Table S2 in the *Supporting Information*).<sup>200</sup>

**Photobleaching and Quantum Yields.** To avoid colored polymers and reach high curing depths efficient photobleaching of the photoinitiator is desirable.<sup>24</sup> Solutions of compounds **1**, **4b**, **4d-f** and the well-characterized bisacylgermane BMDG (Ivocerin®) in a mixture of toluene and methyl methacrylate (MMA) were photolyzed with LEDs. The use of MMA and the additional deoxygenation of the samples (with argon) have the purpose of suppressing the formation of undesired (colored) photoproducts, which interfere with the UV-vis measurements.<sup>24</sup>

First, we photolyzed the solutions with an LED emitting at 385 nm (LED385, see Experimental Section for details), since all the studied compounds absorb strongly at this wavelength (see Figure 5). To ensure good comparability, the concentrations of the compounds were adjusted so that  $A_{385} \approx 0.7$ . The results (normalized absorbance as function of time) are shown in Figure 8a. All compounds show nearly identical time traces when irradiating with LED385, except for the *para*-substituted digermane **4d**, whose absorbance decays much slower than the absorbances of the other compounds, so that a slight yellow color is still visible after 600 s.

Since compounds **4d-f** feature absorbance peaks with considerable tailings up to 500 nm, we also photolyzed solutions of the investigated compounds with a LED emitting at about 470 nm (LED470; mimicking the longest wavelength emission of dental lamps, see Experimental Section for details).<sup>202</sup> The results are shown in Figure 8b – **4e** and **4f** bleach most efficiently, followed by BMDG and **4d**. **1** and **4b** do not show substantial absorbance at 470 nm, hence a slow decay is observed. The UV-vis spectra, which were acquired while irradiating the samples with the LEDs, are found in the *Supporting Information*.



**Figure 8**. Steady-state photolysis of BMDG and **1**, **4b**, **4d-f** with a) LED385 , b) LED470 in toluene/MMA (1/1 v/v). The absorbance traces are normalized to the initial absorptions at the observation wavelengths (maxima of  $n/\sigma - \pi^*$  transitions; BMDG: 412.0 nm; **1**: 378.0 nm, **4b**: 384.0 nm, **4d**: 379.5 nm, **4e**: 380.5 nm, **4f**: 381.0 nm).

From the data obtained in the photolysis experiments with LED385, the decomposition quantum yields were determined following the procedure by Stadler et al.<sup>203</sup> For each compound, the absorbance trace obtained during irradiation with LED385 was converted to a concentration trace using the extinction coefficients given in Table 2 and then fitted with a mono-exponential function ( $y = y_0 + Ae^{-k_{\text{fit}}x}$ ) as shown in the *Supporting Information*. The product of the time constant  $k_{\text{fit}}$  (in s<sup>-1</sup>) and the initial concentration of the compound  $c_0$  (in mol L<sup>-1</sup>) is then divided by the product of the photon flux  $I_0$  (LED385 operated at 45 mA;  $I_0 = 1.7 \cdot 10^{-5}$  mol L<sup>-1</sup> s<sup>-1</sup>) and the factor  $(1 - 10^{-A'_i})$ , where  $A'_i$  is the absorbance at the peak wavelength of the LED (387 nm, see experimental section), to obtain the quantum yield<sup>203</sup>:

$$\phi = \frac{k_{\rm fit}c_0}{I_0(1-10^{-A_i'})}$$
(2)

The calculated quantum yields are shown in Table 2. For BMDG, the obtained quantum yield is almost identical to the value in acetonitrile/MMA.<sup>24</sup> The second highest quantum yield is found for **1**, which is

well in line with values found for other tetraacylgermane compounds ( $\phi = 0.34 - 0.44^{24}$ ; in acetonitrile/MMA). For the oligoacylgermanes **4b** and **4d-f**, the determined quantum yields range from 0.08 (**4d**) to 0.27 (**4b**). Compared to BMDG, the quantum yields of the oligoacylgermanes are comparably smaller; however, the high extinction coefficients of the  $n/\sigma$ - $\pi$ \* transitions compensate for the low quantum yields giving rise to an effective photobleaching.

**Table 2.** Wavelength of  $n/\sigma - \pi^*$  absorption maxima and extinction coefficients at  $\lambda_{max,exp}$  (in toluene/MMA 1/1 (v/v)), and determined quantum yields for BMDG, **1**, **4b** and **4d-f**.

	$\lambda_{max,exp} [nm]$	$\varepsilon$ [M <sup>-1</sup> cm <sup>-1</sup> ] at $\lambda_{max,exp}$	$\Phi$ (385 nm)
			$0.86\pm0.02$
BMDG	412.0	1001	$(0.83\pm0.01$
			<sup>[a]</sup> )
1	378.0	1839	$0.38\pm0.01$
4b	384.0	2280	$0.27\pm0.01$
4d	379.5	3879	$0.08\pm0.01$
<b>4e</b>	380.5	3209	$0.23\pm0.01$
<b>4</b> f	381.0	5035	$0.13\pm0.01$

<sup>[a]</sup> value in acetonitrile/MMA 1/1 (v/v) from ref.<sup>24</sup>

**Photo-DSC Measurements.** Photo-DSC is a versatile method for the fast and accurate evaluation of the performance of PIs in polymerizable resins. Various characteristic kinetic parameters can be obtained with one single measurement including the time to reach the maximum heat flow ( $t_{max}$ ), maximum rate of polymerization ( $R_{p,max}$ ), and time to reach 95% of final conversion ( $t_{95\%}$ ). Furthermore, the double bond conversion (DBC) can be calculated from the overall reaction enthalpy  $\Delta H$  (peak area), providing that the theoretical heat of polymerization ( $\Delta H_{0,p}$ ) is known.

Photo-DSC has been chosen to evaluate the performance of the synthesized photoinitiators in 1,6-hexanediol diacrylate (HDDA) as model monomer system. The previously reported tetraacylgermane **1** was investigated as reference compound.<sup>21</sup>

The PI performance was compared at equal molar PI concentrations (0.30 mol%) as well as equal amounts of photo-cleavable groups (0.15 mol% for 1; 0.2 mol% for 4a, 0.1 mol% for 4b; 0.075 mol% for 4d,e; 0.05 mol% for 4f) (see Figure 9). All investigated PIs show nearly identical behavior for both measurement series. This indicates that the use of lower molar concentrations is possible without negative effects on the observed photoreactivity. Only at very low concentrations, we see a reduction in conversion speed for 1, 4a and 4b as shown in Table S4. 4d exhibits a slightly lower DBC in both

measurement series, which is consistent with the reduced photobleaching ability and low quantum yield (see Figure 8a and Table 2).



**Figure 9.** Photo-DSC (left) and conversion plots (right) for the photopolymerization of HDDA with 0.3 mol% PI (top) and PI concentration with equimolar amounts of photo-cleavable groups (bottom).

#### Conclusion

In summary, we investigated the single electron transfer reactions of tetraacylgermanes induced by potassium or KOtBu. We detected the formation of radicals by EPR spectroscopy, which act as intermediates for the formation of a stable triacylgermenolate **2**. The one-pot synthetic protocol gives **2** at an excellent yield, as confirmed by NMR spectroscopy, UV-vis measurements and X-ray crystallography. Furthermore, we could determine the crystal structure of **2**, which represents the first undistorted structure of a heavier group 14 enolate. The efficiency of **2** to serve as new germanium centered precursor system is demonstrated by the reactions with a variety of electrophiles. In all cases, the salt metathesis reaction gave rise to novel acylgermanes in excellent yields. These new acylgermanes were examined for the application as high performance photoinitiators. In comparison to **1**, **4b-f** show a significant bathochromic shift of the absorption edge. Furthermore, **4b-f** also outperform **1** in terms of extinctions coefficients, resulting in a possible lower consumption of these high priced photoinitiators with the same performance. The data obtained from TR-EPR spectroscopy clearly show that the newly

synthesized oligoacylgermanes **4b** and **4d-f** undergo bond cleavage upon irradiation with UV light ( $\lambda = 355$  nm) forming mesitoyl and germyl radicals. The germyl radicals **Ge(4b)**, **Ge(4d)**, and **Ge(4e)**, show higher rate constants for the addition to butyl acrylate when compared to the "lighter relative" **Ge(1)**. When using styrene with its electron-rich double bond as reaction partner, the rate constants are increased even more. Especially, **Ge(4d)**, as well as **Ge(4b)**, are more reactive towards styrene than **Ge(1)**. Photolysis experiments show that all compounds except **4d**, which is characterized by a very small quantum yield of decomposition ( $\phi = 0.08$ ), bleach efficiently when irradiated with UV light from an LED (emission maximum 387 nm). Due to the substantial absorption around 500 nm, **4e** and **4f** show considerable photobleaching upon illumination with an LED emitting at about 470 nm. The reaction rates and DBC for **4a**, **4b**, **4e** and **4f** are comparable to **1**. Notably, **4e** and **4f** show consistently high photoreactivity even at very low PI concentrations. On the basis of the photochemical characterization of the compounds, we consider **4e** and **4f** as most promising candidates for the use as photoinitiators. Further studies to probe the scope of this new synthetic pathway are currently in progress. In addition, we are currently testing these new type I photoinitiators for visible light induced photopolymerization because they have the substantial advantage of bleaching yielding colorless products.

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## Notes

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## 1.3.3. Synthesis of Mixed Functionalized Tetraacylgermanes

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#### Abstract

Tetraacylgermanes are known as highly efficient photoinitiators. Herein, the synthesis of mixed tetraacylgermanes **4a-c** and **6a-e** with a non-symmetric substitution pattern is presented. Germenolates are crucial intermediates of these new synthetic protocols. The synthesized compounds show increased solubility compared with symmetrically substituted tetraacylgermanes **1a-d**. Moreover, these mixed derivatives reveal broadened  $n-\pi^*$  absorption bands, which enhance their photoactivity. Higher absorption of these compounds at wavelengths above 450 nm causes efficient photobleaching when using an LED emitting at



470 nm. The quantum yields are in the range of 0.15 - 0.57, depending on the nature of the aroyl substituents. On the basis of these properties, mixed functionalized tetraacylgermanes serve as ideal photoinitiators in various applications, especially in those requiring high penetration depth. The synthesized compounds were characterized by elemental analysis, IR spectroscopy, NMR and CIDNP spectroscopy, UV/Vis spectroscopy, photolysis experiments and X-ray crystallography. The CIDNP data suggest that the germyl radicals generated from the new tetraacylgermanes preferentially add to the tail of the monomer butyl acrylate. In case of **6a-e** only the mesitoyl groups are cleaved off, whereas for **4a-c** both the mesitoyl and the aroyl group are subject to  $\alpha$ -cleavage.

## Introduction

Nowadays, photoinitiators (PIs)<sup>204</sup> are of high interest in different industrial application processes, such as 3D printing,<sup>205,206</sup> coatings,<sup>207</sup> and in the medical sector for artificial tissues or dental filler materials.<sup>208,209</sup> The design and the implementation of such PIs are very challenging. Requirements<sup>210</sup> such as low toxicity, sustainability, environmental compatibility, low costs, and the fast bleaching are crucial. Photoinitiators can be classified as type I, type II or multicomponent PIs.<sup>211</sup>

Recently, germanium-based photoinitiators have attracted considerable attention due to their low toxicity and bathochromic shift in their longest wavelength absorption. Thus, they are promising alternatives to the currently widely used phosphorous-based photoinitiators.<sup>212</sup> However, the low

abundance of germanium in the earth's crust results in higher Di(4costs. methoxybenzoyl)diethylgermane (Ivocerin), a commercially available photoinitiator based on germanium, is synthesized via a multi steps pathway.<sup>213</sup> This complex procedure, which relies on a Corey-Seebach reaction followed by column chromatography, results in the high costs of this PI. Another disadvantage is the inefficient curing depth at wavelengths above 500 nm.<sup>18</sup> We have introduced a new one-pot synthetic protocol providing tetraacylgermanes  $Ge[C(O)R]_4$  (R = aryl) in high yields.<sup>21</sup> Furthermore, we found that tetraacylgermanes are more efficient photoinitiators than Ivocerin. Due to the presence of four RC=O chromophores, tetraacylgermanes show increased band intensities, which lead to a more efficient light absorption. Different substituents on the aromatic ring allow tuning of the properties and shifting the absorption band to higher wavelengths, which is ideal for medical applications. However, a huge drawback of symmetrical tetraacylgermanes are their high melting points, which are responsible for the low solubility, limiting the field of applications.

Herein, we introduce two one-pot synthetical pathways towards mixed functionalized acylgermanes. The introduction of different substituents on the germanium leads to increased solubility compared to symmetrical tetraacylgermanes **1a-d** (Scheme 1). The broad absorption bands of these compounds promises a wide variety of applications.



Scheme 1. Chemical structures of symmetrical tetraacylgermanes 1a-d.

## **Results and Discussion**

#### **Introduction of Mixed Functionality**

**Method A:** The entry into this chemistry is provided by tris(trimethylsilyl)acylgermane **2**, conveniently obtainable by reaction of tetrakis(trimethylsilyl)germane with equimolar amounts of KOtBu and acid chloride. Subsequently, **2** was reacted with equimolar amounts of KOtBu generating the crucial germenolate intermediate **3**. To this germenolate a threefold excess of the respective acid fluoride was added in situ to yield the desired nonsymmetric products **4a-c** in good yields. The reaction pathway is shown in Scheme 2. So far, this method turned out to be restricted to electron donating groups (EDGs), while the introduction of electron withdrawing groups (EWGs) was not possible. Due to the introduction of mixed functionalities, the solubility increases drastically, but isolation of a clean product is more complex, and hence yields are reduced.



Scheme 2. Reaction scheme of method A. Synthesis of mixed functionalized tetraacylgermanes 4a-c.

**Method B:** The starting material for method B, depicted (Scheme 3) is tetrakis(trimethylsilyl)germane. By adding equimolar amounts of KOtBu and subsequently 3.1 equiv of mesitoyl fluoride, the stable germenolate intermediate **5** is formed. This reaction could be accomplished via different synthetic routes,<sup>214</sup> but the direct method with KOtBu and mesitoyl fluoride used for this work generally gives higher yields. After the addition of KOtBu, the reaction solution turns yellow, which indicated consumption of KOtBu and the formation of the potassium germanide (Scheme 3). On adding a threefold excess of mesitoyl fluoride the solution turns reddish, which marks the formation of **5**. To the formed germenolate the corresponding acid chlorides were added in situ, and the desired products **6a-d** were isolated in good to excellent yields. A huge advantage of this method is that EWGs can also be introduced. Consequently, this leads to a significant bathochromic shift and tailing of the longest wavelength absorption.





## **UV/Vis Absorption Spectra**

The broad absorption band of each compound centered at about 390 nm (see Figure 1), attributed to the  $n-\pi^*$  transition, is responsible for the photoinduced cleavage of the Ge-C bond. Importantly, these bands extend to >450 nm and show a higher absorbance than the commercial PI, Ivocerin. Mesitoyltri(*o*-toluoyl)germane (**4a**) shows the highest absorption at this wavelength (tailing up to 475 nm) and could therefore play an important role in the medical industry. With **6b** a tailing up to even 525 nm is obtained.



**Figure 1.** Absorption spectrum of synthesized mixed functionalized tetraacylgermanes compared with the commercially available Ivocerin with a concentration of  $1 \times 10^{-3}$  M in acetonitrile.



**Figure 2.** Comparison of the mixed functionalized tetraacylgermanes to the symmetrical tetraacylgermanes. a) **4a** compared to tetramesitoylgermane and tetra(o-toluoyl)germane. b) **4b** compared to tetramesitoylgermane and tetra(*p*-toluoyl)germane. c) **4c** compared to tetramesitoylgermane and tetrabenzoylgermane. d) Mixed functionalized tetraacylgermanes, synthesized via method B, compared to tetramesitoylgermane (**1d**).

As shown in Figure 2a-c, the presence of one mesitoyl group leads to a hypsochromic shift on the one hand. On the other hand, more importantly, the extinction coefficient is increased, which leads to higher efficiency in light absorption. As depicted in Figure 2a-c, the absorption bands of the mixed-functionalized tetraacylgermanes are broader than those of the symmetrical ones. Therefore, excitation can be accomplished in a wider wavelength range, even at slightly higher wavelengths relative to the symmetrical acylgermanes. The only exception is mesitoyltribenzoylgermane (**4c**) (see Figure 2c). Tetraacylgermanes with EWGs show extended tailing of the absorption above 500 nm (see Figure 2d). In general, the mixed derivatives show higher extinction coefficients compared with the symmetrical compounds.

#### **Photobleaching Behavior**

In applications, such as dental restoration, efficient photobleaching is pivotal to avoid the formation of colored polymers. Furthermore, the curing depth also strongly depends on the absorption behavior of the formed polymer: the more effective the discoloration of the Pl/monomer reactive mixture, the greater the curing depth.<sup>18,21,24,73,203,215,216</sup> Hence, we investigated the photobleaching behavior of the mixed acylgermanes and compared it to already published data.<sup>214</sup> Degassed solutions of **4a-c** and **6a-e** (A<sub>385</sub>  $\approx$  0.6 to ensure comparability) in toluene/methyl methacrylate (MMA) (1/1 v/v) were irradiated with two different low power LEDs emitting at wavelengths of 385 or 470 nm (LED385 and LED470; for a detailed description of the LEDs, see Experimental Section and Figure S23 in the *Supporting Information*), which are typical for dental lamps.<sup>217</sup> The normalized absorbance curves as function of time are depicted in Figure 3. On irradiation with LED 385 (see Figure S25 in the *Supporting Informations* for UV/Vis spectra during illumination), most of the compounds are bleached efficiently in presence of MMA, and only **6b-d** show slow decay. On irradiation with LED 470 (see Figure S26 in the *Supporting Information* for UV/Vis spectra during illumination), compounds **4a-c** and **6a-e** are bleached more efficiently than tetramesitoylgermane (**1d**, red line in Figure 3b) due to their higher absorbance at 470 nm (see Figure 1).



**Figure 3.** Steady-state photolysis of Ivocerin, **1d**, **4a**-**c** and **6a**-**e** with **a**) LED385, **b**) LED470 in toluene/MMA (1/1 v/v). The absorbance traces are normalized to the initial absorptions at the observation wavelengths (maxima of  $n/\sigma-\pi^*$  transitions;

Ivocerin: 412.0 nm; 1d: 378.0 nm, 4a: 397.0 nm, 4b: 400.0 nm, 4c: 400.0 nm, 6a: 380.0 nm, 6b: 379.0 nm, 6c: 379.5 nm, 6d: 378.0 nm, 6e: 373.0 nm). Data for Ivocerin and 1d were taken from the literature.<sup>214</sup>

Interestingly, the absorbance for **6c** initially increases and then slowly decays (orange curves in Figure 3). A shift of the absorption maximum from 379.5 nm for **6c** to 382 nm is also observable (see Figure S24 in the *Supporting Information*). These observations point to the formation of a colored photoproduct. Following the procedure by Stadler et al.,<sup>203</sup> we determined the quantum yield of decomposition for the mixed acylgermanes **4a-c** and **6a-e**. For **6e**, which is bleached most efficiently on irradiation with LED385, the highest quantum yield ( $\phi = 0.57$ ) was measured, followed by **4a** ( $\phi = 0.52$ ). These values are considerably higher than the values for symmetrical tetraacylgermanes (0.34–0.44) found in a previous study.<sup>[14]</sup> Compounds **6b** and **6d**, both featuring an EWG (methyl ester and nitrile, respectively) at the *para* position of the second aroyl substituent, show the lowest quantum yields in the series of compounds.

**Table 1.** Wavelength of  $n/\sigma - \pi^*$  absorption maxima and extinction coefficients (in toluene/MMA 1/1 (v/v)) and determined quantum yields.

	$\lambda_{max,exp}$ [nm]	$\varepsilon$ [M <sup>-1</sup> cm <sup>-1</sup> ] at $\lambda_{max,exp}$	$\Phi$ (385 mm)
Ivocerin <sup>[a]</sup>	412.0	1001	$0.86\pm0.02$
<b>1d</b> <sup>[a]</sup>	378.0	1839	$0.38\pm0.01$
<b>4</b> a	397.0	1078	$0.52\pm0.01$
<b>4</b> b	400.0	1323	$0.48\pm0.01$
<b>4</b> c	400.0	1363	$0.42\pm0.01$
6a	380.0	1766	$0.41\pm0.01$
6b	379.0	1675	$0.24\pm0.01$
6c	379.5	1656	[b]
6d	378.0	1865	$0.15\pm0.01$
6e	373.0 <sup>[a]</sup>	2091	$0.57\pm0.01$

[a] shoulder, [b] not determinable

#### **CIDNP Studies**

To elucidate the radical reaction pathways on initiation, the title compounds were investigated by chemically induced dynamic nuclear polarization (CIDNP), an NMR-based technique, that allows detection of short-lived intermediates formed from photoinitiators. A remarkable feature of CIDNP NMR spectra of photoinitiators containing aroyl groups is the detection of aldehydes as products of the

benzoyl-type primary radicals in the presence of monomers.<sup>21,24,190,218,219</sup> Therefore, we employed this technique to determine, which of the aroyl groups are cleaved off preferentially upon irradiation with UV light ( $\lambda = 355$  nm). The CIDNP spectra of solutions of **1a**, **1c**, **1d**, **4a-c** and **6a-e** in toluene-d<sub>8</sub> in presence of the monomer butyl acrylate (BA) were acquired. For the tri(mesitoyl)aroylgermanes (**6a-e**) and tetramesitoylgermane **1d**, the same aldehyde signal was evident, which is assigned to the mesitaldehyde (**MH**,  $\delta = 10.34$  ppm),<sup>24</sup> as shown in Figure 4a for **6e**.

However, this is not the only information that can be extracted from the CIDNP spectra. Furthermore, on the basis of the CIDNP data, the mechanism of the radical addition can be elucidated. The germyl radical formed on cleavage can, in principle, attack both vinyl positions in butyl acrylate ( $\alpha$  or  $\beta$  position) to form two regioisomers **R1** and **R2** (see Figure S38 in the Supporting Information). In a further step, both isomers recombine with a mesitoyl radical to form P1 and P2. In the CIDNP spectrum of 6e (Figure 4a), the signals centered at 4.6 ppm (enclosed in the red rectangle) can be interpreted as a doublet of doublets with J = 7.2 and 8.8 Hz. These coupling constants are also found in the multiplet from 2.29– 2.55 ppm (blue rectangle), which, in fact, consists of two doublets of doublets with J = 13.8 Hz. Such a coupling pattern is typical for a methylene group adjacent to a chiral center. As the difference in chemical shift (ca. 30 Hz) for the methylene protons is in the range of the geminal coupling constant  $(^{2}J$ = 13.8 Hz), a second-order effect ("roof effect") in the spectrum is evident.<sup>220</sup> For both regioisomers **P1** and P2, the same coupling pattern is expected, however, on the basis of the chemical shift of the CH signal (4.6 ppm), the proton can be assigned to the  $\alpha$ -position of two carbonyl groups in **P1** (see Figure S39 in the Supporting Information, see Figure 4a for structure of Ge(6a)-BA-M). This regioisomers, formed by attack at the  $\beta$  position, was also postulated in previous publications by us.<sup>21,24</sup> These coupling patterns can also be found in the CIDNP spectra of 6a-d, 1a and 1c; only for 1d, it is not observable (see Table 2).

In case of the tri(aroyl)mesitoylgermanes (4a-c), two aldehyde signals are observable [MH and *o*-tolualdehyde (*o*-TH) for 4a; MH and *p*-tolualdehyde *p*-TH for 4b; MH and benzaldehyde BH for 4c] in the corresponding CIDNP spectra (see Figures S31 and S32 in the *Supporting Information* and Figure 4b) and this indicates that the corresponding benzoyl-type radicals are formed as intermediates. Moreover, the CIDNP spectra of 4a-c show more than one signal in the region around 4.5 ppm (CH group) and in addition, the multiplet around 2.5 ppm (methylene protons) becomes more complicated, as shown for 4c in Figure 4b. This means that different addition products are formed. The signal enlarged in the red rectangle in Figure 4b can be interpreted as dd (J = 7.4 and 8.5 Hz) and for the signal at 5.05 ppm (green rectangle), 6.8 and 8.9 Hz are obtained as coupling constants. With these data in hand, the multiplet enlarged in the blue rectangle can be deconstructed to four dds, as indicated by the colored circles. As the chemical shift and the coupling constants found for the dd at 5.05 ppm are almost identical to the values obtained for B<sub>3</sub>Ge-BA-B formed from 1c (see Table 2), we expect a similar product (B<sub>2</sub>MGe-BA-B), which features a mesitoyl group (M) instead of a benzoyl group (B) at the Ge center.

The stronger signal at 4.60 ppm is attributed to  $B_3$ GeBA-M. Further small signals in vicinity to the CH and methylene proton signals suggest, that additional (similar) photoproducts (e.g.  $B_2$ MGe-BA-M) are formed. These products clearly mirror the reactivity of the primarily formed germyl radicals.

In case of **4b**, three CH signals can be clearly identified (see Table 2, Figure S32 in the *Supporting Information*), however, only one geminal coupling constant can be extracted from the multiplet at 2.6 ppm. Nevertheless, the dd displaying the highest chemical shift (5.09-5.17 ppm) might be attributed to  $(p-T)_2MGe-BA-(p-T)$ . If a mesitoyl group is located adjacent to the CH group, a smaller chemical shift value will be expected (in accordance with the CH shifts observed for **1d**, **6a-e**). For **4a**, four signals of almost the same intensity are detected in the region typical for the CH proton (red rectangle in Figure S31 of the *Supporting Information*). One of the signals coincides with the signal of the CH proton for the photoproduct of **1a**; hence the formation of a similar photoproduct is expected. Possible addition products are shown in Figure S31.



**Figure 4.** <sup>1</sup>H NMR and CIDNP spectra (excitation at  $\lambda = 355$  nm, ca. 50 mJ per pulse) of a) **6e** in the presence of butyl acrylate (5.8 mM **6e**, 50 mM BA in toluene-d<sub>8</sub>) and b) **4c** in the presence of butyl acrylate (7.6 mM **4c**, 50 mM BA in toluene-d<sub>8</sub>).

Finally, on the basis of the CIDNP data, the question whether the two different aroyl radicals (observed for **4a-c**) are cleaved off from different acylgermane molecules or from the same molecule (i.e. two consecutive cleavages) is answered. In a previous study,<sup>24</sup> it was found that the chemical shift of the methylene protons adjacent to the Ge center is susceptible to the nature of the other substituents at the Ge atom. If alkyl groups are present, a shift to higher field is expected. As the multiplets for **4a-c** are found in the same region as those for **1c**, **1d** and **6a-e** (or even shifted downfield, see Figure S37 of the Supporting Information for comparison), consecutive cleavage (and addition) at the same acylgermane molecule seems unlikely on the timescale of the CIDNP NMR experiment.

compound	$\delta(\mathrm{CH}_2)$ / ppm	$\delta(\mathrm{CH})$ / ppm <sup>[a]</sup>	<i>³J /</i> Hz	$^{2}J/\mathrm{Hz}$
1a	2.34-2.58	4.80-4.88 <sup>[b]</sup>	8.0	13.5
1c	2.44-2.67	5.01-5.08	7.0, 9.0	13.5
1d	2.29-2.33	4.28-4.35	6.5, 8.0	[d]
		4.80-4.88 <sup>[b]</sup>	8.0 <sup>[c]</sup>	[d]
	2 20 2 55	4.64-4.72 <sup>[b]</sup>	8.0 <sup>[c]</sup>	[d]
4a	2.30-2.55	4.48-4.56 <sup>[b]</sup>	8.0 <sup>[c]</sup>	[d]
		4.41-4.49 <sup>[b]</sup>	8.0 <sup>[c]</sup>	[d]
		4.65-4.73	7.0, 9.0 <sup>[c]</sup>	13.6
<b>4</b> b	2.39-2.79	5.09-5.17	7.0, 8.8 <sup>[c]</sup>	[d]
		4.45-4.53	7.0, 8.7 <sup>[c]</sup>	[d]
		4.56-4.64		
4.5	2.42-2.73	5.01-5.09	7.4, 8.5 <sup>[c]</sup>	13.6
40		4.42-4.50	6.8, 8.9 <sup>[c]</sup>	13.4
		4.76-4.80		
6a	2.18-2.46	4.40-4.48	6.5, 9.3	14.0
6b	2.21-2.48	4.42-4.50	6.5, 9.3	13.7
6c	2.23-2.43	4.27-4.35	7.6, 8.5	14.1
6d	2.17-2.42	4.32-4.40	7.0, 9.0	14.0
6e	2.29-2.55	4.55-4.63	7.2, 8.8	13.8

**Table 2.** Chemical shifts in ppm and coupling constants in Hz for the addition products formed from compounds **1a**, **1c**, **1d**, **4a-c** and **6a-e** observed in the CIDNP spectra.

[a] Sorted from most intense to weakest signals (for **4a-c**), [b] Triplet instead of doublet of doublets, [c] Assigned to the respective signal in previous column, [d] Not determinable

## Solubility

Low solubility is a huge drawback of symmetrical tetraacylgermanes. By introducing a mixed substitution pattern at the germanium atom of tetraacylgermanes an increase in solubility was observed (see Table 3). For this reason, as well as the broad  $n-\pi^*$  absorption bands, a huge variety of applications becomes feasible.

**Table 3.** Compared melting points of symmetrical to mixed functionalized tetraacylgermanes synthesized. Compounds synthesized with method B are compared to the tetramesitoylgermane **1d**.

symmetrical	m <sub>P</sub> [°C]	А	m <sub>P</sub> [°C]	В	m <sub>P</sub> [°C]
1a	123-125 <sup>[a]</sup>	4a	92-96	6a	148-150
1b	decomposition >230 <sup>[a]</sup>	4b	95-100	6b	106-108
1c	82.5-83 <sup>[b]</sup>	4c	148-150	6c	190-192
1d	198-199 <sup>[b]</sup>			6d	208-210
				6e	168-170

[a] Ref <sup>215</sup>. [b] Ref <sup>21</sup>

Solubility tests were carried out with methyl methacrylate (MMA), butyl acrylate (BA) and acetonitrile, and the amounts of xompounds dissolved in 100  $\mu$ L of solvent were analyzed for method A (Table 4) and B (Table 5). The results were compared to the symmetrical tetramesitoylgermane **1d**, the data of which can also be found in Table 4.

The mixed functionalized tetraacylgermanes synthesized by method A show exceptionally high solubility, especially **4a**. Switching the methyl group to the *para* position on the benzoyl group leads to a lower solubility compared with the compound with the methyl group in *ortho* position. The compounds synthesized according to method B show a significant decrease in solubility, compared to the derivatives of method A. This can be attributed to the number of mesitoyl groups in the molecule – the higher the number of mesitoyl substituents the lower the solubility and *vice versa*. Moreover, the solubility of compound **6b** increases by 1500 % (replacement of a mesitoyl group with a benzoyl group bearing an ester moiety in *para* position). Even in acetonitrile, which is a non-suitable solvent for the other compounds, a good result could be achieved. We suggest that the reason for this behavior is the presence of the polar ester moiety.

	1d [mg]	4a [mg]	4b [mg]	4c [mg]
BA	9.70	128	23.3	68.7
MMA	4.80	56.7	18.9	69.9
acetonitrile	0.40	0.80	1.70	23.5

Table 4. Amount of compound (synthesized with method A) dissolved in 100  $\mu$ L of the respective solvent compared with 1d.

Table 5. Amount of compound (synthesized with method B) dissolved in 100  $\mu$ L of the respective solvent.

	6a [mg]	6b [mg]	6c [mg]	6d [mg]	6e [mg]
BA	13.2	77.5	1.20	7.20	4.10
MMA	2.60	114	3.40	1.40	2.90
acetonitrile	1.70	5.30	0.10	0.30	0.80

#### NMR Spectroscopy

NMR spectra and detailed characterization for **4a-c** and **6a-e** are provided in the *Experimental Section* and the *Supporting Information*. All derivatives show very similar <sup>13</sup>C chemical shifts for the carbonyl C atom between 209.2 and 233.4 ppm, which is characteristic for carbonyl groups directly linked to a germanium atom. The presence of two different carbonyl groups characteristic for the unsymmetrical tetraacylgermanes is confirmed by the occurrence of two peaks in this region.

## X-Ray Crystallography

Crystals suitable for single-crystal XRD were obtained for compounds **4a-c** and **6a-e**. As two representative examples, the molecular structures of **4a** (method A) and **6b** (method B) are shown in Figures 5 and 6. All other structures can be found in the *Supporting Information*. The torsion angle between the C=O bond and the aromatic plane of the mesitoyl group is much larger than of any other aroyl substituent (Table 6). The evaluated data of the bond lengths are slightly elongated compared to the average Ge-C bond (1.97 Å)<sup>221</sup> and the average C=O bond (1.19 Å).<sup>222</sup> The obtained crystallographic data of the mixed derivatives are similar to those of the symmetrical compounds.



**Figure 5.** ORTEP representation of **4a**. Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. The torsion angle (mean value) between the C=O group and the aromatic ring plane of the *o*-toluoyl group is  $27.76^{\circ}$ . The torsion angle between the C=O group and the aromatic ring plane of the mesitoyl group is  $65.40^{\circ}$ .



**Figure 6.** ORTEP representation of **6b**. Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. The torsion angle between the C=O group and the aromatic ring plane of the ester group is  $21.41^{\circ}$ . The torsion angle (mean value) between the C=O group and the aromatic ring plane of the mesitoyl group is  $56.23^{\circ}$ .

**Table 6.** Mean bond lengths d [Å] and torsion angles between the C=O group and the aromatic ring plane [°] of compounds **4a-c** and **6a-e.**  $R^1$  represents the mesitoyl substituent,  $R^2$  the respective acyl group of each compound.

	d <sub>Ge-C</sub>	$d_{C=O}\left(R^{1}\right)$	$d_{C=O}\left(R^2\right)$	$\angle O = C - R^1$	$\angle O = C - R^2$
4a	2.039	1.209	1.225	65.40	27.76
<b>4</b> b	2.025	1.219	1.215	48.36	8.71
4c	2.028	1.214	1.216	83.20	8.24
6a	2.034	1.213	1.217	66.88	18.79
6b	2.031	1.213	1.218	56.23	21.41
6c	2.039	1.211	1.212	54.66	29.72
6d	2.033	1.214	1.217	62.21	13.89
6e	2.030	1.212	1.219	60.10	4.16

#### Conclusion

We were able to synthesize a variety of mixed-functionalized tetraacylgermanes *via* two different synthetic routes. Purification by column chromatography is crucial for method A, which reduces the yields of that pathway. Therefore, method B was introduced, with which even EWGs can be implemented. The new mixed-functionalized tetraacylgermanes **4a-c** and **6a-e** show lower melting points than symmetrical tetraacylgermanes. The lower melting points result in improved solubility, which was also confirmed by solubility tests in BA, MMA and acetonitrile. The introduction of mixed functionality into tetraacylgermanes leads to a broadening of their absorption band with an increased absorption maximum. Curing of formulations containing Ivocerin is problematic with light above 450 nm, but the synthesized mixed tetraacylgermanes show high absorption even in this range. Remarkably, tailing of the absorption spectrum up to 525 nm was observed.

Photobleaching experiments showed that all compounds except **6b-d** are bleached efficiently on illumination with a 385 nm LED. Due to the higher absorption at wavelengths above 450 nm, solutions of **4a-c**, **6a** and **6e** are bleached significantly faster than Ivocerin and the symmetrical tetraacylgermane **1d** when irradiated with a 470 nm LED. This opens up the possibility of efficient curing with visible-light sources, which is of high importance for medical applications. The highest quantum yield in the series of compounds was found for **6e** ( $\phi = 0.57$ ).

The reaction pathways of the primary radicals (germyl and benzoyl) were investigated by CIDNP NMR spectroscopy. For the trimesitoylaroylgermanes **6a-e** the same aldehyde signal as for the tetramesitoylgermane (**1d**) was detected, which indicates that only the mesitoyl group is cleaved off in **6a-e**. The triaroylmesitoylgermanes **4a-c** feature two aldehyde signals in their CIDNP spectra suggesting that the  $\alpha$ -cleavage can happen at both the aroyl group (*o*-toluoyl in **4a**, *p*-toluoyl in **4b** and benzoyl in **4c**) and the mesitoyl group. On the basis of the coupling patterns seen for the signals in the regions of 2.2–2.8 and 4.3–5.2 ppm in the CIDNP spectra, which are observed for all compounds (except for **1d**), regioselective addition of the germyl radical to the  $\beta$  position of the monomer butyl acrylate, in accordance with previous observations,<sup>21,24</sup> can be suggested. Further studies to probe the scope of these initiators are currently in progress.

#### Acknowledgements

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Keywords: acylgermanes • photochemistry • photoinitiator • solubility • tetraacylgermanes

## 1.3.4. Synthesis, LIFDI Mass Spectrometry and Reactivity of Triacyl-Germenolates

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#### Abstract

The synthesis of stable triacylgermenolates **3a,b** was achieved by using a multiple silyl abstraction methodology. The formation of these new germenolates was confirmed by NMR spectroscopy and UV–Vis measurements. Moreover, for



the triacylgermenolates 2 and 3a LIFDI mass spectrometry was used to characterize these new compounds. Germenolates 3a,b serve as a starting point for a new triaacylgermane 4a and two octaacyldigermanes 4c,d. The formation of these acylgermanes was confirmed by NMR spectroscopy, X-ray crystallography, UV–Vis measurements and mass spectrometry. The UV–Vis absorption spectra of 4c,d show considerably increased band intensities due to the presence of eight chromophores.

#### Introduction

Based on their application as photoinitiators (PIs) acylgermanes were intensively studied in the last two decades, which boosted the number of available compounds significantly.<sup>18,73,213,223</sup> Our group also contributed to this research topic and introduced a new one-pot synthetic protocol providing tetraacylgermanes  $Ge[C(O)R]_4$  (R = aryl) in high yields.<sup>21,215</sup>

Recently, we investigated the redox chemistry of acylgermanes and discovered that upon reduction (i.e. alkali metals or KO'Bu) under inert conditions, the corresponding acylgermane radical anions are formed (Scheme 1), which were characterized by EPR spectroscopy in combination with DFT calculations.<sup>192</sup> While monoacylgermanes display similar reduction potentials as benzaldehyde derivatives, the di- and tetraacylgermanes can be reduced at less negative potentials due to the presence of more electron-withdrawing acyl groups.



Scheme 1. Alkali metal reduction of acylgermanes to the corresponding radical anions.

Based on the accessibility of acylgermanium based radical anions, we could also show that the reduction of tetraacylgermane **1** provides a synthetically attractive reaction pathway towards triacylgermenolate **2** (Scheme 2 SET-Approach).<sup>81,82</sup> We could furthermore establish a direct approach towards triacylgermenolate **2**, which circumvents the usage of alkali metals (Scheme 2 Direct Approach). The efficiency of **2** to serve as new germanium centered precursor system was demonstrated by the reactions with a variety of electrophiles. In all cases the salt metathesis reaction gave rise to novel acylgermanes in excellent yields.

SET-Approach:



Scheme 2. Synthetic pathways towards triacylgermenolate 2.

The aim of this study was to introduce new aromatic groups at the carbonyl moiety in order to determine the group tolerance of this methodology. Moreover, we investigated the isolated products with Liquid Injection Field Desorption Ionization (LIFDI) mass spectrometry (MS) and present the first successful characterization of negatively charged germenolates by LIFDI(-).

#### **Results and Discussion**

**Synthesis of triacylgermenolates 3a,b**. For this study we focused on the direct approach, as the yields of the target compounds were significantly higher. So far, the method turns out to be restricted to derivatives containing *ortho*-substituted aromatic rings with electron-donating groups (EDGs). Up to now, we have not observed the formation of triacylgermenolates when acid fluorides are *un-*, *meta-* or *para-*substituted aromatic rings or carrying electron-withdrawing groups (EWGs), e.g., bromo-, chloro-, iodo-, and cyano-substituted acid fluorides, at the aromatic ring.

For the direct approach the starting material is tetrakis(trimethylsilyl)germane. By adding equimolar amounts of KO'Bu, [18]-crown-6 and dissolving the solids in  $Et_2O$  the corresponding germanium anion is formed quantitatively. Subsequently 3.0 equivalents of the respective acid fluoride were added, which resulted in a color change and the formation of precipitate.

By the usage of *o*-toluoyl fluoride and *o*-methoxybenzoyl fluoride the precipitate was identified as stable triacylgermenolate **3a,b** as [18]-crown-6 adduct (Scheme 3). Here the addition of [18]-crown-6 is necessary in order to isolate pure **3a,b** in good yields. **3a,b** can be stored in the absence of air at room temperature for several months without detection of any degradation products. Analytical and spectroscopic data support the structural assignment, and are given in the Experimental Section and in the *Supporting Information*, together with experimental details. Both derivatives show very similar <sup>13</sup>C chemical shifts for the carbonyl C-atom for **3a**  $\delta = 259.6$  ppm and for **3b**  $\delta = 256.1$  ppm, which is characteristic for carbonyl groups directly linked to a negative charged germanium atom.



Scheme 3. Synthetic protocol for the synthesis of compound 3a,b.

**Mass Spectrometry of 2 and 3a**. As our synthetic protocol is new for germanium compounds and giving the fact that these negative charged germanium species are only characterizable by <sup>1</sup>H- and <sup>13</sup>C-NMR, we investigated **2** (Figure 1) and **3a** (Figure 2 and 3) with LIFDI MS. These compounds can be seen as showcase derivatives for the first successful characterization of negatively charged organometallic compounds by LIFDI(-) MS.





Figure 2. Isotope pattern of 3a acquired in LIFDI(-) mode.



Figure 3. Isotope pattern of the counter ion of 3a acquired in LIFDI(+) mode.

The mass spectrum of 3a also shows an additional mass peak with a higher mass than expected. We identified this as the radical anion 3c (Figure 4). We first thought that this radical anion was formed during the reaction and remains in the isolated germenolate. To proof this, we investigated the isolated compound 3a with the use of EPR-spectroscopy. However, no EPR-signals were found. Consequently, we assume that in the injector a fragmentation reaction to two radicals occurs (Scheme 4). While the germanium centered radical undergoes an uncharacterisable pathway, we assume that the carbon centered radical adds to the germenolate 3a and forms the radical anion 3c.





Scheme 4. Assumed fragmentation produced at the surface of the heated LIFDI emitter.

**Reactivity of 3a,b with selected examples of electrophiles.** In order to test our new precursor systems, we reacted **3a,b** with selected examples of electrophiles. As suitable electrophiles we choose an aryl-substituted di-acyl chloride and a bromo-alkane. All these reactions resulted in the clean formation of a variety of new acylgermanes in good yields (Scheme 5). Compound **4b** is also formed during the reaction, however, due to the unexpected instability on silica gel the compound was not isolable. The reason for the selection of the respective electrophiles is based on the applicability of the formed acylgermanes. We know that alkyl substituted triacylgermanes have good solubility and acceptable absorptions properties. On the other hand, the terephthaloyl group as spacer leads to a significant bathochromic shift of the longest wavelength absorption, which leads to visible light induced type I photoinitiators.<sup>81</sup>

However, the hexamesitoyl substituted derivative of this type has nearly no solubility in a variety of standard acrylates. Therefore, we hoped that the use of higher soluble groups such as the *o*-toluoyl and *o*-methoxybenzoyl groups should lead to more soluble compounds and thus opens up the possible implementation as PI for various applications. An important parameter for the solubility of acylgermanes is their melting point (mp). The higher the melting point, the lower the solubility. Compared to the hexamesitoyl substituted derivative, **4c**,**d** show significantly lower melting points (mp of hexamesitoyl substituted derivative = 245-247°C; mp of **4c** = 145-147°C; mp of **4d** = 210-212°C), which indicates better solubility in various monomers. Analytical and spectroscopic data obtained for **4a**,**c**,**d** are consistent with the proposed structures. NMR spectra and detailed assignments are provided in the Experimental Section and in the *Supporting Information*. All derivatives show very similar <sup>13</sup>C chemical shifts for the carbonyl C-atom between  $\delta = 221.6$  and 224.9 ppm, which is characteristic for carbonyl groups directly linked to a germanium atom. These new compounds represent promising photoinitiators.



Scheme 5. Reaction of 3a,b with selected electrophiles.

**X-ray Crystallography.** The structures of **4c**,**d** were confirmed by single-crystal X-ray diffraction analysis (Figure 5 and 6). Compound **4c** crystallized in the triclinic space group  $\overline{P1}$ , and the unit cell contains one molecules. Compound **4d** crystallized in the monoclinic space group  $P2_1/c$ , and the unit cell contains two molecules. Structural data are in accordance with literature values of other acyl germanium compounds.<sup>21,24,81,82</sup> The torsion angle between the C=O groups and the aromatic ring planes is a structural feature, which significantly influences the optical properties. Table 1 summarizes the two measured torsion angles of the acylgermanes. The smaller the angle, the more pronounced the conjugation between the aromatic ring and the carbonyl group. This results in a bathochromic shift of  $\lambda_{max}$ .



**Figure 5.** ORTEP representation of **4c**. Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted and the tolyl units are displayed as wireframes for clarity. Selected bond lengths (Å) with estimated standard deviations: Ge(1)-C(1) 2.0187 (16), Ge(1)-C(2) 2.0292 (16), Ge(1)-C(3) 2.0240 (16), Ge(1)-C(26) 2.0154 (15), C(1)-O(1) 1.212 (2), C(2)-O(2) 1.2133 (19), C(3)-O(3) 1.2170 (19), C(26)-O(4) 1.2191 (18).



**Figure 6.** ORTEP representation of **4d**. Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted and the anisyl units are displayed as wireframes for clarity. Selected bond lengths (Å) with estimated standard deviations: Ge(1)-C(1) 2.018 (4), Ge(1)-C(5) 2.016 (5), Ge(1)-C(13) 2.017 (4), Ge(1)-C(20) 2.011 (4), C(1)-O(1) 1.213 (5), C(5)-O(2) 1.218 (4), C(13)-O(4) 1.226 (5), C(20)-O(6) 1.231 (5).

**Table 1.** Torsion angles between the C=O groups and the aromatic ring planes [°] of compounds **4c,d.**  $\angle O=C(int)-R$  are the torsion angles of the two internal acyl groups,  $\angle O=C(per)-R$  are the torsion angles of the six peripheral acyl groups.

compound	∠O=C(int)−R	∠O=C(per)−R
4c	6.69	29.16
4d	22.07	10.00

**UV-Vis Spectroscopy.** To further elucidate substituent effects on the absorption behaviour of these new acylgermanes, UV–Vis absorption spectra of **4a,c,d** were recorded and compared with tetra(o-toluoyl)germane **5** (Figure 7). The longest wavelength absorption band is the  $n/\sigma$ - $\pi^*$  transition, which is also responsible for the cleavage of the germanium-carbon bond. As previously shown for this compound class, the absorption behaviour is strongly influenced by the substitution pattern at the aromatic ring system as well as the torsion angles between the carbonyl groups and the aromatic ring planes. *Ortho* substitution reduces the symmetry within the molecule giving more fine structures. Consequently, a broadening of the  $n/\sigma$ - $\pi^*$  absorption band is observed. The same holds true for the torsion angle. The smaller the torsion angle the more bathochromic shifted is the longest wavelength absorption. In comparison to the triacylgermane **4a**, the oligoacyldigermanes **4c,d** showed a significant higher extinction coefficient, which can be attributed to the higher number of chromophores in the molecule. Moreover, **4c,d**, display a substantial red-shift of the absorption edge up to 500 nm.



Figure 7. UV-Vis absorption spectra of 4a,c,d and 5; dichloromethane solution,  $c = 5 \times 10^{-4} \text{ mol/L}$ .

#### Conclusion

In summary we investigated the group tolerance of the multiple silyl abstraction methodology towards triacylgermenolates. The method turns out to be restricted to derivatives containing *ortho*-substituted aromatic rings with electron-donating groups (EDGs). The formation of triacylgermenolates were not

observed when acid fluorides are *un-*, *meta-* or *para-* substituted aromatic rings or carrying electronwithdrawing groups (EWGs). Consequently, two new stable triacylgermenolates **3a,b** were synthesized by this approach. The formation of these new germenolates was confirmed by NMR spectroscopy, UV–Vis measurements and LIFDI mass spectrometry. The reaction with suitable electrophiles gave rise to the formation of a new triaacylgermane **4a** and two octaacyldigermanes **4c,d**, which were characterized by NMR spectroscopy, X-ray crystallography and UV–Vis measurements. The UV–Vis absorption spectra of **4c,d** revealed increased band intensities due to the presence of eight chromophores. On the basis of the absorption properties of the compounds, we consider **4c** and **4d** as the most promising candidates for the use as photoinitiators. Further studies to probe the scope of this new synthetic pathway are currently in progress.

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Keywords: acylgermanes • mass spectrometry • germenolates• photoinitiator • group tolarance•

# **1.3.5.** Isolable Geminal Bisgermenolates: A New Synthon in Organometallic Chemistry

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Dedicated to Professor Matthias Drieß on the occasion of his 60th birthday

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#### Abstract

We have synthesized the first isolable geminal bisenolates  $L_2K_2Ge[(CO)R]_2$  (R = 2,4,6trimethylphenyl (**2a**,**b**), L = THF for (**2a**) or [18]-crown-6 for (**2b**)), a new synthon for the synthesis of organometallic reagents. The formation of these derivatives was confirmed by NMR spectroscopy and X-ray crystallographic analysis. The UV/Vis spectra of these anions show three distinct bands, which were assigned

by DFT calculations. The efficiency of **2a,b** to serve as new building block in macromolecular chemistry is demonstrated by the reactions with two different types of electrophiles (acid chlorides and alkyl halides). In all cases



the salt metathesis reaction gave rise to novel Ge-based photoinitiators in good yields.

The chemistry of metal enolates continues to be a comprehensively researched field in contemporary organic chemistry.<sup>224,225,226–228</sup> Furthermore, the classical aldol reaction is one of the most important biosynthetic tools for life on earth.<sup>229–232</sup> In this context a geminal bisenolate surrogate was introduced as powerful organic substrate for the regioselective  $\alpha$ , $\alpha$ -difunctionalization adjacent to a ketone.<sup>233</sup> This surrogate bypasses the use of  $\alpha$ -diazo carbonyl compounds, which are state-of-the-art reagents for such reactions.<sup>234–238</sup> Here a replacement is highly desirable due to safety concerns and limited functional group compatibility of the latter. There are, however, no reports on the targeted isolation of geminal bisenolates published so far.

Recently heavier group 14 enolates (HG 14 enolates) of silicon and germanium were found to be key intermediates during the synthesis of photoinitiators, as well as during the formation of complex silicon frameworks.<sup>21,22,72,98</sup>
The latest investigation concerning germenolates was the synthesis and characterization of potassium-tris(2,4,6-trimethylbenzoyl)germenolate (1), as a new building block for high-potential photoinitiators PIs.<sup>81,82</sup>

While the chemistry towards tetraacylgermanes has already been thoroughly investigated,<sup>21,72</sup> the class of triacylgermenolates is still in the early stages of development. Owing to the importance of the latter, as highly promising building block for germanium-based PIs, we continued to examine this particular compound class.

During the course of these examinations a new, hitherto unpublished and yet undescribed species was found. Upon addition of 2.0 equivalents of elemental potassium to a solution of 1 dissolved in THF, we established a highly selective electron transfer reaction leading to the elimination of a mesitoyl-substituent. Hence, the dianionic species 2 is formed. This remarkable finding represents the first ever synthesized geminal bisenolate so far and opens up a new highly reactive building block in main group chemistry. Looking at the literature only a handful geminal germyl dianions are reported.



Scheme 1. Types of literature known geminal dianionic germanium compounds 3-4 and germole dianions 5. New isolable geminal bisgermenolate 2 as new building block.

The groups of Mochida, Satgé and Tokitoh pioneered in the synthesis of 1,1-dimetalogermane derivatives of the type  $Ar_2GeM_2$  (compound **3a**, Scheme 1) by the metalation of the corresponding hydrides with alkali metals, 'BuLi or lithium naphthalenide.<sup>69,70,239–241</sup> Vyazankin et al. generated Et<sub>2</sub>GeLi<sub>2</sub> (compound **3b**, Scheme 2) by the reaction of (Me<sub>3</sub>Si)Et<sub>2</sub>GeLi with Me<sub>3</sub>SiLi.<sup>242</sup> However, due to their thermal instability, these compounds were not isolable and

were only identified by trapping reactions. Sekiguchi and Lee used silylated precursor molecules to perform either a reductive cycloreversion or a direct reductive dehalogenation in order to synthesize isolable 1,1-dilithiogermane derivatives (compound **4**, Scheme 1).<sup>243,244</sup> These silyl-substituted geminal dianions are isolable, room-temperature stable, and fully characterizable compounds, which led to their importance as synthetic building blocks in modern main group chemistry.

Another important germanium-based dianion are germole dianions. Since West et al. reported on the first characterized delocalized germole dianion,<sup>245</sup> considerable progress has been made during the last two decades. Especially the groups of Tilley,<sup>246</sup> Boudjouk<sup>247,248</sup> and Müller<sup>249,250</sup> synthesized a variety of germole dianions and discussed their chemistry (compound **5**, Scheme 1). The rare number of geminal dianions available and hence the undeniable interest in these derivatives drove our motivation to contribute to this field. Thereby our intention was the design of a reasonable preparative-scale approach for the synthetically highly attractive geminal bisgermenolate.

The synthesis of **2** can be performed by the use of two different starting materials and two different ligand systems, with equal reaction mechanism for all methods. These reactions resulted in the clean formation of air and moisture sensitive geminal bisgermenolate **2a**,**b** in good yields (Scheme 2). The details of the SET mechanism is depicted on the next page. During the reaction **2a**,**b** precipitated at room temperature from the respective used solvent to give purple crystals. After filtration, the crystals can be stored at room temperature in the absence of air even for prolonged periods. Analytical data are consistent with the proposed structures, as both derivatives show very similar <sup>13</sup>C chemical shifts for the carbonyl C-atom for **2a**  $\delta = 274.7$  ppm and for **2b**  $\delta = 279.4$  ppm, which is characteristic for carbonyl groups directly linked to a negative charged germanium atom. On the basis of the very low solubility of **2a**,**b** in all standard solvents for NMR spectroscopy (highest solubility was observed in THF-d<sub>8</sub> with of 5 mg/mL for **2a** and 12 mg/mL for **2b**) we also performed MAS-NMR spectroscopy to ensure the purity of these compounds. **2a**,**b** show very similar shifts in the <sup>1</sup>H and <sup>13</sup>C MAS-NMR. Moreover, for **2b** we were also observed the shift for the carbonyl group at  $\delta = 278.4$  ppm. The results are presented in the *Supporting Information*.



Scheme 2. Synthesis of 2a,b.

Compound 2 can be described by two resonance structures 2' and 2'', shown in Figure 1. 2' represents the geminal dianion and 2'' represents the bisgermenolate. Moreover, 2 can also be described as 2''', which is an isomer of 2' and 2''



Figure 1. Possible resonance and isomeric structures of 2.

Derivative **2b** afforded crystals of sufficient quality for single crystal X-ray crystallography. The molecular structure is depicted in Figure 2. Compound **2b** crystallizes together with two molecules of [18]-crown-6 in the orthorhombic space group *Pnma* containing four molecules per unit cell. Both acyl groups are stabilized by one potassium atom, while the central Ge-atom is stabilized by the other potassium atom.



**Figure 2.** ORTEP representation for compound **2b** (1:2 adducts with [18]-crown-6). Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (pm) and bond angles (deg) with estimated standard deviations: Ge(1)-C(1) 198.4(3), C(1)-O(1) 125.2(4), Ge(1)-K(1) 396.6(12), Ge(1)-K(2) 333.6(11), O(1)-K(1) 264.8(2), C(1)-Ge(1)-C(1#) 103.64(19).

On the basis of the observed structural features, **2b** adopts in the solid state structure **2**". This is also supported by DFT calculations. The negative charge is mainly confined in the C(O)GeC(O) moiety of **2b** (Figure 3) explaining the rather tight binding of one K<sup>+</sup> counterion towards the two carbonyl oxygen atoms (distance: ca. 265 pm). Owing to the concentration of -0.58 charge units at the Ge center, the second K<sup>+</sup> counterion resides below it at a distance of 334 pm, with the two K cations being slightly tilted along the y-axis.

The Ge-C(O) bonds of 198 pm are slightly shorter compared to values of literature-known germenolates (210-206 pm),<sup>126</sup> but significantly longer then values found for germenes (177-186 pm),<sup>251,252</sup> indicating electron delocalization across the C(O)-Ge-C(O) fragment.

To study the reaction mechanism for the formation of 2a,b, we used a combination of UV/Vis and EPR spectroscopy. A solution of tetraacylgermane 6 in dry THF was prepared in a special EPR tube allowing an in-situ reduction at a potassium mirror (see *Supporting Information* for details).



**Figure 3.** DFT calculated geometry of **2b** including selected charges and bond lengths. Left: view along the x, z plane, right: view along the y, z plane H-Atoms are not displayed for clarity. The red sphere indicates the molecular moiety carrying 85% of the negative charge.

The solution was gradually reduced until the violet color of the dianion appeared. EPR and UV/Vis spectra were recorded after each contact of the solution with the potassium mirror. During the procedure, the characteristic absorption band of tris(mesitoyl)germenolate ( $\lambda_{max} = 427 \text{ nm}^{[7]}$ ) was detected via UV/Vis spectroscopy. Further reduction led to the characteristic UV/Vis spectrum of the dianion **2a** (dark violet solution; see Figure 4). The detailed results are presented in the *Supporting Information*.

Furthermore, we investigated a THF solution of **1** after exposure to metallic potassium and could obtain an EPR spectrum (shown in the *Supporting Information*). The spectrum is unresolved likely based on many small and unresolved coupling constants of protons of the mesityl substitutent. Instead, another reaction mixture (**6** + potassium + [18]-crown-6 in benzene) gave a rather distinct EPR spectrum (*Supporting Information*). In our prior publication on the characterization of the germenolate **1**, an almost identical EPR spectrum was obtained, however, the reduction was performed with KO*t*Bu. We tentatively assigned the spectrum to a follow-up product derived from **1** and the *tert*-butoxy radical.<sup>81</sup> The new experimental results contradict our first assignment and rather suggest, that both reducing agents lead to the same intermediate or by-product. As reducing agent, the use of elemental potassium is essential. With other metals (i.e. lithium or sodium) or bases (i.e. KOtBu) no formation of **2** was observed.

As reported recently, the germenolate **1** is formed by a germa-acyloin condensation.<sup>81</sup> During the formation of **2**, this reaction sequence is repeated for the second acyl-group. Here, once more a radical anion is formed by a SET-reaction (Scheme 3). Hence, two ion-paired radical anions undergo a germa-acyloin condensation followed by a scission of the diketone-moiety. After elimination of the diketone, the bisgermenolate **2** is formed. A second SET-reaction probably leads to the formation of **a** diradical, which undergoes a complex and uncharacterized degradation sequence. The formation of **2a** by method B, depicted in Scheme 2, performs both SET-reactions consecutively, starting from the tetraacylgermane **6**. Herein, the formation of the germenolate **1** is instantly followed by the conversion to the bisgermenolate **2**. In the case of method C, the bisacylgermenolate **2** is stabilized additionally by two equivalents of [18]-crown-6.

THF was used as a solvent to determine the charge transfer behavior for the longest wavelength absorption bands.<sup>195</sup> Figure 4 depicts the measured and calculated UV/Vis spectra of **2b** in THF together with their calculated frontier Kohn-Sham orbitals for the HOMO and LUMO orbital (the UV/Vis spectrum of **2a** can be found in the *Supporting Information*).



Scheme 3. SET reaction of 1 with K<sup>0</sup> (Method A)



**Figure 4.** Measured UV/Vis spectra and calculated contributions of **2b** in THF. Vertical transitions are marked as lines with their respective oscillator strengths (right axis). The orbitals involved in the first bands are presented in the lower part.

The geminal bisgermenolate **2b** exhibits three intense absorption bands with  $\lambda_{\text{max}} = 553$  nm (band I), 416 nm (band II) and 311 nm (band III). Moreover, the calculated data show a reasonable agreement with the measured absorption bands. The band at around 570 nm is dominated by a HOMO $\rightarrow$ LUMO transition. The HOMO has significant coefficients at the Geatom. The LUMO reveals a symmetric electron distribution over both mesitoyl moieties with the negative charge residing mainly at the central part of **2b** (see Figure 4). The absorption centered at 416 nm consists of two main contributions from HOMO  $\rightarrow$ LUMO+6 and HOMO  $\rightarrow$ LUMO+7 transitions (for the orbital representations and the detailed interpretation of the spectrum see *Supporting Information*).

This dianionic species represents an optimal and highly promising building block for the formation of new, hitherto not synthesizable acylgermanes and related species. In order to test our new precursor system, we reacted **2a**,**b** with selected examples of electrophiles. As suitable electrophiles we choose aryl- as well as alkyl-substituted acid chlorides and two haloalkanes. All these reactions resulted in the clean formation of a variety of new acylgermanes in good yields (Scheme 4). A significant correlation between the used method and the yield of the expected product was not observed. Analytical and spectroscopic data obtained for **7a-g** are consistent with the proposed structures. NMR spectra and detailed assignments are provided in the Experimental Section in the *Supporting Information*.



7g: 36% yield

Scheme 4. Reactivity of 2a,b with selected examples of electrophiles.

The UV/Vis spectra of **7a-g** (Figure 5) revealed broad absorption bands centered at around 390 nm for **7a-d** and at around 360 nm for **7e-g**, which can be allocated for the  $n-\pi^*$  transition. This band is responsible for the photo-induced cleavage of the Ge-C bond. In close analogy to previous observations, the mixed functionality of these derivatives leads to broadening of their absorption bands, which is highly beneficial for their application as larger variety of wavelengths can be used to initiate photopolymerization.

All derivatives show very similar <sup>13</sup>C chemical shifts for the carbonyl C-atom between  $\delta = 223.9$ and 243.8 ppm, which is characteristic for carbonyl groups directly linked to a germanium atom. Crystals suitable for single-crystal X-ray diffraction analysis were obtained for compounds **7a**, **7f**, and **7g**. As a representative example, the molecular structure of **7g** is depicted in Figure 6 (see the *Supporting Information* for remaining structures). Structural data are in accordance with literature values of other acyl germanium compounds.<sup>21,72,73,80,88,126</sup>

To explore if the acylgermanes synthesized via the procedure shown in Scheme 3 are suitable photoinitiators, we performed photo CIDNP experiments<sup>253</sup> with **7g** and **7f**. The corresponding <sup>1</sup>H-NMR/CIDNP spectra in the presence of butyl acrylate clearly reveal the growth of polymer chains with Ge-substituted end groups based on the expected  $\alpha$ -cleavage of Ge–C(O) bonds upon n- $\pi^*$  excitation via intersystem crossing (see *Supporting Information*).<sup>21,73,82</sup>



**Figure 5.** Absorption spectra of synthesized compounds **7a-g** compared with the commercially available Ivocerin<sup>®</sup> and tetra(mesitoyl)-germane **6** at a concentration of  $1 \times 10^{-3}$  M in dichloromethane.



**Figure 6.** ORTEP representation for compound **7g**. Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) with estimated standard deviations: Ge(1)-C(1) 2.0057 (15), C(1)-O(1) 1.212 (2), C(11)-O(2) 1.216(2), Ge(1)-C(11) 2.0037 (15), Ge(1)-C(21) 1.9624 (16), Ge(1)-C(24) 1.9644 (16).

In conclusion we have introduced a synthetic strategy for the hitherto unknown geminal bisenolates  $L_2K_2Ge[(CO)R]_2$  (R = 2,4,6-trimethylphenyl (**2a,b**), L = THF for (**2a**) or [18]-crown-6 for (**2b**)), which represents a new synthon for the synthesis of organometallic reagents. Furthermore, the formation of these derivatives was confirmed by NMR spectroscopy and X-ray crystallographic analysis.<sup>[24]</sup> Moreover, the efficiency of **2a,b** to serve as new building block in macromolecular chemistry is demonstrated by the reactions with two different types of electrophiles (acid chlorides and alkyl halides). In all cases the salt metathesis reaction gave rise to potential novel Ge-based photoinitiators in good yields. Further studies to probe the scope of this chemistry are currently in progress.

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Keywords: bisenolates • germenolates • acylgermanes • SET reaction • photoinitiators

## 1.3.6. Isolable Stannenolates Enable the Synthesis of Visible-Light Photoinitiators

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Dedicated to Professor Frank Uhlig on the occasion of his 60th birthday

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## Abstract

Isolable stannenolates  $LKSn[(CO)R]_3$  (R = 2,4,6-trimethylphenyl (1a,b), L = DME for (1a) or [18]-crown-6 for (1b)), a new building block for the synthesis of effective Sn-based photoinitiators, were synthesized. The formation of these derivatives was confirmed by NMR

spectroscopy, UV/Vis spectroscopy as well as X-ray crystallographic analysis. Compound **1a** is employed as a synthon in main group chemistry through reactions with two different types of electrophiles (acid chlorides and alkyl halides). All investigated electrophiles react via the salt metathesis reaction and gave rise to novel acylstannanes in good to excellent yields. The applicability as visible light photoinitiators is demonstrated by photobleaching (UV/Vis



absorption spectroscopic studies) as well as through application in photo-DSC studies.

The reactions of enolates remains to be a heavily investigated field in contemporary organic chemistry.<sup>224,225,226–228</sup> Additionally, the aldol reaction is one of the most important biosynthetic instrument for life on earth.<sup>229–232</sup> Despite the fact that numerous reactions involving enolates have been reported, little is known about their heavier congeners - silenolates, germenolates and stannenolates. Although Bravo-Zhivotovskii and co-workers reported the first synthesis on these heavier group (HG) 14 enolates in 1989,<sup>254</sup> the synthesis and characterization of further compounds has proven to be challenging.

Recently HG 14 enolates were found as decisive intermediates during the formation of photoinitiators, as well as during the synthesis of complex silicon frameworks.<sup>21,22,72,98</sup>

For enolates two resonance structures can be formulated. In the enol form (I) the negative charge is located on the oxygen atom. In contrast, in the keto form (II) the negative charge is found primarily on the central atom (Scheme 1).<sup>255,256</sup>

The dominant resonance structure of enolates is the enol form in solution as well as in solid state.<sup>256</sup> Silenolates and germenolates on the other hand show a significantly different resonance behavior. The site of the equilibrium is more shifted to the keto form, as all stable silenolates

and germenolates (characterized by single crystal X-ray crystallography) have a pyramidal central silicon or germanium atom with elongated single bond to the adjusting carbon atom.<sup>80,126,257–259</sup>



Scheme 1. Resonance Structures of enolates (above) and HG 14 enolates (below).

When this work was in peer-review the group of Bravo-Zhivotovskii and Apeloig published a paper about the isolation and characterization of the first stable lithium stannenolate. On the basis of X-ray analysis, NMR spectroscopy and DFT quantum-mechanical calculations this lithium stannenolate also adopts the keto-form and consequently is best described as an acyl-stannyl anion.<sup>260</sup>

Recently our group succeeded in the isolation of triacylgermenolates,<sup>81,82</sup> which can also serve as a novel building block for high performance HG 14 photoinitiators. The high stability of this triacylgermenolates encouraged us to investigate the implementation of tin as other central atom. Here we report on the synthesis of stable stannenolates by a single electron transfer and a classical multiple silyl abstraction approach. Our results show an innovative aspect of organotin chemistry. The aim of this work is to demonstrate that triacylstannenolates are new synthons for the formation of group-14-based photoinitiators.

Furthermore, this pathway considerably expands the amount of available acylstannanes. Lastly, the performance of these compounds was assessed by photobleaching (employing UV/Vis absorption spectroscopy), and photo-polymerization experiments (by mean of photo-DSC measurements).

The starting point of our investigation is the straightforward reaction of tetraacylstannane 2 with potassium. Compound 2 was dissolved in 1,2-dimethoxyethnae (DME) and solid freshly cleaned potassium was added. It was noted noted that the potassium became red in color immediately, indicating the start of the reaction. After approximately 10 min, the orange reaction solution became red. Complete consumption of the potassium marks the end of the reaction and results in the formation of hitherto unknown triacylstannenolate **1a**. Upon storage at -30°C, clean **1a** 

crystallizes out of the reaction solution as red powder in good yields. Analytical and spectroscopic data that strongly support the structural assignment are given in the *Supporting Information*, together with experimental details.

Based on this findings, Scheme 2 shows the proposed single electron transfer (SET) mechanism for the formation of **1a** employing potassium as a reduction agent. The first reaction step involves the formation of a radical anion by means of a SET reaction. The radical anion undergoes an acyloin condensation and after elimination of the diketone, the stannenolate **1a** is formed. A second SET reaction may lead to the formation of a diradical, which we were not able to characterize.



Scheme 2. SET reaction of 2 with  $K^0$  (method 1).

We furthermore tested other alkali metals in order to isolate other substituted triacylstannenolates. Therefore, we reacted 2 with 2 equivalents of lithium or sodium. Both alkali metals were consumed immediately (for Li approx. 30 min. and for Na approx. 15 min.). While in the case of lithium only uncharacterisable polymer was found, sodium as reducing agent formed the sodium substituted trisacylstannenolate 1c, but the low stability (degradation in solution and in solid state within 24h) prevented a complete characterization (Experimental details are included in the *Supporting Information*). This observation is well in line with previous findings regarding the stability of silenolates and germenolates.<sup>257,261,262</sup>

The multiple silyl abstraction methodology is an easy to perform approach for the synthesis of acylgermanes and moreover for their corresponding germenolates. It also circumvents the use of alkali metals and the overall yields are significantly higher. Therefore, we set out and reacted the potassium stannide **3K** with 3.0 molar equiv. of the mesitoylfluoride, which gave rise to the formation of **1a** within 30 minutes (see Scheme 3). After removal of the solvent and resuspension in *n*-pentane, the product was filtrated of the reaction solution giving an overall yield of 75%. A slightly adopted synthetic procedure was applied for the synthesis of compound **1b**. The only difference was the addition of 1 eq. 18-crown-6 during the synthesis of compound **3K** giving an overall yield of 80%. Compounds **1a,b** can be stored in the absence of air at room temperature

for several months without finding of any degradation products. We were also able to grow crystals of **1a**, which were suitable for single crystal X-ray crystallography. In Figure 1, the molecular structure of the isolated stannenolate is depicted. As for all other structural characterized HG group 14 enolates, the central Sn atom of **1a** is pyramidal and has elongated Sn–C single bonds.<sup>263</sup> Accordingly, in the solid state, **1a** is best described as acyl stannyl anion (keto form **II** in Scheme 1). The DFT geometry agrees well with the crystal structure (see Table S3) with some minor deviations, which are justified by the lattice effect in the crystal not taken into account by our single molecule calculation.



Scheme 3. Multiple silyl abstraction methodology towards 1a.



**Figure 1.** ORTEP representation for compound **1a**. Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) with estimated standard deviations:  $\sum \alpha Sn(1) 290.67$ , Sn(1)-C(1) 2.2598 (17), Sn(1)-C(11) 2.2624 (17), Sn(1)-C(21) 2.2517 (17), C(1)-O(1) 1.224 (2), O(2)-C(11) 1.227 (2); O(3)-C(21) 1.226 (2), Sn(1)-K(1) 5.548, K(1)-O(1) 2.6129 (14), K(2)-O(2) 2.6610 (14), K(2)-O(3) 2.6064 (14).

Furthermore, **1a** adopts discussable structural features with respect to the relative alignment of the three carbonyl groups as well as the distance between the anionic and cationic centers in the

molecule. The bidentate dimethoxyethane is not able to coordinative saturate the potassium metal, consequently all the carbonyl groups orient themselves in order to satisfy the coordination sphere of potassium.

NMR data further confirm the assumption that the dominant resonance structure of **1a**,**b** is the keto form. In close correlation to other HG 14 enolates, where the carbonyl shifts were found in the region of  $\delta = 262$  to  $\delta = 291$  ppm,<sup>80,260</sup> both compounds exhibit very comparable <sup>13</sup>C chemical shifts for the carbonyl C atom between  $\delta = 293.7$  ppm for **1a** and 286.9 ppm for **1b**.

To determine the resonance structure in solution UV/Vis absorption spectra were measured and the longest wavelength absorption bands were assigned for the conformational minimum structures via DFT calculations at the B3LYP-D3/def2-TZVP level. The obtained computational data is summarized in the *Supporting Information* and show reasonable agreement. Figure 2 shows the experimentally obtained UV/Vis absorption spectra together with the calculated frontier orbitals. These bands are indisputably assigned to the HOMO $\rightarrow$ LUMO transition and are centered at 456 nm. The HOMOs of **1a,b** (Figure 2) mainly match to the p<sub>z</sub> orbital of the tin atom with little variation in form and energy. Upon excitation, electron density is displaced into the  $\pi^*$  orbital of the carbonyl moiety (LUMO). Therefore, the stannenolates **1a,b** also adopt the keto form in solution regardless the used ligand.

For the follow up reactions we exclusively used **1a** as precursor molecule, because the removal of the 18-crown-6 is tedious and reduces the yields significantly. As suitable electrophiles we chose to use iodomethane and 1,2-dibromoethane, and giving our ongoing interest in the synthesis of oligoacyl 14 compounds, we also tested di- and triacyl chlorides. The reaction of **1a** with iodomethane led to the formation of the expected triacylstannane **3** in good yields (Scheme 4). Compound **3** represents the first isolable triacylstannane closing the gap from mono- to tetraacylstannanes. The reactions with di- and triacyl-chlorides resulted in the clean formation of a variety of new oligoacyldistannanes **4a-c** in good yields (Scheme 4).

All these new derivatives are promising photoinitiators. Spectroscopic and analytical data obtained for **4a-c** confirm the proposed structures. NMR spectra and detailed assignments are provided in the *Supporting Information*. All derivatives show very similar <sup>13</sup>C chemical shifts for the carbonyl C atom between  $\delta = 233.0$  and 245.5 ppm, which is characteristic for carbonyl groups directly linked to a tin atom.



**Figure 2.** Measured UV/Vis spectra of **1a**,**b** in THF ( $5 \times 10^{-4}$  mol/L; top) and the orbitals (HOMO left, LUMO right) involved in the first band are presented.



Scheme 4. Reactivity of 1a with selected examples of electrophiles.

1,2-dibromoethane is known to be a selective transmetalation agent in main group chemistry. Therefore, we reacted **1a** with 0.55 equiv. of 1,2-dibromoethane and observed the selective formation of a hexaacyldistannane **5** (Scheme 5). Analytical and spectroscopic data obtained for **5** are consistent with the proposed structures. NMR spectra and detailed assignments are provided in the *Supporting Information*. We were also able to grow crystals of **5**, which were suitable for single crystal X-ray crystallography. In Figure 3, the molecular structure of the hexaacyldistannane **5** is depicted.<sup>[16]</sup>



Scheme 5. Reactivity of 1a with 1,2-dibromoethane.



**Figure 3.** ORTEP representation for compound **5**. Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted and the Mes units are displayed as wireframes for clarity. Selected bond lengths (Å) with estimated standard deviations: Sn(1)-Sn(1#) 2.8005(4), Sn(1)-C(1) 2.261(3), Sn(1)-C(11) 2.261(3), Sn(1)-C(21) 2.249(3).

For many applications free-radical photoinitiators require an absorption in the visible spectrum of the light, therefore the UV/Vis absorption spectra of **3**, **4a-c** and **5** were recorded and compared to spectra of structurally related tetraacylstannane **2** and tetraacylgermane **6** (Figure 4). As previously shown for this compounds, the absorption behavior is strongly influenced by the substitution pattern at the aromatic ring system.<sup>22</sup> Interestingly the tetraacylstannane **2** and the triacylstannane **3** show nearly identical extinction coefficients and absorption edges, which is in stark contrast to the results obtained for the corresponding acylgermanes.

In comparison to the tri- and tetraacyl substituted derivatives, the oligoacyldistannanes **4a**,**b** the oligoacyltristannane **4c** and the hexaacyldistannane **5** showed a significant higher extinction coefficient, which can be attributed to the higher number of chromophores in the molecule. Moreover, the oligoacylstannanes **4a** and **4c** display a substantial red-shift of the absorption edge. Similar results are also found for the oligoacylgermanes, however, these new derivatives show absorption up to 600 nm, which can lead to visible light induced photoinitiators.

In order to further investigate the usability of these compounds as radical photoinitiators we have performed photobleaching experiments using previously described setup.<sup>264</sup> To that end compounds **3** to **5** were dissolved in 1:1 (v:v) mixture of toluene methyl methacrylate (MMA) and irradiated using UV LED with maxima of emission centered around 387 nm. The absorbance at  $\lambda_{max}$  of investigated compound was monitored versus time and used to determine quantum yields for decomposition (for further details see Figure S2-S11 in the *Supporting Information*). The change in absorbance for investigated compounds is plotted on Figure 5. The determined decomposition quantum yields range from  $0.66 \pm 0.2$  for **5**,  $0.47 \pm 0.2$  for **4b** and  $0.27 \pm 0.2$  for **4c**. In the case of **3** and **4a** secondary thermal component is of the same order of magnitude as the photochemical component as can be seen from Figure 5. Thus, quantum yield of photochemical decomposition for respective compounds cannot be reliably measured using this method. In addition, the photobleaching experiment was carried out with a blue LED having

emission maxima at 472 nm. This demonstrates the feasibility of compounds **3** to **5** to be used as visible light Pls, for details see *Supporting Information*.



Figure 4. UV/Vis absorption spectra of 2, 3, 4a–c, 5 and 6 toluene solution,  $c=5\times10^{-4}$ mol/L.



**Figure 5.** Steady-state photolysis of investigated compounds using 387 nm LED in toluene/MMA (1/1 v/v). The absorbance traces are normalized to the initial absorptions at the observation wavelengths.

For an evaluation of the performance of the PIs in polymerizable resins, photo-DSC measurements were conducted. One single measurement can give information about the reaction kinetics as well as the double bond conversion (DBC; for further details, see the *Supporting Information*). Glycerol dimethacrylate (GDMA) was used as model monomer system in the polymerization experiments. Besides the synthesized PIs (**3** and **4a-c**), the polymerization behavior of a structurally identical germanium compound (**Ge-4b**) was determined as reference. Compound **5** was not sufficiently soluble in GDMA and was therefore not included in this experiment.

The PI performance was analyzed at (1) equal molar PI (0.15 mol%) as well as (2) equal photocleavable group (PCG) concentration (0.075 mol% for **4a**, **4b** and **Ge-4b**; 0.05 mol% for **4c**; 0.2 mol% for **3**), respectively (Figure 6). Among the synthesized photoinitiators, **4c** provide the highest reactivity in GDMA with a final DBC of  $37.4 \pm 2.6$  and  $37.8 \pm 1.6$ , at 0.15 and 0.05 mol%, respectively. Comparing the Sn-based PI **4b** to a structurally identical germanium compound (**Ge-4b**), the germanium based photoinitiator shows a higher polymerization activity, but is still comparable to other Sn-initiators in its polymerization activity.

Although, the herein studied compounds show unambiguous photo-reactivity, a possible sensitivity to oxygen must be further investigated.



**Figure 6.** Photo-DSC (left) and conversion plots (right) for the photopolymerization of GDMA with 0.15 mol% PI (top) and equal PCG concentration (bottom).

In conclusion we could synthesize and fully characterize the triacylstannenolates **1a,b**. The efficiency of **1a** to serve as tin-based precursor system is confirmed by the reactions with a variety of electrophiles, as all reactions gave rise to novel acylstannanes **3-5** in good yields. In addition, these new acylstannanes were investigated for their suitability as visible light photoinitiators.

On the basis of the photochemical characterization of the derivatives, we consider 3 and 4c to be the candidates with the greatest potential for use as visible light induced photoinitiators. Further studies to probe the scope of this new synthetic pathway are currently in progress.

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# **1.3.7.** Synthesis and Characterization of New Counterion-Substituted Triacylgermenolates and Investigation of Selected Metal-Metal Exchange Reactions

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#### Abstract

The synthesis to obtain triacylgermenolates with alternated counterions by single-electron-transfer reactions or by the direct approach is described. The formation of these



derivatives was confirmed by NMR spectroscopy and UV-vis spectroscopy. Moreover, metal-metal exchange reactions of the potassium substituted triacylgermenolate 2a with MgBr<sub>2</sub>, ZnCl<sub>2</sub> and HgCl<sub>2</sub> are presented. Additionally, 2a was reacted with *n*Bu<sub>4</sub>NBr, which led to the formation of an ammonia-substituted triacylgermenolate 8. Furthermore, we reacted 2a with HCl/Et<sub>2</sub>O in order to obtain the triacylgermane 9. Subsequently, we investigated the reaction of 9 with *t*Bu<sub>2</sub>Zn and *t*Bu<sub>2</sub>Hg. NMR spectroscopy, single-crystal X-ray crystallography, and UV-vis spectroscopy are employed for analysis of structural properties.

#### Introduction

Historically speaking, the synthesis and characterization of heavier group 14 (HG 14) enolates were mainly triggered by fundamental investigations in the field of main group chemistry.<sup>254,257,265–267</sup> Recently, we could demonstrate that HG 14 triacylenolates (M = Ge and Sn) represent innovative building blocks for the formation of high-performance free radical photoinitiators.<sup>81–83</sup> To synthesize these new HG 14 triacylenolates, we established two pathways. The first methodology uses a potassium-induced single electron transfer (SET) approach starting from the respective tetraacyl derivatives. The second method uses the tetrakis(trimethylsilyl) derivatives as starting materials (direct approach). After KO*t*Bu-induced desilylation and reaction with 3 equivalents of an acid fluoride, the respective HG 14 triacylenolates are obtained. The direct approach circumvents the usage of alkali metals and results in higher yields of the target compounds (Scheme 1). In general, the synthesis of HG 14 enolates was focused exclusively on lithium- and potassium-derivatives.<sup>80,126,127,254,257–259,265,266,268,269</sup> Other counterions were not investigated so far, although they can significantly influence the reactivity and the structural properties of these enolates. Consequently, the aim of this study was to introduce new counterions. Therein, we focused on germanium as central atom and used exclusively the 2,4,6-trimethylphenyl moiety as aromatic group at the carbonyl group.



Scheme 1. SET Approach vs. Direct Approach

#### **Results and Discussion**

**Electron-Transfer Reactions of Other Alkali Metals (Method A):** Recently, we have investigated the usage of elemental lithium to induce electron-transfer reactions with tetraacylstannanes. However, only uncharacterisable polymers were found.<sup>85</sup> The same holds true for tetraacylgermanes. At the beginning of the reaction, the reaction solution changed from yellow to orange, which indicates the formation of the target compound. However, on prolonged stirring (approx. 30 min) the color changed to deep black, along with the formation of a precipitate. We assume that the initially formed lithium-substituted germenolate is highly unstable, and therefore, an isolation of the lithium derivative is not possible. On the basis of this observations, we investigated sodium as reducing agent. Consequently, we reacted **1a** with 2.1 equivalents of sodium in tetrahydrofuran (THF). The reaction solution was stirred overnight, and the complete consumption of the metal marks the end of the reaction. This germenolate **3a** is formed with remarkable selectivity, based on performed NMR spectroscopy at the end of the reaction. **3a** was isolated as red solid in 74% yield by adding *n*-pentane to the reaction solution (see Scheme 2). Analytic and spectroscopic data which support the structural assignment, together with experimental details are summarized in the *Experimental Section*.



Scheme 2. SET Reaction of 1a with Na<sup>0</sup>

We further investigated the usage of other alkali metals (rubidium, cesium) to synthesize differently decorated triacylgermenolates. In both cases, compound **1a** was reacted with 2.1 equivalents of the respective metal in THF as solvent (Scheme 3). However, the high solubility of these heavier alkali metals prevented the isolation of these compounds via the SET approach. Experimental details are summarized in the *Experimental Section* and NMR spectra of the reaction solutions are provided in the *Supporting Information*.



Scheme 3. SET Reaction of 1a with Rb<sup>0</sup> and Cs<sup>0</sup>

**Direct Approach towards Triacylgermenolates (Method B):** As outlined in the Introduction section, the direct approach is a convenient method to obtain potassium triacylgermenolates, with various substituents on the carbonyl group in good to excellent yields. Here, we used other metal-*tert*-butoxides (NaO*t*Bu, RbO*t*Bu and CsO*t*Bu) to generate the metal germanide *in situ*.<sup>270-271</sup> These germanides were subsequently reacted with three equivalents of mesitoylfluoride. The addition of [18]-crown-6 is necessary to induce a precipitation of the formed germenolates in Et<sub>2</sub>O (see Scheme 4). Compounds **4a-c** were isolated in good to excellent yields (experimental details are included in the *Experimental Section*).

Stability of 3a and 4a-c. All isolated germenolates can be stored in the absence of air at room temperature for prolonged time (usually months).



Scheme 4. Direct Approach towards 4a-c

UV/Vis spectroscopy of 2a, 3a and 4a-c. To determine the longest absorption band for our isolated germenolates, we used THF as solvent and compared it with the parent compound 2a (M = K). In Figure 1 the measured UV/Vis spectra of the isolated germenolates are depicted. These germenolates exhibit two distinct absorption bands with  $\lambda_{max} = 425-427$  nm (band I [pz- $\pi$ \* excitation]) and 352-353 nm (band II [ $\pi$  - $\pi$ \* excitation]).



Figure 1. Measured UV/Vis spectra of 2a, 3a and 4a-c in THF ( $1 \times 10^{-4}$  mol/L).

**Transmetalation Reactions of 2a.** In contrast to metal enolates where magnesium as counterion is widely used, <sup>272,273</sup> a HG 14 magnesium substituted enolate has not been reported so far. Therefore, we reacted our potassium triacylgermenolate **2a** with 0.55 equivalents of MgBr<sub>2</sub> in THF at -30 °C. After removal of the solvent and resuspension in toluene, the reaction salt was filtered off the reaction solution. Compound **5** was isolated by crystallization in excellent yield (Scheme 5).



Scheme 5. Reaction of 2a with MgBr<sub>2</sub>

Furthermore, we were able to structurally confirm compound **5** by single-crystal X-ray diffraction analysis (compare Figure 2). **5** crystallizes in the monoclinic space group P2<sub>1</sub>/n and the unit cell contains four molecules. In close analogy to other structurally characterized germenolates,<sup>80–83,126,127</sup> the central Ge atoms are pyramidal and have elongated Ge-C single bonds. Noteworthy is an interesting structural feature in the structure of **5**. The relative orientation of the six carbonyl groups is different. While four groups are orientated to the magnesium center, the remaining other two groups do not show any coordination. This coordination is also found in solution, as all signals for the mesityl groups in the <sup>1</sup>H as well as <sup>13</sup>C-NMR are in the ratio 2:1 (solvent for NMR spectra is THF-d<sub>8</sub>). Furthermore, two additional donor molecules of THF coordinate to the magnesium atom (experimental details are included in the *Experimental Section*).



**Figure 2**. ORTEP representation for compound **5**. Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted, mesityl groups and THF molecules are displayed as wireframes for clarity. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations:  $\sum \alpha Ge(1) 308.38$ ,  $\sum \alpha Ge(2) 308.11$ , Ge(1)-C(1) 2.004 (3), Ge(1)-C(11) 2.006 (3), Ge(1)-C(21) 2.029 (3), C(1)-O(1) 1.252 (3), C(11)-O(2) 1.250 (3), C(21)-O(3) 1.223 (4), Mg(1)-O(1) 2.060 (2), Mg(1)-O(2) 2.043 (2), Mg(1)-O(4) 2.055 (2), Mg(1)-O(5) 2.047 (2), Mg(1)-O(THF) 2.093, C(31)-O(4) 1.167 (9), C(41)-O(5) 1.192 (6), C(51)-O(6) 1.220 (7), Ge(2)-C(31) 2.007 (8), Ge(2)-C(41) 1.988 (5), Ge(2)-C(51) 2.036 (6).

The next synthetic target was the synthesis of a HG 14 zinc enolate. Therefore, we reacted **2a** with 0.55 equivalents of ZnCl<sub>2</sub>. However, NMR spectroscopy performed after the addition of the zinc salt showed the formation of a new product alongside with remaining starting material in the ratio 1:1. Consequently we added another 0.55 equivalents of the ZnCl<sub>2</sub> to the reaction solution and observed the complete consumption of the starting material and the formation of one single product. After removal of the solvent, resuspension in toluene, and filtration, compound **6** was isolated in 83% yield (see Scheme 6). In contrast to the magnesium enolate, compound **6** shows only one signal for the three carbonyl groups and four for the aryl carbon atoms in the <sup>13</sup>C-NMR spectrum. This indicates a better solvent separation for this compound. NMR spectra and detailed assignments are provided in the *Experimental Section* and in the *Supporting Information*.



Scheme 6. Reaction of 2a with ZnCl<sub>2</sub>

Single crystals suitable for X-ray analysis were obtained by cooling the concentrated solution of **6** in THF to -30 °C (Figure 3). Compound **6** crystallized in the monoclinic space group *C*2/*c* and the unit cell contains four molecules. Again, the central germanium atoms are pyramidal and the Ge-C bonds are elongated. The structural analysis also sheds light on the experimental observations that no salt was formed. In contrast to the expected transmetalation, the first bimetallic HG 14 enolate is formed. This so-called zincate forms a dimer bridged by two potassium atoms, which have two different coordination

modes. K(1) is coordinative saturated by two chlorine atoms and four oxygen atoms. K(2) is coordinated by two THF molecules and four chlorine atoms. Moreover, the Zn-Ge bond length with 2.448 Å is slightly longer than their covalent radii (2.42 Å) and significantly longer than those of [Ph<sub>3</sub>Ge]<sub>2</sub>Zn,<sup>274</sup> (Me<sub>3</sub>Si)<sub>3</sub>GeZnCl<sup>275</sup> and [(Me<sub>3</sub>Si)<sub>3</sub>Ge]<sub>2</sub>Zn.<sup>276</sup>



**Figure 3**. ORTEP representation for compound **6**. Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted, mesityl groups and THF molecules are displayed as wireframes for clarity. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations:  $\sum \alpha Ge(1) 317.91$ , Ge(1)-C(1) 2.050 (3), Ge(1)-C(11) 2.046 (3), Ge(1)-C(21) 2.048 (3), C(1)-O(1) 1.224 (4), C(11)-O(2) 1.217 (4), C(21)-O(3) 1.221 (4), K(1)-O(1) 2.651 (2), K(1)-O(2) 2.742 (2), Zn(1)-Ge(1) 2.4475 (5), Zn(1)-Cl(1) 2.2793 (9), Zn(1)-Cl(2) (2.2688 9), K(1)-Cl(1) 3.1512 (11), K(2)-Cl(1) 3.1350 (11), K(2)-Cl(2) 3.1236 (9).

**Reaction of 2a with HgCl<sub>2</sub>**. On the basis of the observed reactivity with ZnCl<sub>2</sub> we wanted to investigate the outcome of the reaction of **2a** with mercury dichloride. Therefore, we reacted **2a** with equimolar amounts of HgCl<sub>2</sub> at -70 °C in THF (see Scheme 7). After removal of the solvent and the formed salts, the reaction control by NMR spectroscopy showed the formation of a sole germanium-based product with a characteristic shift for an acylgermane (<sup>13</sup>C NMR shifts for the carbonyl group  $\delta = 227.86$  ppm). We consequently assumed that the expected Ge-Hg-Cl bond was formed. However, structural analysis revealed our preliminary assumption to be wrong. Instead of the expected product a chlorotrimesitoylgermane **7** was formed in good yields (see Figure 4). Here, we assume that the initial compound is thermally instable and eliminates elemental mercury. Satgé and coworkers found a similar reactivity for their germanium-mercury derivative. <sup>277</sup>



Scheme 7. Reaction of 2a with HgCl<sub>2</sub>

Compound 7 crystallized in the monoclinic space group  $P2_1$  and the unit cell contains fourteen molecules. Additionally, this compound represents an interesting new building block as it can be used as precursor for further derivatization.



**Figure 4**. ORTEP representation for compound **7**. Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) with estimated standard deviations: Ge(1)-Cl(1) 2.173(3), Ge(1)-C(1) 2.018(11), Ge(1)-C(11) 2.070(11), Ge(1)-C(21) 2.023(11), C(1)-O(1) 1.215(15), C(11)-O(3) 1.201(14), C(21)-O(2) 1.175(14).

**Reaction of 2a with Tetrabutylammonium Bromide.** In several conferences, we were asked about the reactivity of our germenolates with ammonium salts. As the solubility is always an issue for this type of compounds, we thought that the ammonium counterions can contribute to solve this problem. Consequently, we set out and reacted **2a** with equimolar amounts of  $nBu_4NBr$  in toluene at 0 °C. After removal of the salts, compound **8** was isolated in 83% yield as red oil (see Scheme 8). NMR spectra and detailed assignments are provided in the *Experimental Section* and in the *Supporting Information*. As expected, compound **8** has good solubility in polar as well as unpolar solvents. Moreover, compound **8** is highly stable, as no degradation was observed even at room temperature.



Scheme 8. Reaction of 2a with *n*Bu<sub>4</sub>NBr

**Reaction of 2a with HCl.** Given the well-known reactivity of germanides with protic solvents to form germanes,<sup>278,279</sup> we investigated the reaction of **2a** with MeOH, EtOH as well as H<sub>2</sub>O. With these abovementioned reagents, we observed the formation of the expected product, however, we also found the formation of multiple uncharacterized side products. Therefore, we set out and tested the reaction with HCl dissolved in Et<sub>2</sub>O. To our delight, we found more selective reactivity and compound **9** was isolated in excellent yields (see Scheme 9). NMR spectra and detailed assignments are provided in the *Experimental Section* and in the *Supporting Information*. A Characteristic of compound **9** is the significant low-field-shifted <sup>1</sup>H-NMR signal for the hydrogen bonded to the germanium atom with  $\delta = 6.29$  ppm.



Scheme 9. Reaction of 2a with HCl/Et<sub>2</sub>O

The so-obtained compound 9 is also an interesting precursor molecule, as the labile Ge-H bond can be used for the formation of selected examples of oligoacyldigermanes. Therefore, we reacted 9 with an organozinc and an organomercury reagent.

**Reaction of 9 with tBu<sub>2</sub>Zn.** Following the seminal work of Apeloig and coworkers who presented the first examples of radical activation of Si-H bond with organozinc reagents,<sup>280</sup> we reacted 9 with 0.5 equivalents of tBu<sub>2</sub>Zn. After the addition of the organozinc reagent, an orange precipitate was immediately formed, which was filtered off. However, in the reaction solution we found significant amounts of unreacted starting material and moreover the tBu2Zn was completely consumed. Therefore, we attempted to characterize the orange precipitate and found that the compound decomposes immediately in polar solvents (i.e. THF, Et<sub>2</sub>O) to a complex product mixture with no traces of the desired product. In unpolar solvents, the compound has a very low solubility, which prevented a complete characterization. However, the <sup>1</sup>H-NMR spectrum indicated that compound 9 reacts with  $tBu_2Zn$  to form an unexpected product. Unfortunately, it was not possible to obtain a <sup>13</sup>C-NMR spectrum of sufficient quality due to low solubility. First we assumed that this product is an intermediate as a significant amount of starting material was still found in the reaction solution. Consequently, we prolonged the stirring at room temperature (48h) and changed the reactions conditions (90 °C for 24h), but no other product was found. The structural determination shed light on the structure of this compound. In Figure 5, the structure of compound 10 is depicted. As assumed, the triacylgermane reacts with  $tBu_2Zn$ , but after the first radical reaction, the zinc atom is coordinative saturated by two oxygen atoms and this prevented a further reaction of this compound. Moreover, based on the sterical hindrance, we found three signals for the mesityl protons in the <sup>1</sup>H-NMR spectrum.



**Figure 5**. ORTEP representation for compound **10**. Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted and the mesityl groups are displayed as wireframes for clarity. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations:  $\sum \alpha Ge(1) 313.89$ , Ge(1)-C(1) 2.019 (3), Ge(1)-C(11) 2.026 (18), Ge(1)-C(21) 2.050 (19), C(1)-O(1) 1.242 (2), C(11)-O(2) 1.244 (2), C(21)-O(3) 1.215 (2), Zn(1)-O(1) 2.1211 (13), Zn(1)-O(2) 2.1181 (13), Zn(1)-Ge(1) 2.4902 (3).

Compound **10** crystallized in the triclinic space group P-*1* and the unit cell contains two molecules. The central germanium atoms are again pyramidal and the Ge-C bonds are significantly elongated.

Moreover, the Zn-Ge bond length is significantly elongated in comparison to their covalent radii and to comparable examples.<sup>274–276</sup> On the basis of the structural analysis, we re-evaluated our reaction and reacted **9** with equimolar amounts of  $tBu_2Zn$  to determine the selectivity of this reaction. To our delight, we found the reaction is very selective and that compound **10** was isolable nearly quantitatively (see Scheme 10).



Scheme 10. Reaction of 9 with tBu<sub>2</sub>Zn

**Reaction of 9 with tBu<sub>2</sub>Hg.** With  $tBu_2Hg$ , the metalation of the Ge-H bond was much smoother. Compound **9** was reacted in *n*-heptane with tBu<sub>2</sub>Hg and stirred at 70 °C for 18 h. The corresponding digermylmercury compound **11** was obtained in 81% yield (see Scheme 11). NMR spectra and detailed assignments are provided in the *Experimental Section* and in the *Supporting Information*.



Scheme 11. Reaction of 9 with tBu2Hg

**NMR spectroscopy.** The observed <sup>13</sup>C-NMR shifts of the carbonyl C atoms of all isolated germenolates **2a**, **3a-c**, **4a-c**, **5**, **6** and **8** were found in the region between  $\delta$ =247.83 and  $\delta$ =274.88 ppm, which is typical for carbonyl groups attached to negative charged germanium atoms. In contrast to this, all carbonyl C atoms of acylgermanes **7** and **9-11** were found significantly high field shifted between  $\delta$ =227.86 and  $\delta$ =238.17. Again, this correlates well with all carbonyl C shifts of other known acylgermanes (see Table 1).<sup>72,73,81,82</sup>

Table 1. <sup>13</sup>C NMR shifts of the carbonyl atoms for compounds 3a-c, 4a-c, 5 and 6-11

Com.	<sup>13</sup> C-NMR (ppm)	Com.	<sup>13</sup> C-NMR (ppm)	Com.	<sup>13</sup> C-NMR (ppm)
2a	263.14 <sup>[a]</sup>	4b	261.15 <sup>[b]</sup>	8	261.45 <sup>[b]</sup>
<b>3</b> a	263.75 <sup>[a]</sup>	<b>4</b> c	260.99 <sup>[b]</sup>	9	231.20 <sup>[b]</sup>
3h	262 13 <sup>[a]</sup>	5	247.83 <sup>[a]</sup>	11	238 17 <sup>[b]</sup>
50	202.15	5	274.88 <sup>[a]</sup>	11	230.17
3c	261.66 <sup>[a]</sup>	6	248.75 <sup>[a]</sup>		
<b>4</b> a	262.68 <sup>[b]</sup>	7	227.86 <sup>[b]</sup>		

 $^{\rm a}$  measured in THF-d\_8 at RT;  $^{\rm b}$  measured in C<sub>6</sub>D<sub>6</sub> with 18-crown-6 at RT

## CONCLUSION

In summary, we investigated the synthesis of a variety of new triacylgermenolates by a single-electrontransfer reaction or by a direct approach. The single-electron-transfer reactions were induced by the respective alkali metals (sodium, rubidium or cesium). In all cases the formation of triacylgermenolates (3a-c) was observed. However, the high solubility of the rubidium and cesium derivative prevented the complete isolation. For the direct approach, the respective tris(trimethylsilyl)germanides were synthesized by the base-mediated desilvlation of tetrakis(trimethylsilvl)germane with metal-tertbutoxides (NaOtBu, RbOtBu and CsOtBu) and reacted with three equivalents of mesitoylfluoride. The addition of [18]-crown-6 was necessary to induce a precipitation of the formed germenolate in Et<sub>2</sub>O. Compounds 4a-c were isolated in good to excellent yields and completely characterized. Furthermore, we performed selected transmetalation of the potassium substituted germenolate 2a with MgBr<sub>2</sub>, ZnCl<sub>2</sub> and HgCl<sub>2</sub>. In the case of the magnesium salt, we found the formation of the expected magnesium bridged derivative 5 in excellent yield, which represents the first magnesium coordinated HG 14 enolate. ZnCl<sub>2</sub> reacts with 2a under the formation of the first bimetallic HG 14 enolate 6. The attempted transmetalation with HgCl<sub>2</sub> did not lead to the expected product. Instead the formation of the chlorotrimesitoylgermane 7 was observed. Furthermore, we reacted 2a with  $nBu_4NBr$  and found the selective formation to the corresponding ammonium germenolate 8. The reaction of 2a with HCl/Et<sub>2</sub>O leads to the formation of the corresponding acylgermane 9. Compound 9 was reacted with tBu<sub>2</sub>Zn and tBu<sub>2</sub>Hg in order to synthesize oligoacyldigermanes. While the reaction of 9 with  $tBu_2Hg$  yields the expected digermylmercury compound 11, the reaction with  $tBu_2Zn$  stops after the first radical reaction and compound 10 is formed quantitatively. Further studies to investigate the reactivity of these new germenolates are currently in progress. In addition, we are currently testing compound 7 as new building block for further derivatization.

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# **1.3.8.** Synthesis and Characterization of Diacylgermanes: Persistent Derivatives with Superior Photoreactivity

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## Abstract

Acylgermanes are known as highly efficient photoinitiators. In this contribution, we present the synthesis of new diacylgermanes **4a-e** via a multiple silyl abstraction methodology. The method outperforms the state-of-the-art approach (Corey–Seebach reaction) towards diacylgermanes in terms of group tolerance and toxicity of reagents. Moreover, these compounds are decorated with bulky mesityl groups in order to improve their storage stability. The isolated diacylgermanes were characterized by multinuclear NMR-, UV/Vis spectroscopy and X-ray crystallography, as well as photolysis experiments (photobleaching) and photo-DSC measurements (photopolymerization behavior). Upon irradiation with an LED emitting at 385 nm, all compounds except for **4a** and **4c** bleach efficiently with quantum yields above 0.6. Due to their broad absorption bands, the compounds can be also bleached with blue light (470 nm), where especially **4e** bleaches more efficiently than Ivocerin<sup>®</sup>

# A Series of New Diacylgermanes



## Introduction

State-of-the-art visible light initiators for photo-induced free radical polymerization are used for a variety of different applications such as 3D-printing,<sup>205,206</sup> tissue engineering,<sup>281,282</sup> coatings<sup>207</sup> and dental applications.<sup>208,209</sup> The vast majority of these state-of-the-art initiators decompose into radical species *via* Norrish type I ( $\alpha$ -cleavage). Modern Norrish type I initiators absorb light above 400 nm e.g. acylphosphines,<sup>212,223,283,284</sup> acylstannanes<sup>73,191</sup> and acyl-germanes.<sup>18,21,81,82,190,197,214,215</sup>

Especially the latter were intensively investigated in the last two decades, which boosted the number of available synthetic pathways towards acylgermanes significantly. However, di(4-methoxybenzoyl)diethylgermane (Ivocerin<sup>®</sup>), a commercially available diacylgermane, is synthesized *via* a complex procedure, which relies on a Corey-Seebach reaction followed by column chromatography and consequently results in the high costs of this PI (Chart 1).<sup>213</sup> Another disadvantage is the inefficient curing depth at wavelengths above 500 nm.<sup>18</sup> Our group has introduced a new one-pot synthetic protocol providing tetraacylgermanes Ge[C(O)R]<sub>4</sub> (R = aryl) in high yields (Chart 1).<sup>21</sup> However, most implemented acylgermanes as initiators have stability issues in various solvents limiting the field of applications.



Chart 1: The state-of-the-art germanium-based photoinitiators.

Here, we introduce an easy to perform synthetic pathway towards diacylgermanes **4a-f** with bulky mesityl groups, avoiding the Corey-Seebach reaction. The introduction of these mesityl groups leads to an increased stability in comparison to the state-of-the-art germanium based photoinitiators. Moreover, the broad absorption band of these compounds lead to a good applicability in the field of photopolymerization.

#### **Results and Discussion**

Synthetic Procedures: The entry into this chemistry is provided by the easy to perform synthetic protocol towards dimesityldi(trimethylsilyl)germane 2. Subsequently 2 was reacted with equimolar amounts of KOtBu and [18]-crown-6 generating the germanide 3 as crucial intermediate. On the one hand the addition of [18]-crown-6 is necessary to stabilize the anion and on the other hand the usage of crown ether circumvents the introduction of sulfur protecting groups and therefore is more sustainable. Analytical and spectroscopic data clearly support the structure of 3 (for details consult the Experimental Section and the *Supporting Information*). This germanide was added to the respective twofold excess of acid fluoride *in situ* yielding the desired diacylgermanes 4a-e in good yields (see Scheme 1). Analytical and spectroscopic data that support the structural assignment are given in the Experimental Section, together with experimental details. Particularly striking is the possible synthesis and isolation of compound 4e, where a benzothiophene group is substituted at the carbonyl moiety, as the introduction of heterocyclic groups is not possible with the Corey-Seebach reaction. Compound 4f was also formed with this protocol, unfortunately due to the instability with silica gel it was not isolable.



Scheme 2. Synthetic Protocol towards Diacylgermanes 4a-f. <sup>a</sup>Yield determined by <sup>1</sup>H NMR analysis. <sup>b</sup>Isolated yield.

# **UV-Vis Spectroscopy**

The broad absorption band of compounds **4a-e** are centered at around 410 nm (see Figure 1), which can be allocated to the  $n-\pi^*$  transition. This band is responsible for the photo-induced cleavage of the Ge-C bond. In comparison to Ivocerin<sup>®</sup> these new diacylgermanes show broader absorption bands, which results in a bathochromic shift of their absorption edge. Consequently, **4b-e** absorb light above 450 nm whereas the commercial PI, Ivocerin<sup>®</sup>, has a weak performance at this wavelength. In comparison to tetra(*o*-toluoyl)germane **5** and tetra(mesitoyl)germane **6** as representative examples of tetraacylgermanes, **4a-e** have similar absorption edges, however lower extinction coefficients, which is due to the presence of only two chromophore groups at the diacylgermanes, compared to the four chromophores in the case of tetraacylgermanes.



**Figure 2.** Absorption spectrum of synthesized compounds **4a-e** compared with the commercially available Ivocerin<sup>®</sup>, tetra(*o*-toluoyl)germane (**5**) and tetra(mesitoyl)-germane (**6**) with a concentration of  $1 \times 10^{-3}$  M in chloroform.

#### **DFT** Calculation

Based on the X-ray data, we have optimized the geometries of **4a-4e** by DFT. Basically, the calculated geometries correspond with the experimental data. For **4a**, an additional, more stable conformer ( $E_{rel} = 8.2 \text{ kJ/mol}$ ) was found. However, the electronic transitions calculated for the latter isomer were essentially identical with those computed for that corresponding to the X-ray structure. The vertical excitation energies (TDDFT) and are presented in the *Supporting Information* (Table S3 and Table S4).

The TDDFT calculated excitation spectra of **4a-e** agree well with the experimental UV/Vis spectra (Figure 2). The first absorption band at ca. 420 nm consists of two vertical excitations, HOMO $\rightarrow$ LUMO and HOMO $\rightarrow$ LUMO+1. Both transitions are n-  $\pi^*$  transitions. The HOMO is localized on both oxygen lone pairs of the C=O groups. LUMO and LUMO+1 are both linear combinations of the C=O  $\pi$ -orbitals with contributions of the neighboring aromatic system. The influence of substitution on orbital energies and localization can be explained by considering the electronic donating (EDG) effects of the substituents. The methyl group is inductive electronic donating and the methoxy group is mesomeric electronic donating. Consequently, the presence of EDG groups (Me in **4a** and **4c** and OMe in **4d**) increase the electron density of the HOMO orbital on the aromatic systems. Additionally, both EDG groups reduce the HOMO-LUMO-gap slightly compared to the unsubstituted **4b** (Table S4), and, thus, cause a bathochromic shift (see Table S3 and Figure 2).

The extension of the  $\pi$  system in **4e** by the annelated thiophene also leads to a red-shift compared with **4a–d**. For **4e** the four calculated transitions between 411 and 447 nm are in good consent with the rather broad absorptions between ca. 400 and 470 nm. Whereas the lines at 411, 431, and 447 nm possess two dominating components contributions, that at 443 is dominated by the HOMO-LUMO transition (Table S3).



Figure 3 shows the relevant orbitals for the first two vertical excitations of **4b**. and **4e**. For all other compounds the relevant orbitals can be found in the *Supporting Information* (Figure S34)

Figure 2. Simulated spectrum of 4a-e together with the vertical transitions (vertical lines).

In particular, the dihedral angle between the aromatic substituent and the adjacent acyl group directs the electronic properties of the diacylgermanes. The bulky mesityl group in **4a** causes an almost perpendicular arrangement of the C=O group and the  $\pi$ -plane of the mesityl substituent (dihedral angle = 75.8°) whereas the  $\pi$ -system and the C=O group are almost coplanar in **4e** (3,28°) and **4c** (21.3°) > **4d** (16.36°) > **4b** (12.4°) being "intermediate" cases.

Consequently, in **4a**, the electron density is almost entirely localized at the acyl group (Figure S34). Solely, HOMO-1 indicates distinguishable coefficients at one mesityl group. For **4c–4e** with smaller dihedral angles delocalization is more pronounced rationalizing the red shifts in the UV/VIS spectra.



Figure 3a. (a) Relevant orbitals for the first two vertical excitations of 4b. Figure 3b. (b) Relevant orbitals for the first two vertical excitations of 4e.

#### Photobleaching

Efficient curing of photoinitiator/monomer mixtures is crucial for applications like dental restoration, therefore steady-state photolysis experiments were performed to assess the photobleaching behavior of the compounds. To that end, degassed solutions of **4a-e** in a 1/1 (v/v) mixture of toluene/methyl methacrylate (with absorbance of about 0.7 at 385 nm) were irradiated with two different low power LEDs with emission maxima at about 385 and 470 nm (LED385 and LED470; described in the Experimental Section of the *Supporting Information* in more detail) – emission wavelengths, which are also found in commercial dental lamps.<sup>217</sup>
Figure 4 shows the time traces of the normalized absorbances when irradiating with LED385 or LED470. It can be seen that **4a** and **4c** bleach least efficiently, whereas **4d** is almost comparable to Ivocerin<sup>®</sup> or to **6**. From an exponential fit of the concentration traces, the quantum yields of decomposition can be determined using the procedure by Stadler et al.<sup>203</sup> The compounds **4a** and **4c** feature the smallest quantum yields (0.20 and 0.49, respectively), while the quantum yields of the other compounds are above 0.62 (see Table 1). For compound **4d** a higher quantum yield comparable to the one of Ivocerin<sup>®</sup> ( $\phi = 0.83$  <sup>24</sup>) is obtained. We ascribe this to the electronic properties of the methoxy groups having a compatible effect when residing in either *o*- or *p*-position of the benzoyl substituents. Despite the fact, that **4c** and **4e** show nearly identical extinctions above 450 nm (see Figure 1), photobleaching of **4e** with the blue LED emitting at 470 nm is more efficient due to its higher quantum yield of decomposition and even faster than Ivocerin<sup>®</sup> (see Figure 4b).



**Figure 4:** Steady-state photolysis of **4a-e** with a) LED385, b) LED470 in toluene/MMA (1/1 v/v). The absorbance traces are normalized to the initial absorptions at the observation wavelengths (maxima of  $n/\sigma$ - $\pi$ \* transitions; **4a**: 387 nm, **4b**: 413 nm, **4c**: 413 nm, **4d**: 399 nm, **4e**: 419 nm). Data for Ivocerin<sup>®</sup> and tetramesitoylgermane (**6**) were taken from ref.<sup>81</sup>

compound	$\lambda_{max,exp}$ [nm]	$\varepsilon$ [M <sup>-1</sup> cm <sup>-1</sup> ] at $\lambda_{max,exp}$	Ф (385 mm)
<b>4</b> a	387	903	$0.20\pm0.01$
<b>4b</b>	413	510	$0.68\pm0.02$
<b>4</b> c	413	624	$0.49\pm0.02$
<b>4d</b>	399	495	$0.83\pm0.02$
<b>4e</b>	419	606	$0.62\pm0.01$

**Table 2:** Wavelength of  $n/\sigma - \pi^*$  absorption maxima and extinction coefficients (in toluene/MMA 1/1 (v/v)) and determined quantum yields of **4a-e**.

## NMR spectroscopy

NMR spectra and detailed characterization of **4a-f** are provided in the *Supporting Information*. All compounds show very similar <sup>13</sup>C chemical shifts for the carbonyl carbon between 219.47 ppm and 240.67 ppm, which is characteristic for the carbonyl groups directly linked to the germanium atom.

## Storage stability tests

Low long-term stability in various solvents (such as chloroform, benzene or toluene) is a drawback of Ivocerin<sup>®</sup> and teraacylgermanes limiting the field of applications. By introducing bulky mesityl groups at the germanium atom the storage stability was drastically improved. UV/Vis spectroscopy as well as NMR spectroscopy were used to determine the storage stability of Ivocerin<sup>®</sup>, tetra(*o*-toluoyl)germane **5** and compounds **4a-e**.

For the UV/Vis method, all acylgermanes were measured in chloroform with a concentration of  $1 \times 10^{-3}$  M and the spectra were recorded once a week over a period of 21 days. To confirm the stability in MMA, UV/Vis spectra of Ivocerin<sup>®</sup>, reference compound **5**, compound **4c** and **4d** were recorded once a week over a period of 21 days with a concentration of  $1 \times 10^{-3}$  M. In case of the NMR method, the measurements were performed in degassed CDCl<sub>3</sub> and C<sub>6</sub>D<sub>6</sub> (0.01 M in 0.5 mL). Once a week over a period of 21 days a spectrum of those were recorded.

During these long-term tests, the NMR tubes, as well as the brown glass volumetric flask for the UV/Vis measurements were sealed with parafilm and stored in the dark. As representative example, compound **4e**, as well as the spectra of Ivocerin<sup>®</sup> and tetra(*o*-toluoyl)germane for comparison, are shown in Figure 5 (UV/Vis data) and Figure 8 (NMR data, left: in  $C_6D_6$ , right: in CDCl<sub>3</sub>).

The measurements in MMA are shown in Figure 6. All other spectra can be found in the *Supporting Information*. As shown in Figure 5, the newly synthesized compound **4e** is stable and even after 21 days no degradation is observed. In contrast to that the absorption of Ivocerin<sup>®</sup> and **5** slightly decrease (see Figure 5b-c).

Moreover, we could confirm by our stability tests that all investigated diacylgermanes are stable in MMA (Figure 6a-c). To conclude, the commercial PIs degrade in solution, in particular in chloroform as well as in benzene, whereas the new synthesized compounds **4a-e** are significantly more stable and show no degradation. In monomers, like in MMA, diacylgermanes are stable over time.



**Figure 5:** Comparison of the long-term stability in solution  $(1*10^{-3} \text{ M in chloroform})$  detected by UV-Vis spectroscopy. Zoomed in part of the UV-Vis spectra of **a**) compound **4e**, **b**) Ivocerin<sup>®</sup> and **c**) **5**.



**Figure 6:** Comparison of the long-term stability in solution (1\*10<sup>-3</sup> M in MMA) detected by UV-Vis spectroscopy. **a) 4c, b) 4d** and **c)** Ivocerin<sup>®</sup>.

The same statement can be made after measuring the NMR spectra of all compounds. The newly synthesized compounds (*e.g.* **4e**) do not show any degradation. Even after 21 days, the spectra remain unaffected (see Figure 8a and b). On the opposite, Ivocerin<sup>®</sup> and **5** already show degradation after 7 days.

During the course of this experiments the degradation product, the aldehyde, get more and more dominant, until only the degradation product is present (Table 2 and Figure 8). Although the acute toxicity of aldehydes is low, the exposure to aldehydes causes irritation of the skin, eyes and mucous membranes of the respiratory passage. As our new presented initiators **4a-e** do not show any formation of these degradation product, we think that this is an important step forward in this research field.

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**Table 3:** Formed aldehyde [%] as degradation product during the stability test monitored by <sup>1</sup>H analysis of Ivocerin<sup>®</sup> and compound **5** after 7, 14 and 21 days in benzene and chloroform. In case of **4e** 0 % aldehyde is formed over the measured time.

compound	solvent	days	aldehyde formation [%]
		7	15
	$C_6D_6$	14	28
I		21	50
Ivocerin		7	18
	CDCl <sub>3</sub>	14	32
		21	100
		7	25
	$C_6D_6$	14	62
5		21	100
5	CDCl <sub>3</sub>	7	44
		14	73
		21	100

## X-Ray crystallography

Crystals suitable for single-crystal XRD were obtained for compounds **4a-e**. Compound **4e** is shown as representative example (Figure 7), the other structures can be found in the *Supporting Information*. The torsion angle between the C=O bond and the aromatic plane vary a lot among the different substituents. The evaluated data of the bond lengths are slightly elongated compared to the average Ge-C bond  $(1.97 \text{ Å})^{221}$  and the average C=O bond (1.19 Å) (Table 3).<sup>222</sup>

**Table 4:** Mean bond lengths d [Å] and torsion angles between the C=O group and the aromatic ring plane [°] of compounds **4a-e.** 

compound	d <sub>Ge-C</sub>	d <sub>C=0</sub>	∠O=C-R
<b>4</b> a	2.060	1.213	68.45
<b>4</b> b	2.041	1.219	7.95
<b>4</b> c	2.044	1.217	25.54
<b>4d</b>	2.033	1.217	13.19
<b>4</b> e	2.032	1.223	1.72



**Figure 7:** ORTEP representation of **4e**. Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. The torsion angle (mean value) between the C=O group and the aromatic ring plane of the thiofuran group is  $1.72^{\circ}$ .



**Figure 8**: Representation of the stacked <sup>1</sup>H NMR spectra (300 MHz) of the respective compound (0.01 M in 0.5 mL) in the corresponding degassed solvent, left: in  $C_6D_6$  (61.7 ppm H<sub>2</sub>O) right: in CDCl<sub>3</sub> (26 ppm H<sub>2</sub>O). a) shows

compound **4e** in C<sub>6</sub>D<sub>6</sub>, b) compound **4e** in CDCl<sub>3</sub>, c) Ivocerin<sup>®</sup> in C<sub>6</sub>D<sub>6</sub>, d) Ivocerin<sup>®</sup> in CDCl<sub>3</sub>, e) **5** in C<sub>6</sub>D<sub>6</sub> and f) **5** in CDCl<sub>3</sub>.



**Figure 9:** Photo-DSC (left) and conversion plots (right) for the photopolymerization of HDDA with 0.3 mol% PI (top) and equal PCG concentration (bottom).

#### **Photo-DSC measurements**

Photo-DSC is a versatile method to evaluate the performance of PIs in polymerizable resins. One single measurement can give information about the reaction kinetics (time to reach the maximum heat flow ( $t_{max}$ ), maximum rate of polymerization ( $R_{p,max}$ ), time to reach 95% of final conversion ( $t_{95\%}$ )) and the double bond conversion (DBC, calculated from the overall reaction enthalpy  $\Delta H$  (peak area) and the theoretical heat of polymerization ( $\Delta H_{0,p}$ )).

The photopolymerization experiments were conducted in 1,6-hexanediol diacrylate (HDDA) as model monomer system (for further details consult the *Supporting Information*). Besides the synthesized PIs (i.e. **4a-4e**), the polymerization behavior of Ivocerin<sup>®</sup> and **5** was determined as reference.

The PI performance was analyzed at (1) equal molar PI (0.30 mol%) as well as (2) equal photocleavable group (PCG) concentration (0.15 mol% for **5**; 0.30 mol% for **4a-4e** and Ivocerin<sup>®</sup>), respectively. In general, the synthesized PIs provide kinetics and a DBC comparable to the reference compounds. In more detail, **4b** and **4d** show a slightly faster polymerization initiation than the other synthesized PIs and can be compared in their reactivity with **5** at the same PI concentration. However, measured at similar PCG concentration, they show a slightly slower turnover than Ivocerin<sup>®</sup>, but higher double bond conversion than both Ivocerin<sup>®</sup> and **5**. This correlates to the quantum yields measured at 385nm, where **4b** and **4d** show the highest values (Figure 9).

## Conclusions

To conclude, we were able to synthesize a variety of substituted diacylgermanes **4a-e** with bulky mesityl groups by the multiple silyl abstraction methodology, avoiding the Corey-Seebach reaction. Moreover, these compounds show excellent stabilities in solvents, which was determined by long-term stability tests in chloroform, benzene and MMA *via* UV/Vis spectroscopy and in chloroform and benzene *via* NMR spectroscopy. The new compounds show a broadening in their absorption bands with absorption above 450 nm, which makes photobleaching with blue light (470 nm) quite efficient. With **4e** a tailing up to 490 nm was observed. All compounds show high quantum yields above 0.5, the only exception is compound **4a**. DSC-measurements show good photopolymerization behavior for all synthesized compounds with double bond conversions comparable to or higher than Ivocerin<sup>®</sup>. Therefore, these new derivatives can be implemented in a broad field of applications. Further studies to probe the scope of these initiators are currently in progress.

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## 1.3.9. Synthesis of Stable Dianionic Cyclic Silenolates and Germenolates

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## Abstract

In this contribution a convenient synthetic method to obtain the previously unknown dianionic cyclic silenolates and germenolates is described. These dianions **2a,b** and **4a,b** are easily accessible *via* a one pot synthetic protocol in high yields. Their structural properties were analyzed by a combination of NMR, single X-ray crystallography, and DFT quantum mechanical calculations. Moreover, the reactivity of **2a,b** and



**4a,b** with selected examples of electrophiles was investigated. **2a** and **4a** were reacted with ClSi*i*Pr<sub>3</sub> to new examples of polysilanes and polygermanes with exocyclic double bonds. The reaction of **2b** with ClSiMe<sub>2</sub>SiMe<sub>2</sub>Cl led to the formation of an acyl bicyclo[2.2.2]octasilane **6**. Moreover, the reaction of **2a,b** and **4a,b** with MeI, as an example for a carbon centered electrophile, led to selective alkylation reactions at the negatively charged silicon and germanium atoms. The corresponding methylated structures **9a,b** and **10a,b** were formed in nearly quantitative yields. The competitive reactivity of the silyl and silenolate anion towards 1 equivalent ClSiMe<sub>3</sub> showed that the outcome of the reaction was strongly influenced by the substituent at the carbonyl moiety. **2a** reacted with 1 equivalent ClSiMe<sub>3</sub> to the corresponding cyclic silenolate **S**<sub>1</sub>**a**, which demonstrated that the silyl anion is more nucleophilic than the silenolate with attached aromatic groups. **2b**, on the other hand, reacted with 1 equivalent ClSiMe<sub>3</sub> to the bicyclic compound **11** *via* an intramolecular sila-Peterson alkenation reaction. These findings clearly showed that the alkyl-substituted silenolate is more nucleophilic than the silyl anion. This paper demonstrates that **2a,b** and **4a,b** have the potential to be used as unique building blocks for complex polysilane and polygermane frameworks.

### Introduction

The synthesis of defined polysilanes in which more than five silicon atoms are connected is challenging. The standard approaches for such polysilanes are Wurtz-type coupling<sup>285,286,287</sup> or Lewis acid-catalyzed rearrangement reactions.<sup>288</sup> These two methods generally give raise to structurally simple polysilanes with a low set of functionalities for further derivatization, which prevent the construction of molecules of even moderate complexity.

A potent strategy for the construction of structurally more challenging silicon frameworks is the use of di- or multi-functionalized starting materials such as  $\alpha, \omega$ -dianions. Gilman<sup>289,290</sup> and Hengge<sup>291,292</sup> were pioneers in this area and developed the cleavage of strained cyclosilanes to obtain dianions. Sekiguchi,<sup>293</sup> Tokitoh,<sup>241</sup> Kira<sup>294</sup> and Apeloig<sup>295</sup> also contributed with their groups in this research field and prepared some previously unknown 1,1-, 1,2- and 1,4dilithiooligosilanes. Marschner and Baumgartner, who introduced KOtBu into the field of polysilane chemistry, achieved a milestone in polysilane synthesis. Consequently, the construction of relative complex polysilanes could be accomplished in a straightforward way.<sup>271,296-298</sup> Recently, Klausen and co-workers established new phenyl substituted dianions.<sup>299</sup> These dianions were used as building blocks for the formation of defined polysilanes as well as for the synthesis of heteroelement substituted polysilanes.<sup>300–302</sup> Scheschkewitz et al. treated their hexasilabenzene with lithium naphthalenide and obtained a novel dianionic silicon cluster. This dianion turned out to be a valuable synthon for the generation of unprecedented molecular heterosiliconoids with boron and phosphorus directly incorporated into the cluster scaffold.<sup>303</sup> In addition, we just published a paper about the synthesis of a mixed substituted dianion, which allows the straightforward access to a hitherto unknown tricyclic polysilane (see Chart 1).<sup>304</sup> Nevertheless, the synthesis of mixed functionalized disilanides has not been reported so far, although these substances would represent ideal building blocks for highly complex silicon frameworks.



#### CHART 1.

As we have reported earlier, it is possible to synthesize and characterize cyclic silenolates as well as cyclic germenolates and convert them with suitable electrophiles in order to gain a new set of differently substituted acylsilanes as well as acylgermanes (see Chart 2).



Furthermore, we could show that the reaction of these enolates with chlorosilanes ClSiR<sub>3</sub> allowed straightforward access to silenes and germenes with exocyclic structures.<sup>126,258</sup> Due to the straightforward accessibility of these cyclic enolates, we saw the potential to investigate their chemical behavior in a greater depth. In this context, we have established a novel synthetic strategy for the synthesis of previously unknown dianionic cyclic silenolates and germenolates. The aim of this work is to investigate the spectroscopic properties and the reactivity of this new type of dianions with selected examples of electrophiles.

### **Results and Discussion**

**Synthesis of dianionic silenolates**. The reaction of the acylcyclohexasilanes **1a**,**b** with two equivalents KO*t*Bu led to the formation of compounds **2a**,**b**, whereby two different functionalized anionic silicon atoms were incorporated into one molecule (Scheme 1).



Scheme 1. Synthesis of Dianionic Compounds 2a,b.

To the best of our knowledge, **2a**,**b** represent the first examples of dianionic polysilanes bearing a silyl anion and a silenolate fragment in one molecule. The dianionic compounds **2a**,**b** were formed in the same fashion as previously described for the corresponding silenolates. Two major differences are worth to mention. First, the use of an appropriate solvent is highly important. We observed the formation of **2a**,**b** only in DME, Et<sub>2</sub>O and toluene. In the case of THF, no product was formed, probably due to the reaction of **2a**,**b** with THF leading to degradation. This was also described in the case of  $\alpha$ , $\omega$ -oligosilyldianions by Marschner et al.,<sup>296</sup> who observed that stable dianionic species were only formed under the use of DME or benzene/toluene with the addition of crown ethers. Second, the reaction is characterized by a two-step reaction sequence. The first 1 equivalent of KOtBu is consumed immediately (approximately 10 min), yielding the silenolates **S**<sub>1</sub>**a**,**b**. The second abstraction of the trimethylsilyl group is much slower and takes place within approximately 18 h. For isolation, **2a**,**b** were crystallized from Et<sub>2</sub>O/[18]-crown-6 at room temperature to give orange crystals of the 1:2 [18]-crown-6 adducts, which were obtained in isolated yields > 90 %. After filtration, the crystals can be stored at -30 °C in the absence of air even for prolonged periods. **2a,b** afforded crystals of sufficient quality for single crystal X-ray crystallography. The molecular structures are depicted in Figures 1 and 2; selected bond lengths and the sum of valence angles are summarized in Table 1.



**Figure 1.** ORTEP diagram for compound **2a** (1:2 adduct with [18]-crown-6). Thermal ellipsoids are depicted at the 50 % probability level. Hydrogen atoms are omitted for clarity.



**Figure 2.** ORTEP diagram for compound **2b** (1:2 adduct with [18]-crown-6). Thermal ellipsoids are depicted at the 50 % probability level. Hydrogen atoms are omitted for clarity.

**Table 1.** Selected bond lengths d [Å] and sum of valence angles  $\Sigma \alpha Si_{(1)}$ ,  $\Sigma \alpha Si_{(6)}$  and  $\Sigma \alpha C_{(1)}$  [deg] for **2a**,**b**.

	2a	2b		2a	2b
d Si <sub>(1)</sub> -C <sub>(1)</sub>	1.892	1.916	d Si <sub>(6)</sub> -K <sub>(2)</sub>	3.441	3.458
d Si <sub>(1)</sub> -K <sub>(1)</sub>	5.102	5.215	d Si <sub>(1)</sub> -K <sub>(2)</sub>	4.143	7.361
$d C_{(1)}$ - $K_{(1)}$	3.843	3.672	$\Sigma \alpha Si_{(1)}$	312.5°	314.4°
$d C_{(1)}$ - $O_{(1)}$	1.254	1.254	$\Sigma \alpha Si_{(6)}$	307.8°	306.1°
d K <sub>(1)</sub> -O <sub>(1)</sub>	2.614	2.579	$\Sigma \alpha C_{(1)}$	359.7°	360.0°

On the basis of the observed structural features, 2a,b are best described as acyl silyl anions (keto-form) with Si-C single bonds, C=O double bonds and markedly pyramidal central Si<sub>(1)</sub> atoms.

Interestingly in **2a** the  $K_{(2)}^+$  cation coordinates simultaneously to  $Si_{(1)}$  and  $Si_{(6)}$ . This is probably caused by a packing phenomenon. Furthermore, this simultaneous coordination is also the reason for **2a** to adopt the half boat conformation, while **2b** and **4b** (**4b** is the dianionic germenolate and will be introduced in the next section) adopt chair conformations. Additionally **2a** shows short  $Si_{(2)}$ -CH contacts which are less than the van der Waals radii of silicon and hydrogen. This can also explain its half boat coordination. A similar result in terms of Si-CH contacts was obtained by the group of Klausen.<sup>17</sup>

Synthesis of Dianionic Germenolates. The straightforward synthesis of 2a,b encouraged us to expand our new methodology to other starting materials. As we have reported previously, it is possible to synthesize cyclic acylgermanes 3a,b.<sup>126</sup> The reaction of these cyclic acylgermanes with two equivalents KO*t*Bu led to the formation of dianionic germenolates 4a,b (Scheme 2). Again, the reaction is characterized by a two-step reaction sequence with reaction rates similar to those of the corresponding acylsilanes.



Scheme 2. Synthesis of Dianionic Germenolates 4a,b.

For isolation, **4a,b** were crystallized from  $Et_2O/[18]$ -crown-6 at room temperature to give orange crystals of the 1:2 [18]-crown-6 adducts, which can be stored after filtration at -30 °C in the absence of air even for prolonged periods. **4b** afforded crystals of sufficient quality for single crystal X-ray crystallography. The molecular structure is depicted in Figure 3; selected bond lengths and the sum of valence angles are summarized in Table 2.



**Figure 3.** ORTEP diagram for compound **4b** (1:2 adduct with 18-cr-6). Thermal ellipsoids are depicted at the 50 % probability level. Hydrogen atoms are omitted for clarity.

**Table 2.** Selected bond lengths d [Å] and sum of valence angles  $\Sigma\alpha(Ge1)$ ,  $\Sigma\alpha(Ge2)$  and  $\Sigma\alpha(C1)$  [deg] for **4b**.

	4b		<b>4</b> b
$d Ge_{(1)}-C_{(1)}$	2.047	d Ge(2)-K(2)	3.635
$d Ge_{(1)}-K_{(1)}$	3.427	d Ge(1)-K(2)	6.671
$d C_{(1)}$ - $K_{(1)}$	3.335	$\Sigma \alpha Ge_{(1)}$	314.5°
$d C_{(1)}$ - $O_{(1)}$	1.248	$\Sigma \alpha Ge_{(2)}$	298.2°
d K <sub>(1)</sub> -O <sub>(1)</sub>	2.760	$\Sigma \alpha C_{(1)}$	359.6°

On the basis of the observed structural features, **4b** is best described as acyl germyl anion (ketoform) with a Ge-C single bond, a C=O double bond and markedly pyramidal central  $Ge_{(1)}$  and  $Ge_{(2)}$  atoms.

**NMR spectroscopy of 2a,b and 4a,b.** NMR data also supported that the dominant structure of **2a,b** and **4a,b** in solution is the keto form. Very similar <sup>13</sup>C chemical shifts were observed for the carbonyl C atom of the two compounds between  $\delta = 266.6$  ppm and 280.9 ppm in a typical range for carbonyl groups. Furthermore, **2a,b** and **4a,b** exhibit only two sharp SiMe<sub>2</sub> resonance lines in the <sup>29</sup>Si-NMR, which clearly suggest free rotation around the Si<sub>(1)</sub>-C<sub>(1)</sub> bond (Table 3). It was not possible to use THF-d<sub>8</sub> for **2b** and **4b** because a detectable degradation was found within minutes at room temperature.

	<b>2</b> [ppm]		<b>4</b> [ppm]		
	<b>a</b> Mes <sup>a</sup>	$\mathbf{b} \operatorname{Ad}^{\mathrm{b}}$	<b>a</b> Mes <sup>a</sup>	$\mathbf{b} \operatorname{Ad}^{\mathrm{b}}$	
δ <sup>13</sup> C ( <i>C</i> =O)	266.63	273.96	281.01	280.92	
δ <sup>29</sup> Si (SiMe <sub>3</sub> )	0.05	-1.14	0.93	0.36	
δ <sup>29</sup> Si (SiMe <sub>2</sub> )	-27.69	-26.48	-27.69	-23.45	
	-32.37	-31.31	-29.35	-25.40	
$\delta^{29}$ Si (Sig)	-67.70	-87.33	-	-	
0 'SI ( <i>SIQ</i> )	-189.08	-192.42	-	-	

Table 3. Selected <sup>13</sup>C- and <sup>29</sup>Si-NMR chemical shifts for the silenolates 2a,b and 4a,b.

 $\delta$  values relative to ext. TMS; " in THF-d\_8 at 25 °C; " in C\_6D\_6 at 25 °C.

**UV/Vis spectroscopy and TDDFT-PCM calculations.** Toluene was used as a solvent to determine the charge transfer behavior for the longest wavelength absorption band.<sup>305</sup> Figure 4 depicts the measured UV/Vis spectra of **2a**,**b** and **4a**,**b** in toluene together with their calculated frontier Kohn-Sham orbitals.





**Figure 4.** Measured UV/Vis spectra of **2a,b** and **4a,b** in toluene  $[1 \cdot 10^{-4} \text{ mol.L}^{-1}]$ , and the calculated frontier Kohn-Sham orbitals of **2a,b** at the TDDFT-PCM(toluene) CAM-B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) level of theory. Kohn-Sham orbitals of **4a,b** are similar in shape and energy (see Supporting Information).

In order to examine the differences between aromatic and saturated substituents at the carbonyl moiety, the mesityl- and adamantly-substituted derivatives **2a**,**b** and **4a**,**b** were investigated. All UV/Vis calculations were performed on the geometry-optimized X-ray crystal structures via TDDFT-PCM in toluene at the CAM-B3LYP/6-31+G(d,p) level of theory.<sup>306</sup> Noteworthy, CAM-B3LYP achieved a better consistency for dianions 2a,b and 4a,b in calculated vertical excitations than B3LYP, which was previously applied to UV/Vis calculations on silenolates  $S_1a,b$  and germenolates  $S_2a,b$ .<sup>126,259</sup> The silenolates 2a,b exhibit intense absorption maxima in the range between 433 and 450 nm, which are red-shifted in the order  $2b \rightarrow 2a$ . The same bathochromic trend  $4b \rightarrow 4a$  also applies to the germenolates 4a,b with absorption maxima between 420 and 447 nm. The acyl substituent (aryl vs. alkyl) significantly affects the HOMO orbital density and hence its shape, which ultimately leads to different reaction centers in conversion with electrophiles (see section below). The HOMO-1 and HOMO of 2a (Figure 4) correspond to the p<sub>z</sub>-orbital of the silenolate with a significant part of the corresponding silanide mixed in, respectively. This contribution makes the silanide equally nucleophilic regarding reactions of cyclic silenolates with aromatic acyl substituents. In contrast, the HOMO of **2b** only exhibits the  $p_z$ -character of the silenolate, whereas the HOMO-1 of **2b** shows the silanides orbital alone, allowing a site-specific functionalization. In addition, the energy difference between the HOMO-1 and the HOMO is in 2a significantly larger than in 2b (0.28 eV vs. 0.09 eV). Similar observations were made with the dianionic germenolates **4a**,**b**. Upon excitation, electron density is displaced into the  $\pi^*$ -orbital of the corresponding carbonyl orbitals. In the corresponding LUMOs of the aryl-substituted species 2a and 4a, our calculations additionally showed considerable conjugation of the carbonyl group and the aromatic  $\pi$ -systems, which is not possible for the alkyl-substituted silenolate **2b** and germanolate **4b**. As a consequence of this, the empty orbitals are energetically stabilized in the order  $2b \rightarrow 2a$ . This stabilization results in smaller excitation energies and in the observed bathochromic shifts of the corresponding absorption bands. The obtained experimental and computational data are summarized in Table 4 and show reasonable agreement.

	$\lambda_{max,exp}$	3	$\lambda_{max,calc}{}^a$	f	Assignment
	[nm]	[L.mol <sup>-1</sup> .cm <sup>-1</sup> ]	[nm]	J	Assignment
2a	450	6602	441	0.2102	$p_z \rightarrow \pi^*(CO/Aryl)$
<b>2b</b>	433	3730	428	0.1131	$p_z \rightarrow \pi^*(CO)$
4a	447	5753	435	0.1591	$p_z \rightarrow \pi^*(CO/Aryl)$
4b	420	2178	418	0.0858	$p_z \rightarrow \pi^*(CO)$

**Table 4.** Experimental and TDDFT-PCM(toluene) CAM-B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) calculated absorption bands  $\lambda$  in toluene, extinction coefficients  $\varepsilon$  resp. oscillator strengths f for **2a,b** and **4a,b**.

<sup>a</sup>  $\lambda_{max,calc}$  are corrected by a factor of 5 % due to a consistent overestimation of excitation energies with CAM-B3LYP.

Reactivity of 2a,b versus selected examples of chlorosilanes. The reactivity of 2a,b versus chlorosilanes parallels the observed reactivities for silenolates and silvl anions. The same reactivity was found by Ohshita and Ishikawa, by Marschner et al. and by our group.<sup>258,267,271,296,297,307</sup> Thus, **2b** with an alkyl group attached to the carbonyl moiety reacted with an equimolar amount of tetramethyldichlorodisilane (ClSiMe<sub>2</sub>SiMe<sub>2</sub>Cl) at 0 °C in THF with formation of the acyl bicyclo [2.2.2] octasilane 6. 6 was obtained in nearly quantitative yield (95 % yield). The asymmetrically substituted acylsilane **6** exhibits two  $^{29}$ Si resonance lines for the SiMe<sub>2</sub> groups near -37 ppm, which are not significantly influenced by the nature of the adamantoyl group. The two  $\delta^{29}$ Si values for the bridgehead Si atoms were measured near -131 ppm (characteristic for tetrasilyl-substituted silanes) and -77 ppm (characteristic for acylsubstituted quaternary silanes). The same tendencies were found earlier by Stueger et al. during the synthesis of a series of substituted bicyclo[2.2.2]octasilanes.<sup>308</sup> The aryl-substituted compound 2a exclusively afforded the O-silvlated silene 5 under the same conditions (compare Scheme 3). NMR spectral data of 5 (compare Experimental Section) are also typical for a Brooktype silene. <sup>13</sup>C and <sup>29</sup>Si signals characteristic for Si=C were observed at  $\delta^{29}$ Si = 32.8 ppm and  $\delta^{13}$ C = 198.9 ppm, respectively. **5** was obtained in a good yield (64 % yield).



Scheme 3. Reactivity of Dianionic Compounds 2a,b towards Chlorosilanes.

Reactivity of 4a,b versus selected examples of chlorosilanes. Furthermore, the reactivity of 4a,b versus chlorosilanes was investigated and parallels previously observed for germenolates and germyl anions.<sup>126,254</sup> The reaction of 4a with two equivalents ClSi*i*Pr<sub>3</sub> afforded the formation of the *O*-silylated germene 7 in excellent yields (compare Scheme 4). NMR spectral data of 7 (see the Experimental Section) are again typical for a Brook-type germene. A <sup>13</sup>C signal characteristic for Ge=C was observed at  $\delta^{13}$ C = 210.17 ppm. Interestingly, the reaction of 4b with an equimolar amount of ClSiMe<sub>2</sub>SiMe<sub>2</sub>Cl did not lead to the formation of the expected products 8, instead undefined polymeric material was formed.



Scheme 4. Reactivity of dianionic compounds 4a,b towards chlorosilanes.

The unsuccessful derivatization of **4b** with  $ClSiMe_2SiMe_2Cl$  encouraged us to investigate the reactivity of **4b** with two equivalents  $ClSiiPr_3$ . Again, no expected product formation was observed. The same experiment was furthermore repeated with **2b** and gave also rise to undefined polymer. Therefore, we reasoned that  $ClSiiPr_3$  is too sterically demanding to allow a M-Si (M =Si for **2b** and M=Ge for **4b**) bond formation in the presence of an adamantoyl group.



Scheme 5. Reactivity of dianionic compounds 2b and 4b towards ClSi(*i*Pr)<sub>3</sub>.

**Reactivity of 2a,b and 4a,b versus carbon centered electrophiles.** We selected MeI as a carbon centered electrophile, because it represents a benchmark reagent with numerous examples found in literature.<sup>257,259,307</sup> In the reaction of **2a,b** and **4a,b** with MeI, the same reactivities in terms of reaction sites were observed. In all cases, alkylation of the negatively charged silicon as well as germanium atoms were found in nearly quantitative yields (Scheme 6). Again the same tendency was published in the case of acyclic silenolates and silanides by Ohshita, Ottosson and Marschner earlier.<sup>257,267,296,297,307</sup> The methylated silicon **9a,b** and germanium derivatives **10a,b** were obtained as *cis/trans* mixtures. The silicon atoms of **9a,b** undergo a significant low field shift from -70 to -45 ppm (in the case of the acyl substituted silicon atom) and from -131 to -84 ppm (for the silyl substituted silicon atom). This is caused by

#### Chapter 1

the lower shielding of the methyl group in comparison to the trimethylsilyl group (see the Experimental Section).



Scheme 6. Reactivity of dianionic compounds 2a,b and 4a,b towards MeI.

Competitive Reactivity of the Silyl Anion and the Silenolate. Finally, we investigated which silanide is more nucleophilic, the silval anion or the silenolates. Therefore we reacted 2a,b with 1 equivalent trimethylchlorosilane (ClSiMe<sub>3</sub>) at -30 °C. The outcome of the reaction was again strongly dependent on the substituent at the carbonyl moiety and reflected our predictions from the computational analyses. 2a with an aryl group attached to the carbonyl moiety reacted with an equimolar amount of ClSiMe<sub>3</sub> to form the cyclic silenolate  $S_1a$ , making the silanide the more nucleophilic reaction center. 2b, on the other hand, reacted with an equimolar amount of ClSiMe<sub>3</sub> to the bicyclic oxahexasilabicyclo[3.2.1]octan-8-ide **11**, which clearly showed that the silenolate is more nucleophilic than the silvl anion in the case of an alkyl substitution. The formation of **11** can be rationalized by assuming the intermediate formation of the silanide 12, which subsequently rearranged to give the bicyclic carbanion 13 by an intramolecular sila-Peterson alkenation. Apparently, 13 is very unstable, losing its intense red color within minutes, presumably by the abstraction of one proton from the surrounding media to give **11** as the final product. Analytical and spectroscopic data (see Experimental Section) clearly supported the bicyclic structure of 11 (compare Scheme 7). Moreover, this compound was obtained by a previous study of our group.<sup>259</sup>



Scheme 7. Competitive reactivity of silyl anion and silenolate towards one equivalent CISiMe3.

### Conclusion

In summary, we synthesized the first examples of mixed functionalized compounds **2a**,**b** and 4a,b, which represent ideal building blocks for highly complex silicon frameworks. These dianions are easily accessible, can be isolated, and were fully characterized. Silenolates **2a**,**b** as well as the germenolates 4a,b adopt the keto-form in solution, irrespective of the nature of the R-group attached to the carbonyl moiety. Furthermore, the reactivity of **2a**,**b** and **4a**,**b** versus chlorosilanes was investigated as an example of a silicon centered electrophile. 2a and 4a reacted with ClSi*i*Pr<sub>3</sub> to give new examples of a polysilane and a polygermane with an exocyclic double bond. The reaction of 2b with ClSiMe<sub>2</sub>SiMe<sub>2</sub>Cl led to the formation of an acyl bicyclo[2.2.2]octasilane 6. Moreover, the reaction of 2a,b and 4a,b with MeI, as a carbon centered electrophile, led to selective alkylation reactions at the negatively charged silicon and germanium atoms. The methylated structures **9a**,**b** and **10a**,**b** were formed in nearly quantitative yields. Finally, we examined the competitive reactivity of the silvl anion and the silenolate towards one equivalent ClSiMe<sub>3</sub>. The outcome of the reaction was strongly influenced by the substituent at the carbonyl moiety, which was in alignment with our computational analysis. 2a reacted with one equivalent ClSiMe<sub>3</sub> to the corresponding cyclic silenolate  $S_1a$  and demonstrated that the silvl anion is more nucleophilic than the silenolate. In contrast to that, 2b reacted with one equivalent ClSiMe<sub>3</sub> to the bicyclic compound 11 via an intramolecular sila-Peterson alkenation reaction. This observation clearly showed that the alkyl substituted silenolate is more nucleophilic than the silvl anion. Further studies to probe the scope of these new dianions are currently in progress.

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# **1.3.10.** Synthesis of D-Galactose-Substituted Acylsilanes and Acylgermanes. Model Compounds for Visible Light Photoinitiators with Intriguing High Solubility

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# Abstract

A convenient synthetic method to obtain D-galactose-substituted acylsilanes and acylgermanes is described. These acyl group 14 compounds are easily accessible in good yields. Their structural properties were analyzed by a Visible Light Photoinitiator with good Solubility in Polar Solvents

structural properties were analyzed by a combination of NMR, single X-ray crystallography and UV/Vis spectroscopy. A D-galactose-substituted tetraacylgermane represents a new interesting visible light photoinitiator based on its absorption properties as well as its high solubility.



The demand and application of high performance photopolymers has been immensely growing in the last decades.<sup>204</sup> Today, their use is no longer restricted to the manufacture of microelectronic devices, coatings, adhesives, inks, printing plates, optical waveguides but also emerging fields of medicine (dental filling materials, artificial tissue, heart valves etc.) and fabrication of 3D objects.<sup>205–209</sup> The key component in such formulations is the photoinitiator (PI). On the basis of this, their synthetic pathway is required to be sustainable, environmental friendly and step economical.<sup>210</sup> Especially for medical applications photoinitiators and their photoproducts have to be non-toxic and highly efficient. Among other promising PI systems, acylgermanes have emerged as suitable radical precursors generating acyl- and germyl-centered radicals upon irradiation, which add very rapidly to double bonds of various monomers.<sup>18,190,197,213,309–311</sup> Moreover, they have the advantages of significantly red-shifted absorption bands and reduced toxicity compared to the frequently applied phosphorus-based PIs.<sup>223,284,312,313</sup> The commercially available Ge-based photoinitiator [bis(4methoxybenzoyl)diethylgermane (Ivocerin))]<sup>18</sup> still suffer from inefficient curing depth at wavelengths > 500 nm (compare Chart 1). Furthermore, the synthetic strategy towards Ivocerin relies on a multistep synthesis (based on the Corey-Seebach reactions), which consequently requires a complex purification process.<sup>213</sup>



Chart 2: The state-of-the-Art Germanium-Based Photoinitiators.

Recently, we established a synthetic method to obtain tetraacylgermanes by a facile one-pot synthetic protocol (Chart 1). Their low toxicity and fast photobleaching, even upon irradiation with high-wavelength visible light were demonstrated.<sup>21</sup> Moreover, the good group tolerance of this synthetic protocol enabled us to synthesize a large variety of different substituted tetraacylgermanes. This "fine-tuning" gave us the opportunity to design photoinitiators for different applications (e.g. dental filling, 3D-printing etc.).<sup>215</sup> However, a huge drawback of symmetrical tetraacylgermanes are their high melting points, which are responsible for the low solubility, limiting the field of applications.

Herein, we set out and investigated new synthetic pathways towards acyl group 14 compounds decorated with monosaccharides to induce better solubility. Moreover, the saccharides bear the possibility of subsequent deprotection, which can lead to water soluble compounds. To proof the viability of our project, we first synthesized a monoacylsilane **1** and a monoacylgermane **2**, respectively. The acyl moiety bears a di-*O*-isopropylidene-protected galactose moiety. For both central atoms the entry into this chemistry is provided by the formation of the corresponding potassium tris(trimethylsilyl)-silanide **1K** and –germanide **2K**. These anions are conveniently achievable by reaction of tetrakis(trimethylsilyl)-silane and -germane with equimolar amounts of KO*t*Bu in polar solvents. Subsequently, these anions were reacted with equimolar amounts of 1,2;3,4-di-*O*-isopropylidene- $\alpha$ ,D-galacturonic acid chloride which allows for generating the respective acyl compound **1** and **2**, in good yields (Scheme 1).



Scheme 3: Synthesis of Monoacylsilane 1 and Monoacylgermane 2.

NMR Spectra and detailed characterization for **1** and **2** are provided in the *Supporting Information*. Both derivatives show very similar <sup>13</sup>C chemical shifts for the carbonyl C atom at 246.0 ppm (for **1**) and at 242.5 ppm (for **2**), which is characteristic for carbonyl groups directly linked to silicon or germanium atoms. The <sup>29</sup>Si-NMR spectra of **1** and **2** showed one resonance

for the three trimethylsilyl groups at -11.20 ppm (for 1) and -4.85 ppm (for 2) and for compound 1 one resonance was found for the silicon atom bearing the acyl group near -70 ppm. The molecular structure of 1 and 2, as determined by single-crystal X-ray crystallography, are depicted in Figure 1 and 2. Both compounds crystallized in the orthorhombic space group  $P2_12_12_1$  with unexceptional bond lengths and angles.



**Figure 3:** ORTEP Representation for compound **1**. Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) with estimated standard deviations: Si(1)-Si(4) 2.3549 (14), Si(1)-Si(2) 2.3622 (14), Si(1)-Si(3) 2.3570 (14), Si(1)-C(6) 1.952 (4), O(2)-C(6) 1.222(4).

To determine the position of the longest wavelength absorption, the UV/Vis absorption spectra of compounds 1 and 2 were recorded and compared to a structurally related monoacylgermane 3(1,1,1-tris(trimethylsilyl)-benzoylgermane).



**Figure 4:** ORTEP Representation for compound **2**. Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) with estimated standard deviations: Ge(1)-Si(1) 2.3789 (9), Ge(1)-Si(2) 2.3809 (8), Ge(1)-Si(3) 2.3822 (8), Ge(1)-C(6) 2.024 (2), O(2)-C(6) 1.416 (3).

Both compounds show long-wavelength absorptions bands  $\lambda_{max}$  values between 325 and 400 nm tailing into the visible light region. Compared to compound **3**, an example of an aryl substituted acylgermane, a significantly hypsochromic shift occurs (Figure 3). This is not surprising because it is well known that aliphatic substituents at the carbonyl moieties undergo the same hypsochromic shift.<sup>41,314</sup> Moreover, the absorption spectrum of **1** and **2** exhibits considerable fine

structure consisting of four main bands which is not unusual and parallels the behavior of structurally related acyl group 14 compounds.<sup>23</sup> Nevertheless, in order to synthesize high performance visible light photoinitiators these blue shift significantly lowers the activity of these derivatives, when visible light is used.



Figure 5: Absorption spectrum of compounds 1 and 2 compared with the monoacylgermane 3 with a concentration of  $1 \cdot 10^{-3}$  M in acetonitrile.

On the basis of these results, we introduced a phenyl spacer at the C<sub>6</sub> position of the D-galactose moiety. The starting point of our manipulations was a Mitsunobu reaction of the 1,2:3,4-di-O-isopropylidene- $\alpha$ ,D-galactose with methyl 4-hydroxybenzoate under standard Mitsunobu reaction conditions to give respective 6-O-(4-methyloxycarbonylphenyl)-d-galactose moiety **4** in good yields. The analytical data are consistent with the proposed structure and can be found in the *Supporting Information*. The next step was the hydrolysis of the terminal methyl ester in compound **4** by saponification under conventional Zemplén conditions which led to 6-O-benzoic acid d-galactose derivative **5**. The desired acid fluoride D-galactose moiety **6** was synthesized by the reaction of the carboxylic acid **5** with equimolar amount of diethylaminosulfur trifluoride (DAST) in dichloromethane in excellent yields (Scheme 2). Again the analytical data for **5** and **6** are presented in the *Supporting Information*.



#### Scheme 4: Synthetic Pathway towards 6.

The next reaction step was the attempted multiple silyl abstraction leading to tetraacylgermane **7**. Therefore, the anion KGe(SiMe<sub>3</sub>)<sub>3</sub> (**2K**) was reacted with 4.1 mol equiv. of the corresponding acid fluoride **6**. The reaction sequence used for the preparation of tetraacylgermane **7** is depicted in Scheme 3. (Note: It is not possible to synthesize tetraacylsilanes via the multiple silyl abstraction methodology. Therefore, from here on we will only focus on germanium as central atom)



Scheme 3: Synthetic pathway towards 7.

The air-stable, yellow, crystalline target compound 7 was obtained in 32 % yield. Analytical and spectroscopic data obtained for 7 are consistent with the proposed structure. NMR Spectra and detailed assignments are provided in the Supporting Information. Compound 7 shows very similar <sup>13</sup>C chemical shifts for the carbonyl C atoms at  $\delta$  219.9 ppm, which is characteristic for carbonyl groups directly linked to a germanium atom. To further elucidate substituent effects on the absorption behavior of 7, a UV/Vis absorption spectrum was recorded and compared to a structurally related tetraacylgermane 8 (tetra-*o*-toluoylgermane). We choose to compare compound 7 with 8, because this tetraacylgermane shows "the best" absorption properties (significant bathochromically shifted absorption edge) and, more importantly, the highest solubility of all hitherto reported tetraacylgermanes. Structure 7 exhibits the longest-wavelength absorption band (n/ $\sigma$ - $\pi^*$  transition) between 350 and 450 nm [ $\lambda_{max}$  = 393 nm  $\epsilon \approx 1753$  $mol \cdot L^{-1} \cdot cm^{-1}$ )] tailing well into the visible region. (compare Figure 4). On the one hand the extinction coefficient of the  $n/\sigma - \pi^*$  transition of compound 7 is significantly higher than in comparison to compound 8. But on the other hand, the band is slightly hypsochromic shifted. This is well in line with the spectroscopic properties of other previously isolated and characterized tetraacylgermanes. To determine a solvatochromism, we measured the UV/Vis absorption spectrum 7 in various solvents, which can be found in the Supporting Information. In line with previous observations,<sup>20-22</sup> no solvatochromic effect was found.



Figure 4: Absorption spectrum of 7 and 8 with a concentration of  $1 \times 10^{-3}$  M in acetonitrile.

The low solubility tetraacylgermanes is a huge drawback for multiple applications. By introducing a di-*O*-isopropylidene protected D-galactose component as substituent, we hoped to increase the solubility in a variety of monomers. Therefore, solubility tests with methyl methacrylate (MMA), ethanol, methanol, and acetonitrile were accomplished. 100  $\mu$ L of the respective solvent were used, and the amounts of dissolved compounds were analyzed. To compare the increased solubility, we again choose **8** as benchmark compound. The results obtained are summarized in Table 1. Compound **7** shows significantly higher solubility's in polar solvents. In ethanol and methanol an increase of approximately 106 % was observed. Moreover, in acetonitrile the solubility of **7** increases by approximately 3125 % compared to **8**.

	7 [mg]	8[mg]	Increase in [%]
ethanol	1.30	0.63	106
methanol	1.00	0.56	79
acetonitrile	22.25	0.69	3125
methyl methacrylate	35.40	3.81	829

**Table 1.** Amount of compound dissolved in 100  $\mu$ L of the respective solvent compared with the tetraacylgermane **8**.

As envisaged in the introduction, deprotection of the isoproylidene groups at the sugar moiety should lead to water soluble photoinitiators. However, despite all efforts we have not been able to isolated partly deprotected or fully deprotected acyl group 14 compounds by selective hydrolysis of the isopropylidene groups. Several standard methods under acidic conditions employing aqu. HCl, ion-exchange resin IR 120 H<sup>+</sup> as well as acetic acid anhydride in various solvent mixtures did not lead to sufficient clean compounds for characterization as well as

property evaluation. (for experimental details see *Supporting Information*) Therefore, we aim for changing the protecting group strategy on the sugar moiety in order to continue our studies in a follow up report.

To conclude, we were able to successfully synthesize novel D-galactose-modified acylsilanes and acylgermanes in good to moderate yields. We first synthesized a monoacylsilane **1** and a monoacylgermane **2**. The acyl moiety bears a di-*O*-isopropylidene protected d-galactose moiety. Both compounds show long-wavelength absorptions bands with  $\lambda_{max}$  values between 325 and 400 nm tailing into the visible light region. However, to synthesize high performance visible light photoinitiators, these blue shift significantly, lowering the activity of these derivatives. Therefore, we introduced a phenyl spacer at the C<sub>6</sub> position of the D-galactose moiety. Subsequently, the synthesized acid fluoride **6** was reacted with **2K**, and after multiple silyl abstraction tetraacylgermane **7** was obtained. Compound **7** exhibit the longest-wavelength absorption band between 350 and 450 nm tailing well into the visible region. Moreover, the Dgalactose-substituted tetraacylgermane **7** shows significantly higher solubility in polar solvents related to germanium based photoinitiators, which is one step closer to the free radical polymerization in aqueous media. Synthetic approaches towards water soluble compounds in this respect are currently in progress.

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# **1.3.11.** The Road to Bisacyldigermanes - A New Compound Class Suitable as Visible Light Photoinitiators

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## Abstract

In this contribution we present a novel synthetic procedure towards a variety of bisacyldigermanes *via* the Corey-Seebach approach. All isolated compounds were characterized

by NMR-spectroscopy, mass spectrometry and X-ray crystallography. The target compounds were further analyzed *via* UV/Vis absorption spectroscopy and their longest wavelength absorptions were assigned by DFT calculations. Moreover,



we determined the activity of our new photoinitiators by photolysis experiments (photobleaching). Additionally, CIDNP spectra confirmed the radical pathway of the inverstigated compounds.

## Introduction.

Steadily increasing demands placed on photoinitiators for free radical polymerization make the production of new, improved systems not only of great interest but also a challenging task. These requirements include among others a good storage stability, effective photobleaching, high efficiencies, low to no toxicity of the photoinitiator itself as well as the formed photoproducts, sustainability, environmental compatibility and not to forget a moderate price.<sup>315–317</sup> As a result, various photoinitiator compounds have appeared in literature in the last decades, including new acylphosphine oxides and derivatives<sup>201,318–323</sup>, a number of acylgermane compounds<sup>21,72,81,82,87</sup>, and some tin-<sup>22,85,191</sup> as well as silicon-based compounds<sup>324,325</sup>. Selected examples of the mentioned compounds are shown in Figure 1. In this context, germanium-based photoinitiators, which undergo a Norrish type I reaction ( $\alpha$ -cleavage) upon irradiation, have attracted wide interest. Compared to established photoinitiator systems, such as phosphorus-based ones like Lucirin<sup>®</sup> TPO (2,4,6-trimethylbenzoyldiphenylphosphine oxide), Irgacure<sup>®</sup> 819 (bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide) or the well-known camphorquinone/amine system, germanium-based photoinitiators have the great advantage of being non-toxic or only slightly toxic, as germanium has no element-specific toxicity.<sup>71,91</sup> Their photocuring activity, excellent

bleaching properties and absorption bands that extend into the visible range also make them suitable for various processes. A well-established compound in this field is the so-called Ivocerin<sup>®</sup>, a bisacylgermanium compound, shown in Figure 1.



Figure 1. Selected examples photoinitiators discussed in the text.

This compound meets many of the stringent requirements but, as expected, also has some disadvantages such as insufficient curing depths at wavelengths above 500 nm, a multi-step synthetic pathway and a time-consuming purification process.<sup>18,71</sup> Therefore, symmetrical tetraacylgermans and subsequently mixed derivatives for a better solubility were investigated by our group.<sup>21,82</sup> A major advantage of tetraacylgermanes compared to Ivocerin<sup>®</sup>, resulting in more efficient photoinitiators, is the presence of four RC=O chromophore units, exhibiting higher band intensities further leading to more efficient light absorption.

Therefore, we now want to introduce another class of germanium-based compounds that are suitable as photoinitiators for radical polymerization, the bisacyldigermanes. Compared to Ivocerin<sup>®</sup>, the aim was to double the germanium content, which in turn should lead to an increased number of germanium centered radicals and thus achieving a higher polymerization rate. Also, regarding several poly- and disilanes tested as (co-)initiators in literature,<sup>324,326,327</sup> which when excited lead to a Si-Si bond cleavage and thus to the formation of silyl radicals, the digermane unit seemed to be quite promising with respect to the formation of radicals. Considering that a Ge-Ge bond has a length of approximately 2.41 Å with a bond energy of 188 kJ/mol, compared to a Si-Si bond that has a length of approximately 2.35 Å with a bond energy of 222 kJ/mol, indicating that the Ge-Ge bond is weaker on average and facilitates potential bond dissociation.<sup>328</sup>

#### **Results and Discussion**

**Synthesis of Digermane Synthon.** The entry into this chemistry is provided by the synthetic protocol towards 1,2-dichloro-1,1,2,2-tetraethyldigermane, which was accomplished through two different methods. In method A we used diethyldichlorogermane as starting material. This dichlorogermane was reacted with 2 equivalents of phenylmagnesiumbromide to obtain the

bisphenylated derivative **1**. Subsequently **1** was reacted with equimolar amounts of trifluoromethanesulfonic acid (TfOH) to the corresponding triflate, which *in-situ* was transferred by nucleophilic substitution with an excess of lithium chloride to the chlorogermane **2**. Through a Wurtz-type coupling using equimolar amounts of elemental lithium the corresponding digermane **3** was obtained. Finally compound **3** was reacted with 2 equivalents of TfOH to the corresponding bistriflate. 1,2-dichloro-1,1,2,2-tetraethyldi-germane (**4**) was obtained by a subsequent nucleophilic substitution of the bistriflate substituent with an excess of lithium chloride. (compare Scheme 1).



Scheme 1. Synthesis of 1,2-dichloro-1,1,2,2-tetraethyldigermane (4) following method A.

The air stable and moisture sensitive compound 4 was obtained in isolated yields of 93%. Analytical and spectroscopic data that support the structural assignments are given in the *Experimental Section* together with experimental details.

However, this tedious multistep procedure was replaced by method B, which reduces the necessary synthetic steps by half. In method B, chlorotriethylgermane was coupled with equimolar amounts of elemental lithium to the corresponding digermane **5** in excellent yields of 98% (Wurtz-type coupling). Acetyl chloride as chlorination reagent is well known in organosilicon chemistry.<sup>329–331</sup> Therefore, we adapted the reaction procedure to organogermanium chemistry. To our delight we found a very selective reaction to the desired compound **4** in 92% yield (see Scheme 2). Analytical and spectroscopic data that support the structural assignments are given in the *Experimental Section* together with experimental details.



Scheme 2. Synthesis of 1,2-dichloro-1,1,2,2-tetraethyldigermane (4) following method B.

**Synthesis of 1,2-Bis(1,3-Dithiane)-Digermanes.** The literature contains multiple methods to obtain acylgermanes.<sup>18,21,46,47,332</sup> For this work we used the Corey-Seebach approach. Therefore, we synthesized a variety of 1,3-thioketals **6a-e** according to literature procedures<sup>333–335</sup> (see Scheme 3).



Scheme 3. Synthesis of 1,3-thioketals 6a-e.

Subsequently these compounds were lithiated using *n*-butyllithium (*n*-BuLi) and *in-situ* reacted with compound **4** in THF at 0 °C to get the 1,1,2,2-tetraethyl-1,2-bis(2-aryl-1,3-dithian-2-yl)digermanes (**7a-e**). Compounds **7a-e** were isolated in good yields through recrystallization from acetone at -30 °C (compare Scheme 4). Analytical and spectroscopic data that well support the structural assignment are given in the *Experimental Section* together with the experimental details. Characteristic for this compound class is the <sup>13</sup>C-NMR chemical shift for the protected C-atom between  $\delta = 49.52$  ppm and  $\delta = 50.96$  ppm.



Scheme 4. Synthesis of 1,1,2,2-tetraethyl-1,2-bis(2-aryl-1,3-dithian-2-yl)di-germanes 7a-e.

Single crystals of **7a** suitable for X-ray structural analysis could be grown by cooling a concentrated solution in acetone to -30 °C. The molecular structure is depicted in Figure 2. Compound **7a** crystallized in the orthorhombic space group  $Pca2_1$  with unexceptional bond lengths and angles. The unit cell contains four molecules (see *Supporting Information*).



**Figure 2.** ORTEP representation for 1,1,2,2-tetraethyl-1,2-bis(2-phenyl-1,3-dithian-2-yl)digermane (**7a**). Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) with estimated standard deviations: Ge(1)-C(1) 2.047(3), Ge(2)-C(15) 2.039(3), Ge(1)-Ge(2) 2.4443(4), S(1)-C(1) 1.814(3), S(2)-C(1) 1.824(3), S(3)-C(15) 1.822(3), S(4)-C(15) 1.815(3).

As mentioned several times in literature, dethioketalization is the most challenging step of the Corey-Seebach approach. During this study a variety of methods were tested (DMSO/cat.<sup>336</sup>, conc.  $H_2SO_4^{337}$ ,  $HgCl_2/CaCO_3^{46}$ ,  $I_2/CaCO_3^{338}$ ), whereby all of these gave rise to extensive aldehyde formation as well as degradation of the Ge-Ge bond. Recently, Unterreiner, Barner-Kowollik and co-workers introduced a mild deprotection procedure using boron trifluoride diethyl etherate (BF<sub>3</sub>•OEt<sub>2</sub>) as a catalyst and (diacetoxyiodo)benzene (PIDA) as oxidizing agent.<sup>339</sup> We adopted this method for our system and found that the dethioketalization proceeds at 0 °C in a solvent mixture of dichloromethane and methanol in good to moderate yields depending on the substituent at the carbonyl moiety (see Scheme 5).



Scheme 5. Synthesis of bisacyldigermanes 8a-e.

Moreover, we found that the group tolerance of this method is decent since both, unsubstituted and a variety of substituted aromatic groups can be easily attached. Analytical and spectroscopic data that well support the structural assignment are given in the *Experimental Section* together with the experimental details. All derivatives show very similar <sup>13</sup>C-NMR chemical shifts for

the carbonyl C-atom between  $\delta = 229.83$  ppm and  $\delta = 237.99$  ppm, which is characteristic for carbonyl groups directly attached to a germanium atom.

Single crystals of 1,1,2,2-tetraethyl-1,2-bis(*o*-toluoyl)digermane (**8b**) as well as of 1,1,2,2-tetraethyl-1,2-bis(*p*-toluoyl)digermane (**8c**) suitable for X-ray structural analysis could be grown by cooling concentrated solutions in *n*-pentane to -70 °C. The molecular structures are depicted in Figure 3 and 4. Both compounds crystallized in the triclinic space group *P*-1 with unexceptional bond lengths and angles. The unit cells contain one molecule (see *Supporting Information*).



**Figure 3.** ORTEP representation for 1,1,2,2-tetraethyl-1,2-bis(*o*-toluoyl)digermane (**8b**). Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations: Ge(1)-C(1) 2.0322(10), Ge(1)-Ge(1#) 2.4374(2), O(1)-C(1) 1.2213(12), O(1)-C(1)-Ge(1) 114.42(7), O(1)-C(1)-C(2) 121.87(9), C(1)-Ge(1#) 110.23(3).



**Figure 4.** ORTEP representation for 1,1,2,2-tetraethyl-1,2-bis(*p*-toluoyl)digermane (**8c**). Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations: Ge(1)-C(1) 2.034(4), Ge(1)-Ge(1#) 2.4371(9), O(1)-C(1) 1.224(5), O(1)-C(1)-Ge(1) 115.8(3), O(1)-C(1)-C(2) 121.1(4), C(1)-Ge(1)-Ge(1#) 109.54(12).

#### **UV/Vis Absorption Spectroscopy**

For photoinitiators in general, a good overlap between the emission of the used photo lamp and the absorption of the photoinitiator is required. Moreover, especially for medical applications an absorption in the visible region of the light is highly beneficial. This can be achieved by the usage of germanium-based photoinitiators, as their longest wavelength absorption is between 360 and 407 nm and tails well into the visible region.<sup>18,21,71,72,82,87</sup> However, the state-of-the-art germanium-based photoinitiator, namely Ivocerin<sup>®</sup>, shows insufficient curing with light sources above 450 nm, which is mainly based on the low absorption in this region. To determine the

absorption properties of our new synthesized acylgermanes **8a-e**, we recorded their UV/Vis spectra (see Figure 5). In accordance with literature, the substitution pattern of the aromatic group significantly influences the  $\lambda_{max}$  value, the tailing into the visible region as well as the extinction coefficient  $\varepsilon$ . In comparison to the unsubstituted derivative **8a**, alkyl substitution results in an increase of the extinction coefficient of 57% for **8b** and 53% for **8c**. Interestingly, all three compounds adopt nearly identical  $\lambda_{max}$  values between 419-423 nm. Surprisingly, especially in respect to the absorption behavior of Ivocerin<sup>®</sup>, the *para*-alkoxy substituted derivative **8e** and the mixed substituted (*para*-alkoxy and *meta*-alkyl) derivative **8d** adopt a significant higher extinction coefficient (for both derivatives is  $\varepsilon$  increased by 26% for **8e** and 28% for **8d**). The other two values, however, are nearly identical for all three compounds.



Figure 5. UV/Vis absorption spectra of 8a–e and Ivocerin<sup>®</sup> (toluene solution,  $c = 10^{-3} \text{ mol} \cdot L^{-1}$ ).

The longest wavelength absorption band at around 420 nm was assigned as two  $n/\sigma - \pi^*$  transitions from the carbonyl lone pairs and the Ge-Ge  $\sigma$ -bond to both acyl moieties. The excitations occur with different linear combination from both the HOMO-1 and HOMO to both the LUMO and LUMO+1 orbitals. Compared to Ivocerin<sup>®</sup>, this band is approx. 15 nm red-shifted in **8a-d**. Interestingly, the HOMO orbitals of **8b** and **8c** show some electron localisation at the central Ge-Ge  $\sigma$ -bond. In Figure 6 the HOMO and LUMO orbitals of **8b** and Ivocerin<sup>®</sup> are depicted as showcase, all other molecular orbitals are summarized in the *Supporting Information* (see Figure S37).



Figure 6. HOMO (left) and LUMO (right) of a) 8b and (b) Ivocerin®.

As many conventional LED sources emit light at 450 nm, absorption at and above this wavelength is necessary to ensure efficient photocuring. Figure 5 also shows the tailing of the  $n/\sigma-\pi^*$  transition. While all alkoxy substituted derivatives including Ivocerin<sup>®</sup>, show only a weak to moderate absorption at this particular wavelength, both alkyl substituted derivatives display a significant higher absorption. In respect to the applicability as visible light photoinitiator this spectral property is crucial.

Chemically Induced Dynamic Nuclear Polarization (CIDNP). The CIDNP experiments of newly synthesized compounds in presence of *n*-butyl acrylate (BA) in toluene were performed to investigate primary radicals formed upon photolysis. To that end, initial experiments were performed with 8a (see Supporting Information Figure S22 for possible cleavage sites of compound 8a). The observation of polarization arising from benzaldehyde proton ( $\delta = 9.59$ ppm), the chemical shift of  $\alpha$ -H proton in the product presented as a triplet ( $\alpha$ -H,  $\delta$  = 4.57 ppm), and  $\beta$ -H protons presented as a doublet ( $\beta$ -H,  $\delta$  = 1.83 ppm) in experimental CIDNP spectra of 8a (Figure S23) strongly point out to a cleavage of the Ge-C=O bond rather than the Ge-Ge bond upon photolysis. This fact was confired by the respective bond dissociation energies, which is lower for the Ge-C=O bond for all investigated compounds 8a-e. In addition, the CIDNP spectra of **8a** was compared to the analogous compound **9** [(diethylgermanediyl)bis(phenylmethanone)] under identical conditions (Figure S24). The comparison reveals two distinctly different CIDNP spectra with chemical shifts of  $\alpha$ -H protons in case of 9 ( $\alpha$ -H,  $\delta$  = 4.77 ppm), being slightly downfield shifted as compared to that of **8a**. In both cases,  $\alpha$ -H protons are presented as triplet instead of the expected doublet of doublets owning to the second-order effects influencing the coupling of  $\alpha$ -H proton to the  $\beta$ -H protons in toluene as solvent. The further assignments for the part of the spectrum with  $\beta$ -H protons and aliphatic protons are hindered by a strong overlap of signals, nevertheless, it can be seen that the spectra are different. The only similarity between CIDNP of **8a** and **9** is in the polarization arising from benzaldehyde proton, again pointing out the cleavage of Ge-C=O bond in **8a** rather than Ge-Ge bond. Upon determining the cleaved bond in the unsubstituted compound, a CIDNP experiment was performed for all of the substituted compounds. The chemical shift of  $\alpha$ -H proton for **8b** is found at  $\delta = 4.51$  ppm (Figure S25), for **8c** at  $\delta = 4.60$  ppm (Figure S26) and in **8d** (Figure S27) and **8e** (Figure S28) at  $\delta = 4.58$  ppm and  $\delta = 4.60$  ppm respectively, in all the cases  $\alpha$ -H protons are presented as triplets as is the case in **8a** presumably though to the second-order effects influencing the coupling of the  $\alpha$ -H proton. In all cases, the corresponding benzaldehyde is observed in the CIDNP spectra confirming the cleavage of the Ge-C=O bond in all of the investigated compounds. This is also supported by our quantum chemical calculations, which found that the bond dissociation energy (BDE) for the Ge-Ge dissociation is approx. 0.3 eV larger than for the Ge-C dissociation (see Table S6).

**Photobleaching.** With the formation of primary radical established, steady-state photobleaching experiments were conducted to investigate the dependency of quantum yield for bond cleavage on the substitution. To that end, the compound was irradiated using LED emitting at 387 nm with 15 nm full width at half maximum, in the presence of monomer in toluene. The data is presented in Table S2 and Figure S29. From experimental data, it can be seen that 8a (Figure S30) and **8b** (Figure S31) derivatives display the lowest quantum yield ( $0.58 \pm 0.02$  and  $0.56 \pm$ 0.02 respectively) for bond cleavage. Compound 8a displays a substantially lower quantum yield for cleavage compared to  $0.83 \pm 0.01$  of analogous 9 derivative. Slightly higher quantum yield is obtained by introducing methyl substituent into *para* position as in 8c) (0.64  $\pm$  0.01, Figure S32). The quantum yield can be further increased by introducing stronger electron donating substituents as methoxy into *para* position **8e** (0.69  $\pm$  0.01 Figure S34). Again the comparison is made with analogous monogermanium compound Ivocerin® having a quantum yield of (0.83  $\pm 0.01$ ) whereas compound **8e** displays slightly lower quantum yield. Lastly introducing fused 2,3-dihydrofuran ring as 8d provides the highest cleavage quantum yield (0.75  $\pm$  0.01 Figure S33). The observation of the increased ease for Ge-C=O bond cleavage by introducing electron donating substituents into the aromatic ring can be rationalized by assuming a greater stabilization effect of electron donating substituent on primarily formed radicals.

It is necessary to point out that irradiation using 430 nm emitting LED leads to significantly faster photobleaching for all of the newly reported compounds, which can be attributed to a higher cross-section of the compounds absorbance spectrum and LED emission.

#### **Conclusion.**

In summary, we were able to synthesize a variety of bisacyldigermanes in moderate to good yields *via* the Corey-Seebach approach. In order to synthesize these new compounds, we first established two methods to the digermane synthon. Both synthetic protocols, pave the way for the straightforward synthesis of tetraethyldichlorodigermane in excellent yield.

Tetraethyldichlorodigermane was subsequently reacted with lithiated 1,3-thioketal species to obtain the 1,1,2,2-tetraethyl-1,2-bis(2-aryl-1,3-dithian-2-yl)digermanes **7a-e** in yields of 71-88%. After dethioketalisation using a mild protocol, the target compounds **8a-e** were isolated by recrystallization. Comparing their absorption behavior to Ivocerin<sup>®</sup>, the monogermanium counterpart, we observe, especially for the alkyl-substuituted derivatives and in particular for compound **8b**, a significant longer tailing of the  $n/\sigma-\pi^*$  transition in the visible region. In respect to the applicability as visible light photoinitiator, this spectral property is crucial since many conventional LED sources emit light at 450 nm. In contrast to our assumption in the introduction, CIDNP measurements as well as DFT calculations found that the cleavage of Ge-(C=O) bond is more likely than a Ge-Ge bond cleavage.

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Keywords: acylgermanes • digermanes• photochemistry • photoinitiators
## 1.3.12. Photoisomerizations of Bishypersilyl-1,2-dione: The Wavelength Matters

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#### Abstract

In this contribution, a synthetic approach towards an isolable bissilyl-1,2-dione **3**, a novel acylsilane, is described. The formation of this derivative was confirmed by NMR spectroscopy and X-ray crystallography. The UV/Vis spectrum of **3** shows two distinct  $n \rightarrow \pi^*$  absorption bands, which do not overlap and have differing characters. Therefore, we performed irradiations at  $\lambda = 360-365$  and at  $\lambda$ 



= 590-636 nm, targeting these two different transitions. Remarkably, we found wavelength dependent rearrangements towards two novel examples of complex silicon frameworks. The irradiation with  $\lambda \approx 360$  nm gave rise to the formation of a novel isolable siloxyketene **4**, by a hitherto unknown 1,3-hypersilyl migration. In contrast to that, the irradiation with  $\lambda \approx 600$  nm leads to the quantitative formation of siloxirane **5**, by a 1,4-trimethylsilyl migration.

#### Introduction

Photochemistry has recently gained renewed attention in the fields of synthetic and polymer chemistry as light allows a high spatial and temporal control.<sup>340,341</sup> Moreover, the used wavelength and intensity can be adjusted easily and the performed reactions proceed without producing any waste. It is therefore not surprising that photochemistry is implemented for material science,<sup>342–346</sup> in synthesis,<sup>347–351</sup> various applications such as in in photopolymerization,<sup>73,352,353</sup> supramolecular chemistry<sup>354,355</sup> and in photo-redox for chemistry.<sup>356,357</sup> In the last decades acylsilanes have evolved as widely used reagents in synthetic chemistry and as important intermediates in material science. 42,43,335,358-363

The photochemical reactivity of acylsilanes is an extensively researched and well understood field, with roots dating back to the late 1970s.<sup>364–367</sup> While simple acylsilanes undergo a photo-

chemical induced 1,2-silyl migration (so-called Brook Rearrangement) forming siloxycarbenes,<sup>368</sup> branched acylpoly-silanes undergo a 1,3-silyl migration and form metastable silenes (compound **1**, Scheme 1a).<sup>51</sup>

Recently, Glorius and coworkers showed that acylsilanes neighbored by an additional carbonyl unit react in a completely different way.<sup>369</sup> Instead of a Brook Rearrangement, the scission of the Si-C bond is followed by a 1,3-silyl migration of the complete SiR<sub>3</sub> unit (Si(Me)<sub>2</sub>*t*-Bu), via a highly reactive siloxyketene (compound **2**, Scheme 1b). Indirect evidence for this intermediate was based on the isolation of follow-up products using various trapping agents (methanol, piperidine, and 4-toluenethiol). Triggered by this work and on the basis of our recent studies on light mediated reactions of acyl metalloid,<sup>21,22,325</sup> we decided to investigate the photochemistry of previously unknown bishypersilyl-1,2-diones. To our delight, we found a wavelength dependent rearrangement towards two novel complex silicon frameworks (compound **4** and **5**, Scheme 1c). This remarkable finding represents a new paradigm in the chemistry of acylsilanes and opens up new synthons in main group chemistry.



Scheme 1. Different types of photochemical rearrangements of acylsilanes. a) classical photo-Brook rearrangement, b) photochemical rearrangement of  $\alpha$ -ketoacylsilanes, c) wavelength-dependent photo-rearrangement of 3 presented in this work.

## **Results and Discussion**

The starting material for our investigation (Compound **3**) is obtained by the reaction of alkali metal-substituted tris(trimethylsilyl)-silanides with either diphenyl oxalate (method A)<sup>370</sup> or oxalyl chloride (method B)<sup>271</sup> at low temperature (see Scheme 2). Optimization of reaction conditions revealed a delicate balance between product formation and formation of 1,1,1,4,4,4-hexamethyl-2,2,3,3-tetrakis(trimethylsilyl)tetrasilane by metal-halide exchange of the silanide.<sup>288</sup> Change of the solvent or counterion for the silanide formation did not improve the yield of **3**. Improvement of the yield (3% at  $-30^{\circ}$ C) could only be achieved by lowering the temperature (20% at  $-100^{\circ}$ C). Upon completion, the reaction was immediately quenched using a 10% H<sub>2</sub>SO<sub>4</sub> solution, followed by extraction of the product using diethyl ether. The crude product was purified by flash column chromatography with *n*-heptane. The blue crystalline

product  $\mathbf{3}$  is air-stable and can be stored at room temperature in the absence of light for months without the observation of degradation products.



Scheme 2. Synthesis of compound 3 by two different reaction approaches with a picture of crystals of 3.

NMR spectroscopy of **3** revealed one single resonance in the <sup>1</sup>H spectrum with a chemical shift at  $\delta = 0.32$  ppm. In the <sup>13</sup>C-NMR, besides the signal for the methyl units at 1.62 ppm, the carbonyl shift at  $\delta = 238.9$  ppm is characteristic of a carbonyl group bound to silicon. The <sup>29</sup>Si-NMR spectrum showed two resonances, one at  $\delta = -10.7$  ppm for the trimethylsilyl groups and one at  $\delta = -79.0$  ppm for the two silicon atoms attached to the carbonyl moiety. We were able to grow crystals suitable for single-crystal X-Ray structure analysis by cooling a solution of **3** in ethyl acetate to  $-30^{\circ}$ C (Figure 1). Compound **3** crystallizes in the triclinic space group *P*-1 with 4 molecules per unit cell. Both carbonyl groups adopt a trans orientation (for steric and electronic reasons) and form a plane.



**Figure 1.** ORTEP representation for compound **3**. Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations: C1-C1# 1.539(8), C1-O1 1.237(5), Si1-C1 1.924(4), Si1-Si2 2.355(2), O1-C1-C1#-O1# 180.00.

The UV/Vis spectrum of **3** indicates three characteristic bands centered at  $\lambda = 247$ , 317, and 637 nm, respectively (Figure 2). TD-DFT calculations reveal that the band at  $\lambda = 637$  nm and the shoulder at  $\lambda = 350$  nm correspond to an  $n \rightarrow \pi^*$  transition from the carbonyl-oxygen lone pairs toward the dione  $\pi$  system. The higher-energy bands at  $\lambda = 317$  and  $\lambda = 245$  nm are attributed to excitations from Si-centered orbitals to the dione  $\pi$  system (Figure S1). The absorption bands do

not indicate solvatochromic shifts (increasing solvent by polarity from hexane to methanol, Figure S2).



**Figure 2.** UV/Vis spectra of **3.** a) Experimental spectra in DCM at three different concentrations, b) Computed spectra with vertical transitions marked as lines with their respective oscillator strengths on the right axis.

The absorptions bands at  $\lambda = 317$  and  $\lambda = 637$  nm ( $\Delta\lambda = 320$  nm) are well separated, do not overlap, and have differing characters. Consequently, we performed irradiations with LEDs having emission maxima centered at  $\lambda = 360$  and 365 nm and at  $\lambda = 590$  and 636 nm, to selectively and separately address the two distinct transitions. At first we performed chemically induced dynamic nuclear polarization experiments (CIDNP)<sup>253</sup> in the presence of an excess (10 eq.) of butyl acrylate, to determine if the central bond of **3** undergoes homolytic cleavage. Here we could not establish any addition of radicals to the acrylate double bond (Figure S3), thus basically excluding photo-induced homolytic cleavage.

For compound **3**, <sup>1</sup>H-NMR spectroscopy is hardly suitable to obtain clear-cut information about reactions of the carbonyl moieties, as only a single resonance for the magnetically equivalent trimethylsilyl groups is present. However, with its 1,2-dione (C=O) functional group, **3** is a perfect candidate for IR analysis. The stationary FT-IR spectra of **3** in CCl<sub>4</sub> at room temperature present only a few well-distinguishable bands, owning to the presence of an inversioncenter (Figure 3a). In particular, bands at 2950 cm<sup>-1</sup> and 2895 cm<sup>-1</sup> (asymmetric and symmetric C-H stretching vibrations, respectively), 1635 cm<sup>-1</sup> (asymmetric C=O stretching vibration), and bands from Si-C stretching and methyl group wagging vibrations (Figure S4). We have used our custom-made setup allowing us to record IR spectra during selective (LED) irradiation under inert conditions.<sup>50</sup> Upon irradiation with a 360-nm LED (Figure S5), the time-resolved IR spectra presented in Figure 3b emerged. The decrease of the C=O band (1635 cm<sup>-1</sup>) correlates with the simultaneous appearance of a band at 2046 cm<sup>-1</sup>, attributed to siloxyketene **4**.<sup>371</sup> Additionally the intensity of various Si-C vibration modes changed and a band at 1065 cm<sup>-1</sup> attributed to C-O stretching vibration of **4** emerged (more detailed see Supporting Information).



**Figure 3.** a) The experimental FT-IR spectra of **3** in CCl<sub>4</sub>.  $2200 - 2700 \text{ cm}^{-1}$  region is not shown for clarity. Time-resolved difference FT-IR spectra during the irradiation of **3** with b) LED having emission maxima at 360 nm, and c) LED having emission maxima at 636 nm. The solvent is subtracted from the spectra and the 700 – 828 cm<sup>-1</sup> region is cut out as this is blocked by the high absorption of the solvent.

To proof the synthetic value of this photoisomerization, we performed experiments in preparative amounts with **3** in benzene-d<sub>6</sub> in a photoreactor using 365 nm high-power LEDs. The reaction was monitored by <sup>1</sup>H-NMR spectroscopy and revealed a highly selective reaction with only minor side products, once again pointing toward the formation of siloxyketene **4** (Figure 4a and Figure S7). Compound **4** was isolated by crystallization. Therefore, the crude reaction mixture was dissolved in *n*-pentane and cooled to  $-70^{\circ}$ C, which resulted in the precipitation of pink crystals in excellent yields of 89%. The spectroscopic data are consistent with the proposed structure (Figure S17-19), with one resonance in the <sup>29</sup>Si NMR spectrum for the silicon atoms bearing the ketene moiety at  $\delta = -77.0$  ppm, two signals at  $\delta = -15.8$  ppm and -11.8 for the six SiMe<sub>3</sub> groups and one significantly high field shifted signal at  $\delta = 19.0$  ppm for the silicon atom covalently bonded to the oxygen. Additionally, the <sup>13</sup>C NMR spectrum revealed the characteristic shift at  $\delta = 219.0$  ppm for the ketene group.

Crystals of **4** suitable for single-crystal X-ray crystallography could be grown at low temperature  $(-30^{\circ}C)$  in *n*-pentane (Figure 4b). Computations revealed that the first excited singlet (S<sub>1</sub>) and triplet (T<sub>1</sub>) states have an energy of 198 and 138 kJmol<sup>-1</sup>, respectively. The second excited singlet (S<sub>2</sub>) and triplet (T<sub>2</sub>) states were found to be at 378 and 317 kJmol<sup>-1</sup>, respectively. Accordingly, excitation of **3** at 360 nm (332 kJmol<sup>-1</sup>) should lead to the higher vibrational level of S<sub>1</sub> followed by intersystem crossing (ISC) to the second excited triplet state (T<sub>2</sub>). Internal conversion (IC) from T<sub>2</sub> then populates a higher vibrational level of the T<sub>1</sub> state. In this latter state, compound **3** possesses sufficient energy to undergo a 1,3- hypersilyl migration to the distal carbonyl oxygen.

An ISC between the T<sub>1</sub> and ground state (S<sub>0</sub>) potential energy surfaces then allows a formation of **4** (Figure 4c).<sup>372</sup> This 1,3-hypersilyl migration is contrary to the well known 1,3-trimethylsilyl migration in the common Brook Rearrangement. The large energy separation between the T<sub>1</sub> and T<sub>2</sub> states (14.963 cm<sup>-1</sup>) together with the lack of high-energy vibrational modes necessary for the dissipation of excess energy (*ie*. energy gap law)<sup>373</sup> are likely responsible for the "hot state"  $\mathbf{3} \rightarrow$ **4** photo rearrangement (Figure 4c).



Figure 4. a) Photochemical rearrangement of 3 to 4 using the LEDs with emission maxima centered at 365 nm, pictures of NMR tubes for 3 and 4 are presented as inserts next to the respective compounds. b) ORTEP representation for compound 4. Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations: C1-C1# 1.539(8), C1-O1 1.237(5), Si1-C1 1.924(4), Si1-Si2 2.355(2) c) The proposed mechanism including a schematic depiction of potential energy surfaces for the  $3 \rightarrow 4$  rearrangements induced by the 360 nm light.

Using a 636 nm LED, which matches the band at  $\lambda = 637$  nm (Figure S8), we have recorded distinctly different time-resolved IR spectra than at  $\lambda = 365$  nm (Figure 3c). This demonstrates clearly distinct photochemical behavior as compared to the irradiation using a 360 nm LED. Markedly, the most intense emerging band is that at 1130 cm<sup>-1</sup>, which is assigned to be the C-O bond stretching of 5. At the same time, the C=O vibration band at 1630  $\text{cm}^{-1}$  decreases. Additionally, several bands in the 850–950 cm<sup>-1</sup> region were observed indicating changes in the Si-C stretching vibrations together with altered lines in the 500–650 cm<sup>-1</sup> region, characteristic for Si-C and methyl group waging vibrations (Figure S9). As for the  $\lambda = 360$  nm irradiation, an experiment in preparative amounts was performed (3 in  $C_6D_6$ ) in a photoreactor with high-power 590 nm LEDs. Again, the reaction was highly selective (<sup>1</sup>H-NMR spectra for the product formation 5 during the irradiation, Figure S10). We were able to isolate product 5 as a yellowish oil (the melting point of the compound is around room temperature) with excellent yield (>99%, Figure 5a). Recrystallization from *n*-pentane at  $-70^{\circ}$ C afforded crystals of sufficient quality for single-crystal X-Ray structure analysis, revealing the corresponding structure of 5, shown in Figure 5b. An interesting fact in this context is, that although configurational isomerism is possible, we only found the formation of the E-isomer of 5. This clearly shows that the

photoizomerization towards **5** is stereoselective. The <sup>29</sup>Si-NMR spectrum showed five resonances, which is consistent with the presence of five non-equivalent silicon atoms. On the basis of previous experience with structurally related compounds, we were able to assign all signals (Figure S20-22).<sup>98,374</sup>

We have performed DFT calculations to explore the wavelength-dependent reactivity of **3**. The available energy at  $\lambda = 590$  nm is 203 kJmol<sup>-1</sup>. This is sufficient to excite **3** to a higher vibrational level of the S<sub>1</sub> state, followed by a vibrational relaxation affording the thermalized S<sub>1</sub> state (*ie*. Kasha's rule). Here, ISC leads to the T<sub>1</sub> state, which relaxes toward **5** after 1,4-trimethylsilyl migration. This is in line with the correspondingly small activation barrier of 29 kJmol<sup>-1</sup> (energy barrier on the T<sub>1</sub> surface towards the formation of **5**). The calculations additionally show that a reaction toward **4** via thermalized T<sub>1</sub> requires a too-high activation barrier of 81 kJmol<sup>-1</sup> (Figure 5c, for further details, see supporting information).



Figure 5. a) photochemical rearrangement of 3 to 5 using the LED with emission maxima centered at 590 nm, pictures of NMR tubes for 3 and 5 are presented as inserts next to the respective compounds. b) ORTEP representation for compound 5. Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations: C1-C1# 1.539(8), C1-O1 1.237(5), Si1-C1 1.924(4), Si1-Si2 2.355(2). c) The proposed mechanism including a schematic depiction of potential energy surfaces for the  $3 \rightarrow 5$  rearrangements induced by the 590 (636) nm light.

During the course of our investigations, we also recorded the UV/Vis spectrum of **4**, which showed well-defined absorption maxima centered at  $\lambda = 279$  nm and  $\lambda = 528$  nm (Figure 6 and Figure S11). As the longest wavelength absorption band overlaps with that of **3** (the  $\lambda = 637$  nm absorption, Figure S12) **4** can theoretically serve as an intermediate for the formation of **5**. Consequently, we irradiated a solution of **4** in C<sub>6</sub>D<sub>6</sub> with 550 nm, 590 nm, and 636 nm LEDs (Figure S13), but we could not detect any conversion utilizing both FT-IR and NMR spectroscopy, respectively.



Figure 6. UV/Vis spectra of 4 in THF at three different concentrations.

In order to exclude a hypothetical formation of siloxycarbenes, we performed photolysis experiments of **3** in an excess of dry methanol with catalytic amounts of triethylamine as base at both wavelengths ( $\lambda = 365$  and 590 nm). The photochemical experiment at  $\lambda = 365$  nm showed a color change from blue to purple pointing towards the formation of 4. This was confirmed by NMR spectroscopy monitoring the reaction. Additionally, a new set of signals was observed, indicating that 4 slowly reacts with methanol to a new product. The trapping reaction was finished after 7 days, as monitored by the NMR spectroscopy. We assume that the reason for this long reaction time is steric hindrance by hypersilyl groups, shielding the ketene unit. The crude product was recrystallized from *n*-pentane to separate product **6** from small amounts of an uncharacterized sideproduct. (Figure 7a). The spectroscopic data of  $\mathbf{6}$  are consistent with the proposed structure (see Figure S23-25). Furthermore, we performed a methanol trapping experiment of **5** with catalytic amounts of triethylamine analogously at 590 nm LED irradiation. (Figure 7b). While monitoring the conversion of **3** by NMR-spectroscopy, the formation of two selective products, as an isomeric mixture in a ratio of 2:1 formed by an in situ ring opening of **5** was observed. Isolation of the main isomer as colourless oil was performed by preparative thin-layer-chromatography. Analytical Data corresponds well with the proposed structural arrangement. Additional evidence about the structural conformation of 7a was given by an HSQC-NMR measurement, also confirming the direct bonding between the hydrogen atom and the carbon atom of the C=C bond. (Figure 7b, for further details, see Figure S29-32).



**Figure 7.** a) Methanol trapping experiments of the photoisomerization of **3** at  $\lambda = 365$  nm b) Methanol trapping experiment of the photoisomerization of **3** at  $\lambda = 590$  nm.

In conclusion, we have established a synthetic pathway towards a bishypersilyl-1,2-dione **3**, which represents a novel acylsilane. On the basis of discrete  $n-\pi^*$  transitions, that are well separated from each other, a wavelength dependent rearrangement to hitherto unknown complex silicon frameworks was found. At  $\lambda \approx 360$  nm a yet undescribed 1,3-hypersilyl migration occurs and an isolable siloxyketene **4** was formed. At  $\lambda \approx 600$  nm, a 1,4-silyl migration leads to the formation a siloxirane **5**. The formation of these derivatives was confirmed by NMR spectroscopy and X-ray crystallographic analysis.<sup>[22]</sup> Additionally, trapping experiments of compounds **4** and **5** were performed. Further studies to probe the scope of this chemistry are currently in progress.

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Keywords: acylsilanes • organsilicon • ketenes • photochemistry

# **1.3.13.** Do Germanium-Based Photoinitiators have the Potential to Replace the Well-Established Acylphosphine Oxides?

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## Abstract

In the last decades, there has been an increasing demand for photoinitiators with growing requirements. Nowadays, photoinitiators need to fulfill several requirements such as a low level of toxicity, biocompatibility, fast polymerization rates, high activities, good photobleaching and much more



in order to remain competitive on the market. Accordingly, we compare acylphosphine oxides and acylgermanes, two common classes of photoinitiators, with respect to their various synthetic pathways, their toxicity, availability and performance.

## Introduction

Photopolymerization has been an essential method for a variety of industrial processes for over more than 30 years. During the last century, there has been an immense increase in the demand and application of photochemically produced high-performance polymers. Today, their use is no longer limited to the production of microelectronics, coatings, microlithography, optics and many more, but also applies in the medical field, e.g. as dental filling material or for artificial tissues and for the production of 3D objects. As the demand for photoinitiators (PIs) has increased over the last decades, the production of new initiators with improved properties are of great interest, but also an enormous challenge.

The stringent requirements for various applications include fast polymerization rates, high activities and excellent storage stability along with efficient photobleaching, sustainability, environmental compatibility and low to no toxicity of the PI and the photoproducts formed.<sup>375–377</sup> Acylphosphine oxides represent a class of PIs that meet several of the above-mentioned requirements. It is represented mainly by the monoacylphosphine oxides (MAPOs) and their bis(acyl) analogues (BAPOs). Due to their excellent properties, such as their high degree of whiteness, good thermal stability, and their high curing efficiency, they almost seem unbeatable.<sup>378</sup> However, they also come with some disadvantages. For instance, some acylphosphine oxide compounds have been described as toxic, which limits their applications in the medical field.<sup>379,380</sup> In addition, some of them show limited solubility in aqueous media.<sup>381</sup>

However, Grützmacher and co-workers accomplished a breakthrough in solubility with functionalized acylphosphine oxides.<sup>382–385</sup>

Recently, more and more germanium-based photoinitiators have been developed and investigated. Compared to phosphorus-based PIs, these initiators provide lower toxicity as well as a significant bathochromic shift of the longest wavelength absorption. However, not to be ignored is the low abundance of germanium in the Earth's crust, which leads to significantly higher costs of germanium-based PIs.<sup>21,82,386</sup> Both compound classes, the acylphosphine oxides as well as the germanium-based PIs follow a Norrish type-I cleavage mechanism upon light irradiation generating radicals and initiating the polymerization process. In the case of the former, a benzoyl- and a phosphinoyl-radical<sup>218</sup> is generated, while in the case of the latter, a benzoyl- and a germyl-radical<sup>387</sup> is generated. Type-I PIs can be defined as molecules that undergo homolytic bond cleavage in the triplet state and typically contain a benzoyl moiety as a chromophore. Primary radicals subsequently add to the double bond of an alkene initiating the polymerization. Quantum yield as well as the rate of addition of the initiator radicals to monomers are important for the efficiency of the reaction process.<sup>377</sup>

This frontier article focuses on the state-of-the-art synthetic methods of acylphosphine oxides and germanium-based PIs to examine their advantages and disadvantages. Toxicity as well as availability and performance as type-I PI for both compound classes will be discussed.

### Syntheses

### **Acylphosphine Oxides**

Several commercially available MAPOs are readily obtained by an Arbuzov-type reaction of airand moisture-sensitive alkoxyphosphanes with acyl chlorides (compare Scheme 5).<sup>388–391</sup> However, the starting material for their synthesis are chlorophosphines, which are not easily available and their industrial production is a highly polluting process.<sup>392</sup> Furthermore, the production of acylphosphine oxides gives rise to stoichiometric amounts of the toxic low-boiling alkyl chlorides e.g. EtCl, as undesirable byproducts.<sup>393</sup> These are released as volatile organic compounds (VOCs) that are difficult to handle and environmentally harmful.<sup>394</sup>



Scheme 5: Classical synthetic route towards acylphosphine oxides.

An alternative route for the preparation of acylphosphine oxides is the addition of disubstituted phosphine oxides to aldehydes in presence of bases and subsequent oxidation of the  $\alpha$ -hydroxyphosphine oxides (shown in Scheme 6).<sup>393,395</sup> The disadvantage of this process is the nevertheless often low oxidation efficiency, which leads to a high amount of oxidant consumption to achieve good yields.<sup>396</sup>



Scheme 6: Synthetic route towards acylphosphine oxides through oxidation of  $\alpha$ -hydroxyphosphine oxides.

However, on the basis of this methodology new acylphosphine oxides substituted with polycyclic aromatic hydrocarbons (PAHs) were recently investigated (Scheme 2).<sup>397–399</sup> The driving force of this development is the availability of powerful light emitting diodes (LEDs), which emit light around 400 nm. Therefore, the introduction of this new acylphosphine oxides with bathochromic shifted absorption maxima is of high interest.

In this context, a new synthetic procedure for acylphosphine oxides was published by Han and Zhang nearly a year ago. Here a direct coupling of hydrogen phosphine oxides with acyl chlorides is mediated by chlorosilanes. (see Scheme 7). The advantage of this synthetic route is the fact that it is environmentally friendlier and safer since no volatile alkyl halides are generated. It also eliminates the use of oxidizing agents used in conventional methods.<sup>400</sup>



Scheme 7: Synthetic route towards acylphosphine oxides using chlorosilanes as catalyst.

While MAPOs are readily accessible through the reactions outlined above, the synthesis of BAPOs is more challenging. Typical synthetic routes to BAPOs involve the double acylation of either a primary phosphine (RPH<sub>2</sub>) or the corresponding metallated derivative (RPH<sub>2-x</sub>M<sub>x</sub>) with an acid chloride in the presence of a base. Subsequent oxidation with e.g. hydrogen peroxide leads to the corresponding bisacylphosphine oxide as shown in Scheme 8. However, this route suffers from inherent safety issues as well as low group functionality. In addition, only aryl or alkyl substituents can be attached to the phosphorus.<sup>391,401</sup>



Scheme 8: Synthetic route towards BAPOs starting from primary phosphanes or metallated derivatives.

Since acylphosphine oxides are mainly water-insoluble initiators, scientists are currently working on modifying the already known initiators. In recent years, the research group of Prof. Grützmacher has developed a convenient one-pot process for the conversion of elemental phosphorus to sodium bis(mesitoyl)phosphide NaP(COMes)<sub>2</sub>. For this purpose, a sodium tert-butylate aggregate NaPH<sub>2</sub>(NaOtBu)<sub>x</sub> is first obtained from elemental phosphorus, sodium and tert-butanol.<sup>402</sup> Subsequent reaction with mesitoyl chloride without prior isolation of the aggregate leads to the formation of NaP(COMes)<sub>2</sub>. A straightforward method for obtaining P-functionalized BAPO derivatives is provided by nucleophilic substitution of NaP(COMes)<sub>2</sub> with alkyl halides followed by oxidation (compare Scheme 9).<sup>201,384</sup>



Scheme 9: Synthetic route towards P-functionalized BAPOs.

With regard to the desired water solubility of acylphosphine oxides, both MAPO and BAPO salts represent new photoinitiators with these properties.<sup>382,385,403</sup> The first research concerning this topic was performed by Schnabel et al. in 1991, where the water-soluble initiator lithium phenyl-2,4,6-trimethylbenzoyl phosphinate, which is a diphenyl(2,4,6-trimethylbenzoyl)-phosphine oxide (TPO) derivative, was reported.<sup>404</sup> The typical synthesis to MAPO salts starts from the commercially available 2,4,6-trimethylbenzoyl-ethoxylphenyl-phosphine oxide (TPO-L), which is synthesized by e.g. the procedure shown in Scheme 5. Further on, it is reacted with sodium iodide or lithium bromide, respectively, to give the corresponding MAPO salts, namely Li-TPO and Na-TPO (shown in Scheme 10).<sup>404–406</sup>



Scheme 10: Synthesis of MAPO salts (Li-TPO and Na-TPO) starting from TPO-L.

In the case of BAPO, the bis(mesitoyl)phosphinic acid (BAPO-OH) is first prepared by the procedure already outlined above (compare Scheme 9). By subsequent reaction with appropriate salts such as sodium hydrogen carbonate or lithium carbonate in low boiling alcohols, BAPO salts, namely BAPO-OLi<sup>385</sup> or BAPO-ONa<sup>403</sup>, can be prepared (shown in Scheme 11).



Scheme 11: Synthesis of BAPO-OH and subsequent reaction to obtain BAPO salts (BAPO-ONa and BAPO-OLi).

## Acylgermanes

Although acylgermanes have been known for more than 60 years, their excellent performance as free radical photoinitiators had long been overlooked. It was not until the seminal work of Liska and Moszner in 2008 with the implementation of acylgermanes as photoinitiators, that research in this field was revived.<sup>407,408</sup> These monoacylgermanes were synthesized from hexamethyldigermane and acid chlorides in the presence of a Pd-catalyst and triethyl phosphite (see Scheme 12).



Scheme 12: Synthesis of monoacylgermanes via palladium-catalysed cross-coupling.

A high activity was also reported for other monoacylgermanes.<sup>197</sup> These compounds were synthesized by the reaction of  $Ph_3GeLi$  with the respective ester,<sup>409</sup> or from the corresponding germyl-1,3-dithiane (compare Scheme 13).<sup>410</sup>



R = Ph, Me; R = Me

Scheme 13: Synthesis of monoacylgermanes via germyl anions and Corey-Seebach approach.

Recently, Wu and co-workers implemented an alternative pathway towards monoacylgermanes.<sup>411</sup> These monoacylgermanes were synthesized from hexamethyl-digermane, carbon monoxide and (hetero)aryl iodides in the presence of a Pd-catalyst and triorgano phosphite (shown in Scheme 14).



Scheme 14: Synthesis of monoacylgermanes via palladium-catalysed carbonylative reaction.

Almost simultaneously with the introduction of monoacylgermanes as promising PIs, the investigation of bisacylgermanes was initiated. The synthetic protocol towards bisacylgermanes is based on a Corey-Seebach type reaction, which was adapted for higher homologues of carbon by A. Brook (compare Scheme 15).<sup>18,408,410</sup>



Scheme 15: Synthesis of bisacylgermanes via Corey-Seebach approach.

On the basis of the synthetic approach presented in Scheme 15 the first bisacylgermane was a commercially available photoinitiator [Bis(4-methoxybenzoyl)implemented as diethylgermane] Ivocerin<sup>®</sup>. In comparison to monoacylgermanes, bisacylgermanes show significantly enhanced extinction coefficients resulting in reduced curing times and increased curing depths of the final composite material.<sup>386,412,413</sup> However, the multi-step synthesis and the tedious purification cause high production costs and prevent - so far - the application as PI apart from dental composites. In 2017 tris- and tetraacylgermanes were synthesized and implemented as long-wavelength PIs.<sup>23,73,82</sup> During the course of these studies, a synthetic protocol allowing a straightforward access to these highly desirable compounds was developed (see Scheme 16). Here, the reaction of a tristrimethylsilyl-substituted germanide with 4 equivalents of acid fluorides leads to the formation of tetraacylgermanes via a multiple silyl abstraction methodology. Trisacylgermanes are formed via the same manner upon reaction of a bissilylsubstituted germanide with the respective acid fluoride.



R = Ph, o-Tol, Mes, p-Tol etc.

Scheme 16: Synthesis of tetraacylgermanes via multiple silyl group abstraction methodology.

Due to the presence of four RC=O chromophores, tetraacylgermanes show increased band intensities in comparison to bisacylgermanes, resulting in more efficient light absorption. A high group tolerance allows the tuning of the properties and shifting of the absorption band to higher wavelengths, which is ideal for medical applications. However, a major drawback of symmetrical tetraacylgermanes are their high melting points, which are responsible for low solubility, limiting the field of applications. Therefore, mixed-functionalized tetraacylgermanes have been implemented (compare Scheme 17).<sup>82</sup> The introduction of different substituents on the germanium centre leads to increased solubility compared with symmetrical tetraacylgermanes.



Scheme 17: Synthesis of mixed-functionalized tetraacylgermanes.

#### **Toxicity of Acylphosphine Oxides**

Testing of various commercially applied photoinitiators for their cytotoxicity as well as biocompatibility has become increasingly important in recent years, as the number of applications in the biomedical field has grown. Earlier this year, Xiao, Liu, Xing et al. published a report in which, among other photoinitiators, bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide (IRGACURE® 819), TPO and TPO-L were examined for their cytotoxicity, using MTT and CCK8 assays, and cytocompatibility towards four tissue types, in particular human cells, mouse cells, normal cells and cell lines. In this study, the tested PIs showed different degrees of cytotoxicity at concentrations ranging from 1 to 50  $\mu$ M under a non-irradiation condition. BAPO exhibited the highest cytotoxicity (IC<sub>50</sub> = 26.68  $\mu$ M; concentration leading to a reduction of cell viability to 50%) among the seven PIs, while TPO appears cytotoxic in a concentration-dependent manner but with a much lower toxicity than that of BAPO. TPO-L, together with another PI, showed the lowest cellular toxicity and at the same time better cytocompatibility with excellent transparency. Upon exposure to 455 nm blue light, these PIs resulted in increasing cytotoxicity to varying degrees, consistent with the trend towards non-irradiation conditions.<sup>380</sup>

In comparison, the water-soluble MAPO and BAPO salts, which were tested for cytotoxicity several years ago, were found to be virtually non-toxic. They were described by the LC<sub>50</sub> (lethal concentration), i.e. the concentration required to kill half of the members of a tested population, in this case a cell culture, after a certain test duration, specifically 24 h. During this study, only Na-TPO was found to have very low biocompatibility (LC<sub>50</sub> < 0.56 mM). In contrast, the cytotoxicity of Li-TPO (LC<sub>50</sub> = 3.1 mM), BAPO-ONa (LC<sub>50</sub> = 2.8 mM), and BAPO-OLi (LC<sub>50</sub> = 2.6 mM) was found to be very low.<sup>385</sup>

According to ECHA (European Chemicals Agency), TPO is classified as Repr. (repoductive toxicity) 2 H361f, indicating that it is suspected of damaging fertility or the unborn child and

causing atrophy of the testes. The classification is included in Annexure VI of CLP (Classification, Labelling and Packaging) regulation.<sup>414</sup> TPO is listed in the Community Rolling Action Plan (CoRAP), which means that the member state Sweden will re-evaluate it in 2022, as it is proposed to further investigate reproductive toxicity and endocrine disrupting properties, persistence, terrestrial bioaccumulation and ecotoxicological properties.<sup>415</sup> ECHA has indicated that they will increasingly use grouping of similar substances, as this is an alternative approach to fill data gaps in registrations submitted under REACH. This approach uses relevant information from analogous substances to predict the properties of target substances. This could of course mean that compounds such as BAPO (IRGACURE® 819) and TPO-L are grouped together with TPO in the dossier review, leading to subsequent restrictions in their use.<sup>416</sup>

#### **Toxicity of Acylgermanes**

Ge-based photoinitiators are repeatedly described in the literature as only very slightly toxic to non-toxic.<sup>21,386,408</sup> In 2008, for example, Ivocerin<sup>®</sup> was found to be non-cytotoxic. Also, the bacterial reverse mutation test (so-called Ames test) revealed that the compound did not induce gene mutations.<sup>407,408,43</sup>

In compliance with the data presented, Ivocerin® has also no harmonized classification according to ECHA and there are no reported hazards from manufacturers, importers or downstream users for this substance.<sup>417</sup>

## Availability

Phosphorus, the 12th most common element in the Earth's crust, is fundamental for life on earth. It is crucial for the formation of DNA, cell membranes and bones. It is vital for food production since it is one of three nutrients (nitrogen, potassium, and phosphorus) used in commercial fertilizer. Consequently, high amounts of phosphorus are consumed every year for food production. Moreover, the Earth's population is growing each year and so is the demand for phosphorus. On the basis of these facts, there has been an ongoing debate about whether or not we are running out of phosphorus. However, this debate was largely dismissed after United States Geological Survey (USGS) and other organizations increased world estimates on available phosphorus resources in 2021.418 Nevertheless, exact reserve quantities remain uncertain, as does the possible impacts of increased phosphate use on future generations. As outlined in numerous papers about germanium-based photoinitiators, the low abundancy of germanium in the Earth's crust (1.6 ppm) results in the high price of these new type of initators.419 Additionally, germanium is recovered mainly as a by-product from sphalerite zinc ores where it is concentrated in amounts up to 0.3%.<sup>420</sup> Since germanium is not a primary resource, the market price of germanium metal is highly fluctuating. Therefore,

these initiator systems cannot fully meet the requirements for photoinitiators in high-throughput polymer synthesis.

## Performance

Acylphosphine oxides as well as acylgermanes are so called Norrish type-I photoinitiators or one-component systems. Upon photocleavage, a benzoyl radical and, in the case of acylphosphine oxide compounds, a phosphinoyl-radical<sup>218</sup> or, in the case of acylgermanes, a germyl-radical<sup>387</sup> are generated. The radical formation is caused by an  $\alpha$ -cleavage from the excited triplet state after photoexcitation and intersystem crossing (ISC) (compare Scheme 18 & Scheme 19). In both cases the phosphinoyl- as well as the germyl-radicals react multiple times faster than the benzoyl radical in the conversion of acrylate double bonds.<sup>377,421</sup> Notably, germyl-radicals show significantly higher reactivity towards monomers than related phosphinoyl-radicals.<sup>201</sup>



Scheme 18: Photocleavage of type-I PIs on the example of TPO generating benzoyl- and phosphinoyl-radicals.



Scheme 19: Photocleavage of type-I PIs on the example of benzoyltrimethylgermane generating benzoyl- and germyl-radicals.

The symmetry forbidden n- $\pi^*$  transitions are responsible for the photoinduced  $\alpha$ -cleavage of the Ge-C(O) or P-C(O) bond and thus the formation of reactive radical sites. In light-induced free radical polymerization, it is important that the emission spectrum of the LED- or UV-lamp overlaps with the absorption spectrum of the corresponding PI. Acylphosphine oxides show low absorption in UV-Vis spectroscopy, around 370-420 nm. Above ~ 420 nm, respectively, no absorption is observed for these compounds, making these initiators unsuitable for long wavelength curing applications. The MAPO and BAPO salts, i.e. Na-TPO, Li-TPO, BAPO-ONa, BAPO-OLi, in turn have their absorption maxima of the n- $\pi^*$  transition approx. at 380 nm. Additionally, they show strong absorption bands well above 400 nm. When irradiated with visible light (400-500 nm), both MAPO and BAPO salts show high reactivity.<sup>385</sup>

In contrast to acylphosphine oxides, acylgermanes exhibit a significant red shift of the longest wavelength absorption. Benzoyltrimethylgermane, for example, exhibits a red shift of 30 nm compared to TPO, i.e., from a  $\lambda_{max}$  value of 380 nm for the phosphorus compound to a  $\lambda_{max}$  value of 411 nm for the germanium compound.<sup>18</sup> Accordingly, acylgermanes, such as tetraacylgermanes or dibenzoyldiethylgermanes, show long-wavelength absorption bands with  $\lambda_{max}$  values between 363 and 419 nm, which extend far into the visible range.<sup>21</sup> This is particular important for the photopolymerization of biocompatible materials, which require non-toxic PIs and non-toxic irradiation sources (visible light).

The high reactivity and excellent efficiency make the two classes of compounds well-suited photoinitiators for industrial purposes. Both initiator systems impress by excellent deep curing and high quantum yields of decomposition.

## Conclusions

To answer the title question "have germanium-based photoinitiators the potential to replace the well-established acylphosphine oxides?", yes and no, both compound classes have their advantages and drawbacks. On the one hand, acylphosphine oxides exhibit cytotoxicity and will be examined more closely by ECHA in the future. On the other hand, they are cost-effective and have been established in industry for decades for high-throughput polymer synthesis. In comparison, acylgermanes have no or only very low cytotoxicity, but germanium is very expensive due to its low abundance in the Earth's crust. Consequently, acylgermanes were so far only implemented as photoinitiators for medical applications. However, improved synthetic pathways and better availability may allow acylgermanes to compete with acylphosphine oxides. The future will show in which direction the development of photoinitiators will move, it only remains to wait and research.

## **Conflicts of interest**

There are no conflicts to declare.

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## 1.4. Outlook

The chemistry of acyl metalloids has evolved in the last decades from a fundamental research field thriven, mainly driven by main group chemists, to a highly interdisciplinary experimental and spectroscopic field focusing on various applications. At the same time, the detailed mechanistic knowledge gained paved the way for new synthetic methods that significantly expanded the synthetic library of acyl metalloids.

Although photoinduced radical polymerization is a well-established technique, there are still challenges, which have to be mastered. The curing depth is still an issue since it depends on the wavelength at which the photoinitiator becomes active. The higher the wavelength, the higher the penetration of the light. It is therefore not surprizing that an important focus has been put on developing initiators with absorptions shifted to  $\lambda$ >>400 nm. We have made important prograss here, but type I photoinitiators that cleave effectively above 600 nm and have a good storage stability are still not available today.

Another major challenge is the development of a high performance biocompatible water-soluble photoinitiator. Although interest for water soluble photoinitiators has existed for almost half a century, all commercial available photoinitiators have at least one major drawback and therefore completely new systems are necessary. In addition, modern approaches in medicine (nanomedicine), such as targeted drug therapy, modern analysis, and diagnostics of diseases, and the production of materials for cell or tissue culture, will require new and increasingly improved initiators that will meet all the criteria for the introduction of materials into the medical market

## 2. Photochemistry of Higher Silicon Hydrides

## 2.1. Introduction

Silicon-hydride derivatives, or simply silanes, are the analogous of hydrocarbons. However, it is these silanes that impressively demonstrate the significant reactivity differences between silicon and carbon.<sup>422,423</sup> While hydrocarbons are chemical inert, silanes are highly reactive molecules that react with oxygen in a spontaneous combustion. Moreover, based on the  $\sigma$ - $\sigma$ \* UV-light can induce a oligomerization. Additionally, under basic conditions a fast degradation occurs. The reason for this different behavior can be traced back to their electronegativities (carbon 2.50, hydrogen 2.20, silicon 1.74 on the Pauling scale), which results in an inverse polarity of the silicon-hydrogen bond. Consequently, this means that the Si-H bond can be easily cleaved by nucleophilic attacks on the silicon atom. Several review articles cover the state of the art of the synthesis and the chemical and physical properties of hydrosilanes.<sup>424-427</sup> Recently, the interest in hydrosilanes and related derivatives has increased, mainly due to recent developments in the semiconductor sector that can be summarized under the term "macroelectronics". Here, electronic circuits with relatively low complexity should be able to cover large areas or flexible substrates and also be inexpensive. These properties play an essential role in the development and research of new photovoltaic (PV) solar cells. The liquid phase deposition (LPD) and processing of silicon films starting from higher silicon hydrides is in this context an attractive procedure.<sup>428</sup> The state-of-the-art LPD based approach for silicon deposition is presented in Scheme 1 using cyclopentasilane (Si<sub>5</sub>H<sub>10</sub>) as a starting material.<sup>35</sup> After a photochemical induced oligomerization this precursor is transformed to a mixture of liquid silane oligomers with an average molar mass of 2600 g/mol. This material is solved in organic solvents to obtain the so-called "liquid silicon material", which is spin coated or printed on a surface of choice. After a thermal treatment at 300-450°C an amorphous silicon film is produced that can additionally be crystallized by laser irradiation.



Scheme 1: Schematic Representation of LPD Processing of Functional Silicon Layers.

## 2.2. Literature

## Synthesis

In general, higher silicon hydrides are obtained by the acid hydrolysis of  $Mg_2Si$  or by the pyrolysis or photolysis of mono- and disilanes. However, both approaches lead to the formation

of a complex product mixture, which contains besides the starting material also insoluble Sicontaining polymer. The state-of-the-art method towards higher hydrosilanes is the hydrogenation of the corresponding chlorosilanes with LiAlH<sub>4</sub> or *i*-Bu<sub>2</sub>AlH. On the basis of this protocol Si<sub>2</sub>H<sub>6</sub>,<sup>429</sup> Si<sub>3</sub>H<sub>8</sub>,<sup>430</sup> HSi(SiH<sub>3</sub>)<sub>3</sub>,<sup>431</sup> Si(SiH<sub>3</sub>)<sub>4</sub><sup>432-434</sup> and the cyclic silicon hydrides Si<sub>5</sub>H<sub>10</sub><sup>435</sup> and Si<sub>6</sub>H<sub>12</sub><sup>436-438</sup> are accessible. In particular, the neopentasilane Si(SiH<sub>3</sub>)<sub>4</sub> can now be prepared in > 100 g quantities by an easy-to-perform procedure starting from perchlorooligosilane such as Si<sub>2</sub>Cl<sub>6</sub> or Si<sub>3</sub>Cl<sub>8</sub> (Scheme 2). This synthetic protocol is an important prerequisite for detailed studies of the chemical properties in this habilitation.

$$Si_nCI_m \xrightarrow{R_3N} CI_3Si \xrightarrow{SiCI_3} iBu_2AIH \xrightarrow{SiH_3} H_3Si \xrightarrow{SiCI_4} Si-SiCI_3 \xrightarrow{iBu_2AIH} H_3Si \xrightarrow{SiH_3} H_3Si \xrightarrow{Si-SiH_3} SiH_3$$

Scheme 2: Synthetic Approach towards Neopentasilane

## Derivatizations

On the basis of their unfavorable properties, the chemical conversion of higher silicon hydrides are still in the early stage of development. Some scattered reports on chemical transformations involving higher silicon hydrides include the partial halogenation of di-, tri-, tetra-, cyclopentaand cyclohexasilanes with BX<sub>3</sub>, HX/AlX<sub>3</sub>, AgX, SnX<sub>4</sub>, HgX<sub>2</sub>, or X<sub>2</sub> (X = Cl, Br, I).<sup>427,439</sup> The partial hydrogenation of perchlorooligosilanes by treatment with substoichiometric amounts of hydrogenating agents such as LiAlH<sub>4</sub> or Me<sub>3</sub>SnH was found to be rather unselective.

A milestone in the chemistry of higher hydrosilanes is the successful synthesis of tetrachloroneopentasilane **5** in multigram quantities recently accomplished in our laboratories (Scheme 3).<sup>440,441</sup> To the best of our knowledge this was the first example for a direct and selective functionalization of a higher silicon hydride on a preparative scale.

*Feher et al.* reported on redistribution reactions of  $Si_2H_6$  or  $Si_3H_8$  under the influence of MSiH<sub>3</sub> (M = Na, K) to give sodium and potassium silanides  $MSi_nH_{2n+1}$  (n = 3–5).<sup>442</sup> Associated studies showed that  $MSi_nH_{2n+1}$  type silanides are also accessible directly from the reaction of SiH<sub>4</sub> with finely dispersed sodium or potassium.<sup>443</sup> The resulting silanide mixtures subsequently could be reacted with C<sub>4</sub>F<sub>9</sub>SO<sub>3</sub>SiH<sub>3</sub>, PhSO<sub>3</sub>H and p-MePhSO<sub>3</sub>H to the corresponding silanes and organosilanes. Treatment with GeH<sub>4</sub>, PH<sub>3</sub> or SnH<sub>4</sub> lead to silyl-substituted sodium or potassium germanides, phosphides or stannides. These methods, however, generally afforded product mixtures, which only could be separated in small amounts by preparative gas chromatography. In a recent paper Stueger et al. presented an alternative method for the synthesis of alkali metal

silanides  $MSi(SiH_3)_3$  (M = Li, Na, K) by treating neopentasilane with bases such as MeLi, MOtBu or  $LiiPr_2$  (Scheme 4). This approach makes silanide accessible in sufficient purity in preparative quantities for the first time and already allowed for the synthesis and the isolation of  $-SiR_3$  and  $-GeR_3$  (R = Ph, Me) derivatives of isotetrasilane.<sup>444</sup>

Scheme 4: Synthesis of a Perhydrogenated Hypersilanide and Reaction with Electrophiles

Recently, we discovered that this silanide undergoes a selective redistribution reaction under formation of the highly branched octasilane as the major product after treatment with halogen sources such as  $BrCH_2CH_2Br$ ,  $SiCl_4$  or  $GeCl_4$  (Scheme 5).<sup>38</sup>

Scheme 5: Synthesis of a Perhydrogenated Hypersilanide and Reaction with Electrophiles

The synthesis and derivatization of this anion and related compounds was also the starting point of this part of my habilitation.

## 2.3. Publications

The following section covers the publications on this topic submitted during this habilitation. The starting point of this work was the isolation and characterization of new perhydrogenated hypersilanides published in *ZAAC*. The second publication was the introduction of a new strategy towards higher silicon hydrides in *Eur. J. Inorg. Chem.* The third paper uses this new developed methodology to generate a variety of single source precursors for Si-C films.

## 2.3.1. The Synthesis of Tris(silyl)silanides Revisited. A Study of Reactivity and Stability

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## Abstract

In this contribution, we investigated the stability of  $(H_3Si)_3SiLi$  (**2a**) in the presence of tetramethylethylenediamine (TMEDA) and 1,2-bis(diphenylphosphino)ethane (DPPE). Moreover, the synthesis to obtain tris(silyl)silanides with alternated counter ions by the base mediated desilylation approach was described. Additionally, metal-metal exchange reactions of **2a** with MgBr<sub>2</sub>, ZnCl<sub>2</sub>, HgCl<sub>2</sub> were examined. Subsequently, we reacted **2a** with 1.0 and 0.5 equivalents of ZnCl<sub>2</sub>[TMEDA] and could obtain the isolable zinc substituted silanides **5a**,**b**. Finally, we reacted **2a** with equimolar amounts of [(<sup>Mes</sup>Nacnac)MgI(OEt<sub>2</sub>)] and [(<sup>Dipp</sup>Nacnac)MgI(OEt<sub>2</sub>)] and found the selective transmetalation to the corresponding magnesium substituted silanides **6a**,**b** in good yields. Interestingly, for compounds **5a**,**b** and **6a**,**b** 

the removal of the reaction solvents did not induce a degradation. For compound **6a** crystals suitable for X-ray analysis could be grown, which represents the first structural characterization of an isolable perhydrogenated hypersilanide.



## Introduction

In contrast to the chemically inert hydrocarbons, their silicon congeners are often pyrophoric upon exposure to air and readily hydrolyze under basic conditions. These unfavorable properties to a large extent impeded the investigation of hydrosilanes in the past. Especially mono- to trisilanes are highly pyrophoric, based on their low boiling points. Therefore, there is an ongoing search for pathways to higher hydrosilanes, which can be performed on a multiple gram scale and result in the formation of pure compounds.

The state-of-the-art approach to higher hydrosilanes on a laboratory scale is the hydrogenation of the appropriate chlorosilanes with LiAlH<sub>4</sub> or *i*-Bu<sub>2</sub>AlH. However, the application of this protocol is more or less restricted to the synthesis of  $Si_2H_6$ ,<sup>429</sup>  $Si_3H_8$ ,<sup>430</sup>  $Si_5H_{12}$  (1)<sup>432–434</sup>, isotetrasilane HSi(SiH<sub>3</sub>)<sub>3</sub><sup>431</sup> and the cyclic silicon hydrides  $Si_5H_{10}^{435}$  and  $Si_6H_{12}$ .<sup>436–438</sup> In particular, neopentasilane 1 now can be prepared in > 100 g quantities by an easy-to-perform procedure starting from perchlorooligosilanes such as  $Si_2Cl_6$  or  $Si_3Cl_8$  (Scheme 1).<sup>432–434</sup>



Scheme 1. Synthesis of neopentasilane 1.

This finding is an important prerequisite for detailed studies of the chemical properties of **1**. Stueger and coworkers showed that **1** undergoes a selective base induced desilylation to the corresponding alkali metal silanides  $MSi(SiH_3)_3$  **2a-c** (M = Li, Na, K). As suitable bases MeLi, MOtBu (M = Na or K) or Li*i*Pr<sub>2</sub> were investigated (Scheme 2).<sup>444</sup>

$$\begin{array}{ccc} SiH_3 & base & SiH_3 \\ H_3Si-Si-SiH_3 & & \\ SiH_3 & M=Li, Na, K & \\ \end{array} \begin{array}{ccc} SiH_3 & \\ SiH_3 & \\ 2a: M=Li \\ 2b: M=Na \\ 2c: M=K \end{array}$$

Scheme 2. Synthesis of tris(silyl)silanides 2a-c.

However, all attempts to isolate or crystallize these silanides failed, due to the tendency to oligomerize upon storage or evaporation of the solvents. On the basis of the recent advances in the field of main group chemistry, we wanted to investigate different bases and use the widely applied kinetic and/or electronic stabilization methods in order to isolate these silanides. This is a prerequisite for further derivatization of this nucleophile.

#### **Results and Discussion**

**Lithium-Silanide 2a.** First, we investigated the stability of **2a** in the presence of tetramethylethylenediamine (TMEDA) and 1,2-bis(diphenylphosphino)ethane (DPPE), two well-known chelate ligands. Therefore, we added equimolar amounts of the respective chelate ligand to a reaction solution of **2a**. Scheme 3 shows the addition reaction of TMEDA. Upon removal of the reaction solvents **3a** degrades to an uncharacterized polysilane. However, at -30 °C pure **3a** precipitates from the reaction solution in good yield. Analytical data are consistent with the proposed structure, exhibiting one resonance line in the <sup>29</sup>Si-NMR spectrum for the three SiH<sub>3</sub>-groups at  $\delta = -77.8$  ppm and one signal for the quaternary silicon atom at  $\delta = -265.9$  ppm. Interestingly, the <sup>1</sup>H-NMR shows besides the expected two signals for the chelate ligand only one sharp signal for the SiH<sub>3</sub>-groups at  $\delta = 4.13$  ppm, which is significantly low field shifted by more than 0.6 ppm to the unsubstituted silanide **2a**. We assume that the chelate ligand leads to more pronounced solvent separation and thus consequently induce more charge distribution of the negative charge through negative hyperconjugation. Unfortunately, all attempts to grow crystals, which were suitable for X-ray analysis failed.



3a, 61% Yield

Scheme 3. Synthesis of tris(silyl)silanides 3a.

In contrast to the selective coordination of TMEDA to **2a**, the DPPE adduct of **2a** was not observed. All attempts to crystalize the DPPE substituted silanide resulted in the crystallization of the free ligand.

Therefore, we moved on to examine the reactivity and stability of other counter ions. The preparation of potassium silanides is an easy to perform method and boosted the number of new polysilanes significantly.<sup>271</sup>

However, as outlined by the seminal work of Ruhlandt-Senge and coworkers the use of KO*t*Bu comes always with the formation of small amounts of elemental silicon, indicating redox chemistry.<sup>445</sup> Therefore we set out and investigated the synthesis of the heavier alkali metal silanide (M = Rb and Cs). Treatment of **1** in THF-d<sub>8</sub> solution at -30 °C with equimolar amounts of the bases (RbO*t*Bu or CsO*t*Bu) results in the formation of the expected tris(silyl)silanides **3b** and **3c** alongside with the corresponding silylether. (compare Scheme 4). This silylether undergoes a rearrangement to SiH<sub>4</sub> and *t*BuO*t*Bu, which is observed by NMR measurements as well as gas evolution (see *Supporting Information* Figure S3 and S5).

## Scheme 4. Synthesis of tris(silyl)silanides 3b,c.

The obtained THF solution could be used directly for further derivatizations or stored at -70 °C for a prolonged time (usually days). Analytical and spectroscopic data that strongly support the structural assignment are summarized in the *Experimental Section*, together with experimental details. Again upon removal of the solvent the silanides undergo a degradation process to uncharacterized polysilanes. Additionally, all attempts to grow crystals by the addition of 18-crown-6 failed.

Recently, it has been found that the transmetalation from lithium silanides to the corresponding magnesium derivatives is beneficial for the stability.<sup>446</sup> Consequently, we transferred this method to the hydrosilane system. The reaction of equimolar amount of **2a** with MgBr<sub>2</sub> results in the formation of small amount of the bis-[tris(silyl)silanide]-magnesium compound **4** as sole isolable product in low yield (Scheme 5). The reaction with 0.5 equivalent of **2a** and MgBr<sub>2</sub> also gave rise to the same product formation and nearly identical yield. Analytical and spectroscopic data that strongly support the structural assignment are shown in the *Experimental Section*, together with experimental details. The compound is also unstable and forms uncharacterized polysilanes at room temperature in days.



Scheme 5. Metal-metal exchange reaction of 2a with MgBr<sub>2</sub>.

The next target was the transmetalation to obtain zincio- and mercurio-oligosilanes. Therefore, we reacted 2a with 0.5 equivalents of ZnCl<sub>2</sub> or HgCl<sub>2</sub>. However, no selective transmetalation was observed. In all cases the formation of elemental zinc and mercury were observed alongside with the polymerization of the silicon skeleton. In order to synthesize a zinc substituted silanide we coordinated ZnCl<sub>2</sub> with TMEDA to stabilize this reagent.<sup>447</sup> Subsequently we reacted **2a** with 1.0 and 0.5 equivalents of ZnCl<sub>2</sub>[TMEDA] and could obtain in both cases isolable zincioisotetrasilanides. The reaction with equimolar amounts of both reagents resulted in the formation of the monosubstituted derivative 5a. The reaction of 2a with 0.5 equivalents of ZnCl<sub>2</sub>[TMEDA] gave rise to the selective formation of the disubstituted zinc species 5b (compare Scheme 6). Analytical data are consistent with the proposed structures for both compounds (see *Experimental Section*). For **5a**,**b** nearly identical signals for the three SiH<sub>3</sub>-groups at  $\delta = -85.2$ ppm for **5a** and  $\delta = -84.7$  ppm for **5b** were found in the <sup>29</sup>Si-NMR spectra. Also the signals for the quaternary silicon atom are in the same region with  $\delta = -202.4$  ppm for 5a and  $\delta = -203.1$ ppm for 5b. Interestingly, in solution 5a undergoes a fast rearrangement process to 5b and ZnCl<sub>2</sub>[TMEDA] (see Scheme 7). In contrast to the alkali metal substituted derivatives of this type, **5a**,**b** do not show any detectable degradation upon removal of the reaction solvents. The isolated white solids can be stored under inert condition for prolonged time. Moreover, on the basis of this **5a**,**b** represents ideal precursors for a further investigation. Nevertheless, all attempts to grow crystals, which were suitable for X-ray analysis failed. Giving our aim to obtain the first structure of a perhydrogenated hypersilyl-silanide we once more changed the cation.



5**b**, 79% yield

#### Scheme 6. Reaction of 2a with ZnCl<sub>2</sub>[TMEDA].



#### Scheme 7. 5a Solution rearrangement process of 5a.

On the basis of the observed reactivity with the TMEDA stabilized  $ZnCl_2$  we wanted to investigate the outcome of the reaction of our silanide with magnesium(II) iodide complexes incorporating  $\beta$ -diketiminate ligands. Therefore, we reacted **2a** with equimolar amounts of  $[(^{Mes}Nacnac)MgI(OEt_2)]$  and  $[(^{Dipp}Nacnac)MgI(OEt_2)]$  and found the selective transmetalation to the corresponding magnesium substituted silanides **6a,b** in good yields (see Scheme 8).



Scheme 8. Reaction of 2a with [(<sup>Aryl</sup>Nacnac)MgI(OEt<sub>2</sub>)].

Again, for both compounds the removal of the reaction solvents does not induce a degradation. Compound **6a,b** can be isolated as slightly yellow powder and stored at room temperature without the formation of any degradation products. In solution a very slow formation of SiH<sub>4</sub> occurs. Analytical data are consistent with the proposed structure, exhibiting one resonance line in the <sup>29</sup>Si-NMR spectrum for the three SiH<sub>3</sub>-groups at  $\delta = -82.7$  ppm and one signal for the quaternary silicon atom at  $\delta = -231.6$  ppm for **6a**. For **6b** the signals for the SiH<sub>3</sub>-groups appear at  $\delta = -85.7$  ppm and for the quaternary silicon atom at  $\delta = -228.7$  ppm. The quaternary signal appears significantly low field shifted in comparison to 2a-c. Finally, with the <sup>Dipp</sup>nacnac ligand system we were able to grow crystals suitable for X-ray analysis, which were obtained by cooling the concentrated solution of **6a** in toluene to -30 °C. Compound **6a** crystallized in the monoclinic space group  $P = 1 2_1/n = 1$  and the unit cell contains four molecules. The Mg1-Si1 bond length (2.6261(11) Å) in **6a** is unexceptional in comparison to other reported magnesium-silanide complexes (2.628-2.800 Å).<sup>448–451</sup> Moreover, in close analogy to other structurally characterized silanides,<sup>452</sup> the central silicon atom is pyramidal with a sum of angle of 296.4°. In comparison to **1** the mean Si-Si bond length with 2.32 Å is slightly elongated.<sup>[15b]</sup> The structural characterization of this compound ends a long series of experiments to gain a structural information for these elusive silanides.



**Figure 1.** ORTEP representation of **6a**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms except the hydrides are omitted and 2,6-Diisopropylphenyl (Dipp) groups and Et<sub>2</sub>O are wireframed for clarity. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations:  $\sum \alpha Si(1) 296.4$ , Si(1)-Mg(1) 2.6261(11), Si(1)-Si2 2.3293(12), Si(1)-Si(3) 2.3243(12), Si(1)-Si(4) 2.3181(13), Mg(1)-N(1) 2.046(2), Mg(1)-N(2) 2.048(2), C(1)-N(1)-Mg(1) 115.49(16), C(3)-N(2)-Mg(1) 115.85(16), Si(3)-Si(1)-Mg(1) 113.20(4), Si(3)-Si(1)-Si(2) 100.03(5), Si(2)-Si(1)-Mg(1) 124.80(5), Si(4)-Si(1)-Mg(1) 118.06(5), Si(4)-Si(1)-Si(3) 99.05(5), Si(4)-Si(1)-Si(2) 97.31(6).

## Conclusion

In summary, we investigated the synthesis of a variety of new tris(silyl)silanides by the addition of chelate ligands, base induced desilvlation and metal-metal exchange reactions. With the addition of TMEDA to the lithium substituted silanide 2a, the TMEDA adduct 3a was isolated. The base mediated desilylation approach was performed to obtain tris(silyl)silanides with different counter ions. Therefore, the reaction of 1 with equimolar amounts of the bases (RbOtBu and CsOtBu) resulted in the formation of the expected tris(silyl)silanides **3b** (M = Rb) and **3c** (M = Cs). Additionally, metal-metal exchange reactions of 2a with MgBr<sub>2</sub>, ZnCl<sub>2</sub>, HgCl<sub>2</sub> were examined. Only MgBr<sub>2</sub> showed a selective transmetalation to the bis-[tris(sily1)silanide]magnesium derivative 4 in low yield. Furthermore, we reacted 2a with 1.0 and 0.5 equivalents of ZnCl<sub>2</sub>[TMEDA] and could obtain the isolable zinc substituted silanides **5a**,**b**. However, the monosubstituted compound **5a** undergoes a fast rearrangement to the disubstituted derivative **5b** alongside with the formation of ZnCl<sub>2</sub>[TMEDA]. As a final point, we reacted 2a with equimolar amounts of [(MesNacnac)MgI(OEt<sub>2</sub>)] and [(DippNacnac)MgI(OEt<sub>2</sub>)] and found the selective transmetalation to the corresponding magnesium substituted silanides 6a,b in good yields. For the zinc-substituted derivatives **5a**,**b** and the magnesium compound **6a**,**b**, the removal of the reaction solvents did not induce a degradation. On the basis of their higher stability, these compounds were isolable as stable solids with a defined amount of solvents attached. Consequently, we are now able to prepare homogeneous stock solutions in non-polar solvents, that are stable and storable in the fridge. For compound **6a** crystals suitable for X-ray analysis could be grown, which represents the first example of an isolable perhydrogenated hypersilylsilanide.

## **Experimental Section**

All experiments were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried using a column solvent purification system.<sup>453</sup> MeLi (1.6M in Et<sub>2</sub>O), THF-d<sub>8</sub> (99.5 atom% D) and C<sub>6</sub>D<sub>6</sub> (99.5 atom%, D) were used without any further purification. Salts were dried before usage. TMEDA was dried by 6-hour reflux above sodium. For the measurement of air sensitive samples deuterated solvents were additionally dried (C<sub>6</sub>D<sub>6</sub> was dried by 24-hour reflux above a sodium/potassium alloy; THF-d<sub>8</sub> was dried by 6-hour reflux above lithium aluminium hydride). Cesium-*tert*-butoxide<sup>454</sup>, rubidium-*tert*-butoxide,<sup>454</sup> ZnCl<sub>2</sub>[TMEDA],<sup>[13]</sup> [(<sup>Mes</sup>Nacnac)MgI(OEt<sub>2</sub>)]<sup>455</sup> and [(<sup>Dipp</sup>Nacnac)MgI(OEt<sub>2</sub>)]<sup>455</sup> were prepared according to published procedures. <sup>1</sup>H- and <sup>13</sup>C- and <sup>29</sup>Si-NMR spectra were recorded on a 200 MHz Bruker AVANCE DPX spectrometer in C<sub>6</sub>D<sub>6</sub> or THF-d<sub>8</sub> solutions and referenced versus TMS using the internal 2H-lock signal of the solvent. Melting points were determined using Stuart SMP50 apparatus and are uncorrected. Elemental analyses were carried out on a Hanau Vario Elementar EL apparatus. UV absorption spectra were recorded on a Perkin Elmer Lambda 5 spectrometer.

X-ray Crystallography. The crystal suitable for single-crystal X-ray diffractometry was removed from a vial or Schlenk flask 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 a cold  $N_2$ stream. XRD data collections for compound 6a was performed on a Bruker APEX II diffractometer with use of an Incoatec microfocus sealed tube of Mo K $\alpha$  radiation ( $\lambda$ = 0.71073 Å) and a CCD area detector. Empirical absorption corrections were applied using SADABS or TWINABS.<sup>456,457</sup> The structure was solved with the use of direct methods and the intrinsic phasing option in SHELXT and refined by the full-matrix least-squares procedures in SHELXL.<sup>458-460</sup> or Olex2.<sup>461</sup> The space group assignment and structural solution was evaluated using PLATON.<sup>462,463</sup> Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were either located in a difference map or in calculated positions corresponding to standard bond lengths and angles. Disorder was handled by modeling the occupancies of the individual orientations using free variables to refine the respective occupancy of the affected fragments (PART).<sup>464</sup> Table S1 in the Supporting Information contains crystallographic data and details of measurements and refinement for compound **6a**. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre (CCDC) under the following number: 2163774.

**Synthesis of 3a**. 4.1 mL of a 1.6 M Et<sub>2</sub>O solution of MeLi (6.6 mmol) were slowly added to a solution of 1.0 g of Si(SiH<sub>3</sub>)<sub>4</sub> (6.6 mmol) in 15 mL Et<sub>2</sub>O at -30 °C. After additional stirring for 30 min at room temperature 1 mL of tetramethylethylenthediamine (6.6 mmol) were added. The

solution was stirred for another 30 min at room temperature and then filtered. Subsequently, 5 mL of THF were added and placed in the refrigerator at -30 °C. The next day the product was precipitated out of solution and subsequently filtrated off, giving the product as a white solid. **Yield**: 2.1 g of **3a** (5.4 mmol; 83%). <sup>1</sup>**H-NMR** (C<sub>6</sub>D<sub>6</sub>, TMS, ppm): 4.13 (s, 9H, Si*H*<sub>3</sub>), 3.62 (m, 8H, OC*H*<sub>2</sub>), 2.04 (s,12 H, NC*H*<sub>3</sub>), 1.99 (s, 4H, NC*H*<sub>2</sub>), 1.61 (m, 8H, C*H*<sub>2</sub>). <sup>13</sup>**C-NMR** (C<sub>6</sub>D<sub>6</sub>, TMS, ppm): 68.22(s, OCH<sub>2</sub>), 56.60 (s, NCH<sub>2</sub>), 46.15 (s, NCH<sub>3</sub>), 25.45 (s, CH<sub>2</sub>). <sup>29</sup>**Si-NMR** (C<sub>6</sub>D<sub>6</sub>, TMS, ppm): -77.76 (q, <sup>1</sup>J<sub>Si-H</sub> = 169.71 Hz, hep, <sup>3</sup>J<sub>SiH</sub> = 7.34 Hz, *Si*H<sub>3</sub>); -265.87 (m, <sup>2</sup>J<sub>Si-H</sub> = 6.25Hz, Li*Si*(SiH<sub>3</sub>)<sub>3</sub>). **mp**: 60-63 °C

Synthesis of 3b. 104 mg of RbO*t*Bu (0.66 mmol) were slowly added to a solution of 100 mg of Si(SiH<sub>3</sub>)<sub>4</sub> (0.66 mmol) in 0.6 mL THF-d<sup>8</sup> in a young tube NMR-tube. After reaction time of 30 min NMR analysis showed quantitative formation of **3b** alongside the formation of silyletherderivates. <sup>1</sup>H-NMR (THF-d<sup>8</sup>, TMS, ppm): 3.25 (s, 9H, SiH<sub>3</sub>). <sup>29</sup>Si-NMR (THF-d<sup>8</sup>, TMS, ppm): -77.04 (q, <sup>1</sup>J<sub>Si-H</sub> = 165.74 Hz, hep, <sup>3</sup>J<sub>SiH</sub> = 8.03 Hz, *Si*H<sub>3</sub>); -281.07 (m, <sup>2</sup>J<sub>Si-H</sub> = 6.74Hz, Rb*Si*(SiH<sub>3</sub>)<sub>3</sub>).

**Synthesis of 3c**. 135 mg of CsO*t*Bu (0.66 mmol) were slowly added to a solution of 135 mg of Si(SiH<sub>3</sub>)<sub>4</sub> (0.66 mmol) in 0.6 mL THF-d<sup>8</sup> in a young tube NMR-tube. After reaction time of 30 min NMR analysis showed quantitative formation of **3c** alongside the formation of silylether-derivates. <sup>1</sup>**H-NMR** (THF-d<sup>8</sup>, TMS, ppm): 3.27 (s, 9H, SiH<sub>3</sub>). <sup>29</sup>**Si-NMR** (THF-d<sup>8</sup>, TMS, ppm): -76.08 ppm (q, <sup>1</sup>J<sub>Si-H</sub> = 165.01 Hz, hep, <sup>3</sup>J<sub>SiH</sub> = 8.16 Hz, *Si*H<sub>3</sub>); -279.64 (m, <sup>2</sup>J<sub>Si-H</sub> = 6.32 Hz, Cs*Si*(SiH<sub>3</sub>)<sub>3</sub>).

**Synthesis of 4**. 4.1 mL of a 1.6 M Et<sub>2</sub>O solution of MeLi (6.6 mmol) were slowly added to a solution of 1.0 g of Si(SiH<sub>3</sub>)<sub>4</sub> (6.6 mmol) in 15 mL Et<sub>2</sub>O at -30 °C. After additional stirring for 30 min at room temperature the solution was slowly added to 0.6 g of MgBr<sub>2</sub> (3.3 mmol) in 20 ml Et<sub>2</sub>O at -30 °C. The mixture was stirred for one hour at room temperature. Subsequently, the solvent was removed via vacuum. 20 mL of *n*-pentane were added and the salts and the formed polysilanes were filtered of. The removal of the solvent afforded an oil, which could be identified as compound **4**. **Yield**: 0.14 g of **4** (0.2 mmol; 8%). <sup>1</sup>**H-NMR** (C<sub>6</sub>D<sub>6</sub>, TMS, ppm): 3.82 (s, 18H, SiH<sub>3</sub>), 3.36 (q, 16 H, CH<sub>2</sub>), 0.85 (t, 24H, CH<sub>3</sub>). <sup>29</sup>**Si-NMR** (C<sub>6</sub>D<sub>6</sub>, TMS, ppm): -84.26 (*Si*H<sub>3</sub>), -299.22 (Mg*Si*(Si(H<sub>3</sub>)<sub>3</sub>).

Synthesis of 5a. 4.1 mL of a 1.6 M Et<sub>2</sub>O solution of MeLi (6.6 mmol) were slowly added to a solution of 1.0 g of Si(SiH<sub>3</sub>)<sub>4</sub> (6.6 mmol) in 15 mL Et<sub>2</sub>O at -30 °C. After additional stirring for 30 min at room temperature the solution was slowly added to 1.72 g of ZnCl<sub>2</sub>[TMEDA] (6.6 mmol) in 20 mL Et<sub>2</sub>O at -30 °C. The mixture was stirred for one hour at room temperature. Subsequently, the solvent was removed via vacuum. The crude product was resuspended in 20 mL of toluene and filtered via a syringe filter. Then, the toluene was removed and washing of the solid with *n*-pentane giving the product as a white solid. **Yield**: 1.7 g of **5a** (5.0 mmol; 76%).

**Anal. Calc.** (%) for C<sub>6</sub>H<sub>25</sub>ClN<sub>2</sub>Si<sub>4</sub>Zn: C, 21.29; H, 7.45, **Found**: C, 21.56; H, 7.67. <sup>1</sup>**H-NMR** (C<sub>6</sub>D<sub>6</sub>, TMS, ppm): 3.95 (s, 9H, Si*H*<sub>3</sub>), 2.11 (m, 16 H, NC*H*<sub>3</sub> and NC*H*<sub>2</sub>) <sup>29</sup>Si-NMR (C<sub>6</sub>D<sub>6</sub>, TMS, ppm): -85.20 (q, <sup>1</sup>J<sub>Si-H</sub> = 187.65 Hz, hep, <sup>3</sup>J<sub>SiH</sub> = 5.04 Hz, *Si*H<sub>3</sub>); -202.39 (m, <sup>2</sup>J<sub>Si-H</sub> = 5.37 Hz, Zn*Si*(SiH<sub>3</sub>)<sub>3</sub>). **mp**: 116-118 °C

**Synthesis of 5b.** 4.1 mL of a 1.6 M Et<sub>2</sub>O solution of MeLi (6.6 mmol) were slowly added to a solution of 1.0 g of Si(SiH<sub>3</sub>)<sub>4</sub> (6.6 mmol) in 15 mL Et<sub>2</sub>O at -30 °C. After additional stirring for 30 min at room temperature the solution was slowly added to 0.86 g of ZnCl<sub>2</sub>[TMEDA] (3.3 mmol) in 20 mL Et<sub>2</sub>O at -30 °C. The mixture was stirred for one hour at room temperature. Subsequently, the solvent was removed via vacuum. The crude product was resuspended in 20 mL of toluene and filtered via a syringe filter. Then, the toluene was removed and redissolved in 10 mL of *n*-pentane. The clear solution and subsequently filtrated off, giving the product as a white solid. **Yield**: 1.1 g of **5b** (2.6 mmol; 79%). **Anal. Calc.** (%) for C<sub>6</sub>H<sub>34</sub>N<sub>2</sub>Si<sub>8</sub>Zn: C, 16.98; H, 8.08, **Found**: C, 17.22; H, 8.15. <sup>1</sup>**H-NMR** (C<sub>6</sub>D<sub>6</sub>, TMS, ppm): 3.97 (s, 18H, SiH<sub>3</sub>), 2.01 (s, 12 H, NCH<sub>3</sub>), 1.72 (s, 4H, NCH<sub>2</sub>). <sup>29</sup>Si-NMR (C<sub>6</sub>D<sub>6</sub>, TMS, ppm): -84.70 (q, <sup>1</sup>J<sub>Si-H</sub> = 186.99 Hz, hep, <sup>3</sup>J<sub>SiH</sub> = 5.10 Hz, *Si*H<sub>3</sub>); -203.11 (m, <sup>2</sup>J<sub>Si-H</sub> = 5.68Hz, Zn*Si*(SiH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>, TMS, ppm): 48.70 (s, *C*H<sub>3</sub>) 56.98 (s, *C*H<sub>2</sub>). **mp**: 120-123 °C.

Synthesis of 6a. 3.3 mL of a 1.6 M Et<sub>2</sub>O solution of MeLi (5.4 mmol) were slowly added to a solution of 0.8 g of Si(SiH<sub>3</sub>)<sub>4</sub> (5.4 mmol) in 15 mL Et<sub>2</sub>O at -30 °C. After additional stirring for 30 min at room temperature the solution was slowly added to 3.0 g of [(<sup>Dipp</sup>Nacnac)MgI(OEt<sub>2</sub>)] (5.4 mmol) in 20 mL Et<sub>2</sub>O at -30 °C. The mixture was stirred for one hour at room temperature. Subsequently, the solvent was removed via vacuum. The crude product was resuspended in 20 mL of boiling *n*-heptane and filtered via a syringe filter. The clear solution was placed in the refrigerator at -70 °C. The next day the product was precipitated out of solution and subsequently filtrated off, giving the product as a slightly yellow solid. **Yield**: 2.3 g of **6a** (3.6 mmol; 68%). Anal. Calc. (%) for C<sub>33</sub>H<sub>60</sub>MgN<sub>2</sub>OSi<sub>4</sub>: C, 62.17; H, 9.49, Found: C, 62.34; H, 9.67. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>, TMS, ppm): 7.27 (s, 6H, CH), 4.87 (s, 1H, CH) 3.77 (m, 4H, CH), 3.55 (s, 9H, SiH<sub>3</sub>), 3.26 (q, 4H, CH<sub>2</sub>), 1.68 (s, 6H, CH<sub>3</sub>), 1.43 (d, 12H, CH<sub>3</sub>), 1.36 (t, 6H, CH<sub>3</sub>) 1.26 (d, 12H, CH<sub>3</sub>) <sup>29</sup>Si-NMR (C<sub>6</sub>D<sub>6</sub>, TMS, ppm): -82.66 (q,  ${}^{1}J_{Si-H} = 184.02$  Hz, hep,  ${}^{3}J_{SiH} = 5.64$  Hz,  $SiH_{3}$ ); -231.64 (m,  ${}^{2}J_{Si-H} = 4.84$  Hz, MgSi(Si(H<sub>3</sub>)<sub>3</sub>).  ${}^{13}$ C-NMR (C<sub>6</sub>D<sub>6</sub>, TMS, ppm): 169.65, 144.57, 141.92, 128.09, 125.66, 124.11, 95.39, 65.41, 28.09, 25.47, 24.50, 24.15, 13.33 ppm. mp: 112-114 °C. Synthesis of 6b. 3.3 mL of a 1.6 M Et<sub>2</sub>O solution of MeLi (5.4 mmol) were slowly added to a solution of 0.8 g of Si(SiH<sub>3</sub>)<sub>4</sub> (5.4 mmol) in 15 mL Et<sub>2</sub>O at -30 °C. After additional stirring for 30 min at room temperature the solution was slowly added to 3.0 g of [(<sup>Mes</sup>Nacnac)MgI(OEt<sub>2</sub>)] (5.4 mmol) in 20 mL Et<sub>2</sub>O at -30 °C. The mixture was stirred for one hour at room temperature. Subsequently, the solvent was removed via vacuum. The crude product was resuspended in 20 mL of boiling *n*-heptane and filtered via a syringe filter. The clear solution was placed in the refrigerator at -70 °C. The next day the product was precipitated out of solution and subsequently filtrated off, giving the product as a slightly yellow solid. **Yield**: 2.0 g of **6a** (3.6 mmol; 68%). **Anal. Calc**. (%) for C<sub>27</sub>H<sub>48</sub>MgN<sub>2</sub>OSi<sub>4</sub>: C, 58.61; H, 8.74, **Found**: C, 58.88 H, 8.93. <sup>1</sup>**H-NMR** (C<sub>6</sub>D<sub>6</sub>, TMS, ppm): 6.85 (s, 4H, C*H*), 4.86 (s, 1H, C*H*) 3.67 (s, 9H, Si*H*<sub>3</sub>), 3.27 (q, 4H, C*H*<sub>2</sub>), 2.18-2.22 ppm (d,18H, C*H*<sub>3</sub>), 1.60 (s, 6H, C*H*<sub>3</sub>), 0.67 (t, 6 H, C*H*<sub>3</sub>) <sup>29</sup>**Si-NMR** (C<sub>6</sub>D<sub>6</sub>, TMS, ppm): -82.67 (q, <sup>1</sup>J<sub>Si-H</sub> = 183.20 Hz, hep, <sup>3</sup>J<sub>SiH</sub> = 5.63 Hz, *Si*H<sub>3</sub>); -228.72 (m, <sup>2</sup>J<sub>Si-H</sub> = 4.95 Hz, Mg*Si*(Si(H<sub>3</sub>)<sub>3</sub>). <sup>13</sup>**C-NMR** (C<sub>6</sub>D<sub>6</sub>, TMS, ppm): 168.48, 144.80, 133, 47, 129.42, 128.09, 94.98, 65.39, 23.06, 20.63, 19.24, 13.32 ppm. **mp**: 118-120 °C.

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In addition, M.H. is pleased that crystals of **6a** suitable for X-ray analysis were obtained by using the (<sup>Dipp</sup>Nacnac)MgI salt, which he first worked with during his Schrödinger fellowship in the Jones group

Keywords: silanides • hydrides • metallation • silanes • silicon

## **2.3.2.** Dodecamethoxyneopentasilane as a new Building Block for defined Silicon-Frameworks

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## Abstract

In this contribution, a convenient synthetic method to obtain tris(trimethoxysilyl)silanides (M = Li, Na, K, Cu) **5a-d** is described. **5a-d** are easily accessible deriving from dodecamethoxyneopantasilane **4** in excellent yields and could be fully characterized *via* NMR spectroscopy and X-ray crystallography. The efficiency of **5a-d** to serve as a new building block



in silicon chemistry is demonstrated by the reactions with two different types of electrophiles (carbon- and silicon-electrophiles). In all cases the salt metathesis reaction gave rise to novel polysilanes in excellent yields. The possibility of a post-functionalization to perhydropolysilanes as well as perchloropolysilanes enables the synthesis of new precursors for silicon deposition.

#### Introduction

The chemistry of silyl anions and in particular its power in the formation of silicon-silicon or silicon-element bonds is one of the most important tool in silicon chemistry. Based on this, significant advances in this field of chemistry have been made during the last twenty years. Today silyl anions play an important role as protecting groups, building blocks for the formation of defined polysilanes as well as reactive intermediates.<sup>465,466</sup>

Although the first reports on the synthesis and derivatization of silyl anions was in the early 1930s, these compounds remained a laboratory curiosity.<sup>467,468</sup> This changed drastically with the pioneering works of Gilman *et al.*, who demonstrated that silyl anions are excellent buildings blocks for the synthesis of organosilanes.<sup>469,470</sup> Another milestone again achieved by Gilman and his group was the generation of the first oligosilyl anions **1** by reacting the corresponding oligosilane with methyllithium (Scheme 1).<sup>471,472</sup> Due to its easy accessibility **1** became a valuable reagent in main group and transition metal chemistry.<sup>473</sup> However, the synthesis of more complex silicon frameworks using methyllithium is not possible, because this base has a tendency to cleave internal Si-Si bonds (instead of peripheral ones). This was circumvented by the work of Marschner and Baumgartner, who introduced potassium *tert*-butoxide as a more selective base.<sup>271</sup> With this method they were able to create a library of different

polysilanes.<sup>296,297,474–476</sup> Additionally, Stueger *et al.* succeeded in the synthesis of perhydrogenated oligosilyl anions 2,<sup>444</sup> which were used for the preparation of highly branched oligosilicon hydrides. These compounds are found to be ideal precursors for the liquid-phase deposition of silicon films.<sup>39,477</sup>

On the basis of this general strategy a lot of emphasis was put into the synthesis of functionalized silyl anions. So far hydrogen-,<sup>478–481</sup> halogen-,<sup>481–484</sup> aryl-,<sup>485–487</sup> alkyl-,<sup>488,489</sup> amino-<sup>490–492</sup> and silyl- (especially trialkylsilyl-<sup>469,471</sup> or triarylsilyl-<sup>493,494</sup>) substituted silyl anions were synthesized. Recently, Krempner *et al.* introduced alkoxy groups as new substituents for the stabilization of silyl anions **3**.<sup>495,496</sup> Furthermore, they demonstrated that alkoxy groups facilitate the selective Si-Si bond cleavage by a nucleophilic attack. While the chemistry of these derivatives was neglected, this type of silyl anions can be seen as a potent building block for the formation of new types of silicon-frameworks.



Scheme 1. Types of literature known alkali metal silanides 1-3. Synthesis of tris(trimethoxysilyl)silanides 5a-d as a new building block for silicon frameworks.

## **Results and Discussion**

Based on previous observations, we considered dodecamethoxyneopentasilane **4** as an ideal starting point for our chemical manipulations, as these products bear the possibility for a post functionalization to perhydropolysilanes (which are precursors for Liquid Phase Deposition (LPD) applications) or perchloropolysilanes (which are precursors for Atomic Layer Deposition (ALD) or Chemical Vapour Deposition (CVD) processes). Although **4** was prepared decades ago,<sup>497</sup> a further functionalization was never accomplished. Thus, we now were able to achieve
the synthesis of tris(trimethoxysilyl)silanides (M = Li, Na, K) **5a-c** by reacting **4** with one equivalent of suitable bases. These reactions resulted in the clean formation of air and moisture sensitive silanides **5a-c** in nearly quantitative yields (Scheme 2). **5a-c** represent an optimal and highly promising building block for the formation of new hitherto unknown polysilanes. Analytical data are consistent with the proposed structures, exhibiting one resonance line in the <sup>29</sup>Si-NMR spectrum for the three trimethoxysilyl-groups near -3 ppm, one signal for the quaternary silicon atom between -270 to -280 ppm (depending on the counter ion). See the *Supporting Information* for experimental details.



Scheme 2. Synthesis of 5a-c.

For **5c** (synthesized *via* method B) single crystals suitable for X-ray structure analysis could be grown in toluene at -30 °C. The structure is depicted in Figure 1 alongside with selected average bond lengths and angels in Table 1. Potassium silanide **5c** is formally composed of two zwitterionic isotetrasilanide units  $[Si{Si(OMe)_3}_3K]$ , which are associated in a head to head fashion. Moreover, the structure reveals two different potassium coordination environments. One octahedral potassium is coordinated tripodally to two isotrasilanides units to give a zig-zag infinite network. The two different potassium ions adopt relatively long silicon-potassium bonds (average 406 pm for tripodally K<sup>+</sup> and average 526 pm for dipodally K<sup>+</sup>), which are significantly longer than related dimeric and monomeric hypersilanides [{MeOMe<sub>2</sub>Si}<sub>3</sub>Si-K]<sub>4</sub> (approx. 356 pm),<sup>495</sup> [{(Me<sub>3</sub>Si)<sub>3</sub>Si(µK)}<sub>2</sub>] (337–342 pm),<sup>498</sup> [(Me<sub>3</sub>Si)<sub>3</sub>SiK-(C<sub>6</sub>H<sub>6</sub>)<sub>3</sub>] (332–335 pm),<sup>498</sup> and [(Me<sub>3</sub>Si)<sub>3</sub>SiK(18-crown-6)] (345 pm).<sup>445</sup> The detailed structural information is summarized in the *Supporting Information*.

Following the seminal work of Hoveln and coworkers using NHC: <sup>Dipp</sup>CuO*t*Bu as selective base for the generation of monosilanides,<sup>499</sup> guided us to investigate this base for the generation of oligosilanides. To our delight we found that the reaction of **4** with equimolar amounts of the carbene stabilized copper-*tert*-butoxide results in the clean formation of air and moisture sensitive silanide **5d** in nearly quantitative yields (Scheme 3). The analytical data is consistent

with the proposed structure, exhibiting one resonance line in the <sup>29</sup>Si-NMR spectrum for the three trimethoxysilyl-groups near -19 ppm, and one signal for the quaternary silicon atom at - 181 ppm. The quaternary silicon in **5d** is significantly low field shifted in comparison to those of **5a-c**.



**Figure 1.** ORTEP representation of **5c**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted and carbon atoms are displayed as wireframes for clarity.

For **5d** single crystals suitable for X-ray structure analysis could be grown in toluene at -30 °C. The structure is depicted in Figure 2 alongside with selected average bond lengths and angels in Table 1. The carbene stabilized copper-silanide **5d** showed Si-Cu bond lengths and C-Cu-Si bond angles that are well in line with those of recently published (NHC)CuSiR<sub>3</sub> complexes (compare Table 1).<sup>499–502</sup>



**Figure 2.** ORTEP representation of **5d**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted and the NHC:<sup>Dipp</sup> unit is displayed as wireframes for clarity.

Comp.	M(1)-O	M(1)-Si(1)	M(2)-Si(1)	Si-Si	Si-O	Si(1)
5c	266	406	526	230	165	312
5d	422	228	-	233	164	318

**Table 1.** Selected average bond lengths [pm] and angles [°] of compounds **5c,d**.

The colorless silanides **5a-d** are very persistent. **5a-d** can be stored at -30 °C in the absence of air even for prolonged periods (usually months). Even upon removal off the solvent the silanides do not undergo detectable degradation reactions. Moreover, according to NMR spectroscopy and X-ray crystallography **5a-d** can be isolated completely solvent free, which is for many follow up reactions (strong Lewis acids, for example, result in ether cleavage) highly beneficial.<sup>503</sup> All four silanides are easily soluble in THF, but nearly insoluble in Et<sub>2</sub>O or other more unpolar solvents, such as toluene and *n*-pentane. Addition of crown ether leads to an increase in their solubility in unpolar solvents (i.e. *n*-pentane). The reactivity of selected examples towards different electrophiles was tested with all silanides. A significant correlation between the used silanide and the yield of the expected product was not observed. Experimental details can be found on the *Supporting Information*.

We first probed the reactivity of our new silyl anions **5** towards carbon electrophiles. Therefore, we used iodomethane, iodobenzene and giving our ongoing interest in the synthesis of acylsilanes, we also tested mesitoyl chloride. The reaction of **5a-c** with iodomethane yielded the expected methylisotetrasilane **6** in excellent yields. The selective formation of **6** was not surprising for us, as also **1** and **2** reacts with iodomethane to the corresponding methylisotetrasilanes.<sup>444,471</sup> Interestingly, the reaction with iodobenzene also gave rise to the selective formation of **7** in isolated yields >70% (Scheme 3). This is in stark contrast to the reactivity of **1** and **2**. These silanides do not react selectively with iodobenzene, instead extensive transmetalation reaction and oligomerization were observed.<sup>504</sup> This further demonstrates that permethoxy substituted silanides are significantly more selective reagents then all other literature known silanides. Moreover, **7** and related compounds are promising reagents for transition metal catalyzed cross coupling experiments (i.e. Hiyama coupling).

Compound **8** was obtained by the reaction of **5a-c** with mesitoyl chloride and represents an ideal precursor for the formation of silenes. NMR data obtained for **6-8** are consistent with the proposed structures and were fully assigned (*see Supporting Information*). The quaternary silicon nucleus for **6-8** exhibit a signal in the range at  $\delta = -99$  to -112 ppm in the <sup>29</sup>Si NMR spectrum. In comparison to the already known similar fully methylated compounds, the methoxylated compounds **6-8** show a significant shift to higher field. Furthermore, the <sup>29</sup>Si resonance of the analog fully hydrogenated compound of **6** also exhibits a down field shift as the methylated silanes.

To verify our experimental observations, we also performed density functional theory (DFT) calculations. Natural bond orbital (NBO) analyses of 1 ((Me<sub>3</sub>Si)<sub>3</sub>Si<sup>-</sup>anion), 2 ((H<sub>3</sub>Si)<sub>3</sub>Si<sup>-</sup>anion), and 5 (((MeO)<sub>3</sub>Si)<sub>3</sub>Si<sup>-</sup>anion) at the PCM(THF) B3LYP/6-311+G(2df,p)//PCM(THF) B3LYP/6-31+G(d,p) level of theory revealed natural population analysis (NPA) charges of -0.71 e for 1, -0.68 e for 2, and -0.79 e for 5, respectively. In all three anions, charge stabilization occurs *via* delocalization into the adjacent, anti-bonding silicon-element orbitals (sum of calculated interaction energies in 1: 17.8 kcal.mol<sup>-1</sup> for n(Si)  $\rightarrow \sigma^*(Si-C)$ ; in 2: 16.1 kcal.mol<sup>-1</sup> for n(Si)  $\rightarrow \sigma^*(Si-H)$ ; in 5: 21.9 kcal.mol<sup>-1</sup> for n(Si)  $\rightarrow \sigma^*(Si-O)$ ). However, only anion 5 shows a stabilizing effect due to back donation from the non-bonding oxygen orbitals *via* negative hyperconjugation (sum of calculated interaction energies in 5: 14.0 kcal.mol<sup>-1</sup> for n(O)  $\rightarrow \sigma^*(Si-Si)$ ). The higher nucleophilicity of the negatively charged silicon-atom of silanide 5 compared to 1 and 2 ultimately results in a cleaner reaction profile with different electrophiles.



Scheme 3. Reactivity of **5a-c** with selected examples of carbon electrophiles.

As the reaction of silyl anions with chlorosilanes represents the most important Si-Si bond formation pathway in polysilane chemistry we also reacted **5a-c** with selected examples of silicon centered electrophiles. The air-stable, slightly moisture sensitive and crystalline target compounds **9-11** were obtained in isolated yields of >80% (Scheme 4). Analytical and spectroscopic data that well support the structural assignment are given in the *Supporting Information*, together with experimental details. Similarly, the <sup>29</sup>Si resonance of the quaternary silicon nucleus of **9-11** exhibits in a higher field ( $\delta = -153$  to -160 ppm) than the fully methylated compounds.



Scheme 4. Reactivity of 5a-c with selected examples of silicon electrophiles.

These silvlated products **9-11** bear the possibility of a post functionalization to perhydropolysilane (which are precursors for LPD applications) or perchloropolysilanes (which are precursors for ALD or CVD processes). To demonstrate this, we chose compound **9** as showcase. For the synthesis of the perhydropolysilane **13**, **9** was reacted with 9 equivalents of DiBAL-H and after recondensation the desired product was isolated in good yields. The perchloropolysilanes **14** was synthesized by the reaction of **9** with an excess of BCl<sub>3</sub> in heptane (Scheme 5).



Scheme 5. Postfunctionalization of 9 to perhydropolysilane 12 and perchloropolysilane 13.

In conclusion we have introduced a synthetic strategy for novel permethoxylated silicon frameworks starting from **5a-d**. Furthermore, we have demonstrated that this new silanides exhibit a slightly different behaviour due to their higher nucleophilicity as previously literature known silanides. This results in high yields and enables the introduction of previous unavailable pathways for the synthesis of polysilanes. Moreover, the possibility of post-functionalisation to perhydro- or perchlorosilanes enables the synthesis of new precursors for LPD, ALD, CVD and other deposition applications. These silanides provide a significant addition to the synthetic methods available for the formation of new defined silicon-frameworks. Further studies to probe the scope of this chemistry are currently in progress.

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Keywords: silyl anions • methoxysilanes • silicon frameworks • polysilanes

# **2.3.3.** Fabrication of Carbon Doped Amorphous Silicon Films using Single Source Precursors (submitted)

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### Abstract

The aim of this study was the preparation of different carbon doped amorphous silicon thin layer materials according to the Liquid Phase Deposition (LPD) process using single source precursors. In our study, 2-methyl-2-silyltrisilane (methylisotetrasilane; **2**), 1,1,1-trimethyl-2,2-disilyltrisilane (trimethylsilylisotetrasilane; **3**), 2-phenyl-2-silyltrisilane (phenylisotetrasilane; **4**), as well



as 1,1,2,2,4,4,5,5-octamethyl-3,3,6,6-tetrasilylcyclohexasilane (cyclohexasilane; **5**) were utilized as precursor materials and compared with the parent compound 2,2-disilyltrisilane (neopentasilane; **1**). Compounds **2-5** were successfully oligomerized at  $\lambda = 365$  nm in the presence of catalytic amounts of neopentasilane oligomer (**NPO**). These oligomeric mixtures (**NPO** and **6-9**) were used for the preparation of thin layer materials. Optimum solution and spin coating conditions were investigated and carbon doped amorphous silicon films were obtained. All thin layer materials were characterized via UV/Vis spectroscopy, light microscopy, spectroscopic ellipsometry, SEM and SEM/EDX. Our results show that the carbon content and especially the band gap can be easily tuned by using these single-source precursors via LPD.

#### Introduction

Recently, solution processing of silicon based electronic devices has attracted much attention as an alternative to chemical vapor deposition (CVD), owing to the possibility of low-cost fabrication by printing processes. Moreover, it opens the possibility for large area depositions and patterning materials.<sup>33,34,505</sup> Recent studies in our laboratories and by others have demonstrated the principal feasibility of the liquid phase deposition (LPD) and processing of silicon films of satisfactory quality.<sup>35–37,39,477,506,507</sup> Therefore, open chained and cyclic silicon hydrides such as compound I - IV (Chart 1) were used as precursors and decomposed to elemental silicon upon heating to temperatures above 300 °C.



Chart 1. Currently used precursors for LPD processing of silicon films.

To be valid for an industrial application, solution processing of silicon based devices has to allow continuous manufacturing of all circuit components by successive deposition and printing steps in the same environment. Therefore, the deposition of silicon-heteroelement thin layer structures is of great interest. Silicon carbide (SiC) or carbon doped silicon has evolved from a high potential wide bandgap semiconductor to a widely acknowledged material in power electronics.<sup>508,509</sup> Here, carbon and other heteroelements are usually added to silicon to perform bandgap engineering. Since carbon provides a very wide bandgap compared to silicon, the bandgap width of the assembled thin SiC layer material can be varied by changing the concentration of carbon in the blend, thus the higher the carbon concentration the wider the bandgap. The difference in the emitter region of amorphous silicon and SiC layers can be seen by comparing the bandgaps of a heavily carbon doped SiC layer (2.2 eV - 3.3 eV) to the bandgap of silicon (1.12 eV).<sup>510</sup> Since the difference seems quite high, bandgap engineering of thin layer materials is of high interest. Those wide bandgap materials (SiC) are therefore used as a wide bandgap field effect transistor device and are more mechanically, thermally and chemically stable than silicon devices.<sup>510</sup> However, until now, most known SiC layer materials were achieved by alloying silicon with carbon and using remote plasma-enhanced CVD, whereas the main obstacle is the extremely low solubility of carbon in silicon.<sup>511,512</sup> So far, literature only contains a small amount of reports on LPD processed functional silicon layers. In those studies, the use of more than one precursor raised considerable problems, thus using hydrosilanes as a precursor for the deposition of functional silicon films which contain one or more heteroatoms covalently linked to silicon (single source precursor) could offer the right solution. <sup>513–516</sup> In many cases single-source precursors were shown to be ideal for producing thin films since they provide a simple route to these materials and therefore reduce the likelihood of side-reactions and the associated formation of contamination of non-stoichiometric films of inferior quality.<sup>517-519</sup>

However, in comparison with carbon chemistry, the systematic functionalization of higher silicon hydrides for silicon based single-source precursors has not been accomplished so far. Therefore, the synthesis of different single-source precursor materials with carbon as heteroelement to achieve thin layer materials via LPD and their characterization was the main target of this work.

## **Results and Discussion**

Synthesis and Characterization of Precursor Molecules. The branched precursor molecules 2-4 were synthetized according to our previously reported method (Scheme 1). Therefore, dodecamethoxyneopentasilane was reacted with equimolar amounts of KO*t*Bu and the anion thus formed was reacted in situ with the respective electrophiles. These derivatives were isolated and subsequently reacted in substance with nine equivalents of DIBAL-H. Finally, compound 2-4 were isolated by vacuum condensation (See Experimental Section and our previous publication<sup>520</sup> for details). Compound 2 and 3 are already reported, but never used as precursor for LPD approaches. Compound 4 was not reported so far. Analytical data is consistent with the proposed structure, exhibiting one resonance line in the <sup>29</sup>Si-NMR spectrum for the three SiH<sub>3</sub>-groups at  $\delta = -93.12$  ppm and one signal for the quaternary silicon atom at  $\delta = -90.13$  ppm. Moreover, proton-coupled <sup>29</sup>Si NMR spectrum of 4 allowed the determination of the coupling constants, which are in the range of previously reported perhydridosilanes (the H<sub>3</sub>Si-groups display a quartet of multiplets (<sup>1</sup>J<sub>Si-H</sub> = 197.2 Hz, <sup>3</sup>J<sub>Si-H</sub> = 3.3 Hz); the quaternary silicon atom shows a multiplet (<sup>2</sup>J<sub>Si-H</sub> = 5.0 Hz).<sup>521</sup>



Scheme 1. Synthesis of precursor molecules 2-4.

As outlined in the introduction, cyclic precursors are also important LPD precursors. Consequently, we developed a synthetic approach towards the cyclic precursor **5** (see Scheme 2). Therefore, the branched hexasilane was reacted with two equivalents of KO*t*Bu to the corresponding dianion. This dianion was in situ reacted with 1,2-dichloroteramethyldisilane and the cyclohexasilane was obtained in good yields by crystallization. The cyclic hydrosilane was

successfully formed in excellent yield (97%) by using DIBAL-H to exchange all methoxygroups with hydrids. Again, analytical data is consistent with the proposed structure, exhibiting one resonance line in the<sup>29</sup>Si-NMR spectrum for the four SiMe<sub>2</sub>-groups at  $\delta = -34.13$  ppm, one signal for the four SiH<sub>3</sub> groups at -97.15 ppm and one signal for the quaternary silicon atom at  $\delta = -146.76$  ppm. The proton-coupled <sup>29</sup>Si NMR spectrum of **5** allowed the determination of the coupling constants, which are also in the range of previously reported perhydridosilanes (the H<sub>3</sub>Si-groups display a quartet of multiplets (<sup>1</sup>J<sub>Si-H</sub> = 193.53 Hz, <sup>3</sup>J<sub>Si-H</sub> = 4.3 Hz); the quaternary silicon atom shows a multiplet (<sup>2</sup>J<sub>Si-H</sub> = 4.7 Hz).



Scheme 2. Synthesis of precursor 5.

Finally, for compound **5** we were able to grow crystals suitable for X-ray analysis, which were obtained by slowly evaporating a benzene solution at room temperature (see Figure 1). Compound **5** crystallized in the monoclinic space group  $P2_1/n$  and the unit cell contains two molecules.



**Figure 1.** ORTEP representation of **5**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms except the hydrides are omitted. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations: Si(1)-Si2 2.3450(3), Si(1)-Si(3) 2.3473(3), Si(1)-Si(4) 2.3393(3), Si(1)-Si(5) 2.3348(3), Si(2)-Si(3) 2.3417(3), Si(2)-Si(1)-Si(3) 113.099(10), Si(4)-Si(1)-Si(2) 112.887(10), Si(4)-Si(1)-Si(3) 109.711(10), Si(5)-Si(1)-Si(2) 105.836(10).

As the LPD method requires a thermal or photochemical oligomerization of the precursor molecules, the UV/Vis absorption spectra of **2-5** were measured and compared to the parent compound **1** (Figure 2a). In order to determine the involved orbitals of the longest wavelength absorption excitation, we used DFT calculations and simulated the vertical excitations. A good qualitative agreement between experimental and calculated absorption maxima could be achieved. For all compounds except for compound **4**, the longest absorption band consist of  $\sigma$ - $\sigma$ \* excitations of the silicon skeleton from HOMO-2, HOMO-1, HOMO and HOMO+4 into LUMO, LUMO+1, LUMO+2 orbitals with different mixing. On the other hand, for compound **4**, the first excitation consists of a  $\pi$ - $\pi$ \* transition from HOMO-1 and HOMO into LUMO and LUMO+1 orbitals. (see Supporting Information for details). As representative example, the calculated frontier Kohn–Sham orbitals for compounds **4** and **5** are depicted in Figure 2b,c.



**Figure 2.** a) UV/Vis spectra of compounds 1-3 and 5 ( $c = 1*10^{-4}$  M; solvent = *n*-hexane) and of compound 4 ( $c = 1*10^{-5}$  M; solvent = *n*-hexane), b) Orbitals involved in the first transition for compound 4 (with a contour value of 0.04 a.u.), c) orbitals involved in the first transition for compound 5 (with a contour value of 0.04 a.u.).

**Oligomerization experiments.** In previous literature reports, the oligomerization process of branched hydropolysilanes was only achievable at a wavelength of  $\lambda = 254$  nm in a quartz tube since the different precursor materials **1-5** show an absorbance at 200-275 nm (Figure 1).<sup>37,477</sup> However, we were able to successfully achieve oligomerization for compound **1** in substance using a wavelength of  $\lambda = 365$  nm in a non-quartz tube with our assembled reactor (see Scheme 3). See Experimental Section and Supporting Information for details.



Scheme 3. Oligomerization of compound 1 at  $\lambda$ =365 nm to form NPO (left). Photolysis reactor used for the oligomerization at  $\lambda$ =365 nm of precursor materials (right).

This was very surprising for us, since no absorption is detectable according to the UV/Vis spectrum of **1**. Consequently, we recorded a UV/Vis spectrum of **1** in substance and found a significant tailing of the absorption until 375 nm (Figure 3). The tailing is responsible for the possible oligomerization at this wavelength. The photochemical oligomerization was stopped as soon as solid polymer was precipitating out of the liquid phase, indicating an average mol mass of approximately 800-2000 g/mol. Encouraged by this finding we wanted to adopt this method and irradiate our new single source precursors at  $\lambda = 365$  nm. For compounds **2-5**, the same conditions as for **1** were applied, however no or a very slow oligomerization was observed.



Figure 3. UV/Vis spectra of compound 1 (neat).

For compound 2 we found were slow oligomerization process. Here, we assume that the low extinction coefficient is the main reason for the low photochemical activity. In addition, compounds **3** and **5** are solids, which were dissolved in benzene or *n*-pentane prior to irradiation. Again, no photochemical induced oligomerization was observed at  $\lambda = 365$  nm. Looking at the orbitals involved in the longest wavelength absorption for compound **4**, we immediately realized that the  $\pi$ - $\pi$ \* excitation is responsible for the inhibited photochemical oligomerization, as this band significantly overlaps the  $\sigma$ - $\sigma$ \* band. Consequently, we used our oligomerized neopentasilane (**NPO**) as catalyst to induce an oligomerization at this wavelength. On the basis of screening experiments, we found out that 0.01 wt% of **NPO** is sufficient to induce a photochemical oligomerization for **2-4** and 0.1 wt% for precursor **5** (see Scheme 3). See Experimental Section and *Supporting Information* for details.



Scheme 3. Oligomerization of compound 1-5 at  $\lambda$ =365 nm to form the oligomeric mixtures 6-9.

The successful oligomerization was characterized via <sup>1</sup>H-NMR spectroscopy. By comparison of the precursor materials to the oligomerized mixtures **6-9** a significant broadening of the peaks was detected, which indicates the formation of oligomers. As an example, Figure 4 shows the formation of the oligomeric mixture **7**. After 10 h of photolysis ( $\lambda = 365$  nm) only slightly broader peaks were visible. However, after 20 h of photolysis two broad peaks right next to the signals of SiH<sub>3</sub> and Si(CH<sub>3</sub>)<sub>3</sub> were observed which indicated the formation of the oligomeric mixture **7** (**TMSISO**).



**Figure 3.** <sup>1</sup>H-NMR spectra of the oligomerization process of compound **3** to **TMSISO** (7) (top: photolysis for 0 h at  $\lambda$ =365 nm; middle: photolysis for 10 h at  $\lambda$ =365 nm; bottom: photolysis for 20 h at  $\lambda$ =365 nm).

Another indicator for oligomerization of those compounds was the change in color after irradiation from a clear solution to a milky yellow/yellow color. For **PhISO** (**8**) no specific broad peaks in the <sup>1</sup>H-NMR spectrum were detectable. In addition, we found various sharp signals in the Si-H region indicating the formation of multiple photoproducts. Moreover, the color of **8** changed from a clear solution to a milky yellow color indicating oligomerization. Similar to **PhISO** (**8**), no broad peaks in the <sup>1</sup>H-NMR spectrum were visible for **CHSO** (**9**). However, similar as to other oligomeric mixtures (**6-8**) a change in color after irradiation from a clear solution to milky yellow was visible. It is important to mention that all the obtained oligomeric mixtures still contain a significant amount of starting material. This is based on the necessity that the respective monomers serve also as solvent for the formed oligomers.

**Thin layer materials.** With the successfully synthesized oligomeric mixtures **6-9**, thin layer materials were fabricated (see Figure 5) and fully characterized.



Figure 5. General procedure of the LPD process of the oligomeric mixtures 6-9 and NPO.

Therefore, glass substrates were cut accordingly to fit the mask for the spin coating process (25x25 mm). Those substrates were cleaned with deionized water, as well as acetone and isopropanol (ultrasonic bath for 1-2 h) to be then transferred into the glove box. All compounds were spin coated on glass substrates in nitrogen atmosphere. The first issue was the usage of the right solvent. Oligomers **6-9** and **NPO** are soluble in tetrahydrofuran, toluene, as well as cyclooctane. To achieve optimum solvent conditions for the LPD process **NPO** was used as benchmark to ease the optimization process of all other compounds.

Figure 6 offers the taken picture of the thin layer itself, as well as light microscopy images (200x magnification) of different solutions of **NPO**. As outlined in Figure 5, we observed the adsorption of small particles on the **NPO** layer. These particles can be attributed to our glovebox, since the synthesis and oligomerization was also performed in this glove box. Since our study can be seen as a proof of concept, we can neglect these particles in later experiments. At 30 wt% of **NPO** in toluene a thin layer with varying layer thickness visible in the microscope was

determined. Therefore, the next experiment was executed with a higher concentration of **NPO** (50 wt% and a different mixture of solvent: 40°wt% toluene + 10 wt% cyclooctane) to eliminate the difference in layer thickness. With those conditions, holes throughout the thin layer were determined via light microscopy, thus changing the solvent to toluene only. According to the change of solvent, no visible holes or cracks were visible with 50 wt% of **NPO** dissolved in toluene. Spin coating parameters did not vary for the different solutions. All solutions needed high acceleration of 9000 rpm for 20 s and a deposition process at 500 °C for 60 s. Lowering the rotations per minute would only lead to irregular spreading of the solutions, thus pour quality layers were obtained.



**Figure 6.** Picture of the successfully formed thin layer of 50 wt% **NPO** (scratches on the surface for analytical measurements) and light microscopy images at 200x magnification (top right: 30 wt% of **NPO** in toluene; bottom left: 50 wt% of **NPO** in 40 wt% toluene and 10 wt% cyclooctane; bottom right: 50 wt% of **NPO** in toluene).

These optimized solvent conditions were then used to optimize the deposition of the oligomeric mixtures 6-9. Therefore, the first experiments for 6-9 were carried out in the same way as the optimized solvent conditions, as well as the same spin coating parameters. In addition, different solvents and concentrations were investigated to achieve further improvements. However, Figure 7 shows that different conditions led to poorer quality layer surfaces. An additional step is required to achieve a high quality thin layer material. The solution of compound  $\mathbf{6}$  had to be cooled down to -30 °C before spin coating. Otherwise, no coating of the glass substrate was observable. The microscopic pictures offer information about the surface of each thin layer materials. Therefore, it was visible that the optimized conditions for **NPO** were applicable for **MeISO** (6). However, due to lower solubility of the oligomers of  $\mathbf{6}$  in toluene, fine particles were observed via microscope. Those particles were removed via filtration of the solution and a thin SiC layer without holes, cracks or particles was obtained. The additional experiment with higher concentrations (70 wt% of 6) and different solvent (cyclooctane) shows, that the usage of solvent and the difference in concentrations makes a huge impact on the quality of the surface of the thin layer material. In this films we found different layer thicknesses and in addition particles of different sizes, as well as cracks/holes throughout the layer. Additionally, as for NPO, spin coating parameters did not vary for the different solutions. All solutions needed high acceleration of 9000 rpm for 20 s and a deposition process at 500 °C for 60 s. Differences in rotations per minute or deposition temperature and time only leads to pour quality layer materials.



**Figure 7.** Picture of the successfully formed thin layer of 50 wt% **MeISO** (6) and light microscopy images of 200x magnification (top right: 50 wt% of 6 in toluene at -30 °C (high oligomeric/polymeric compounds not filtrated); bottom left: 50 wt% of 6 in toluene at -30 °C (filtrated); bottom right: 70 wt% of 6 in cyclooctane at -30 °C).

Next, **TMSISO** (7) was used to achieve thin SiC films. Therefore, the optimized conditions of **NPO** were used. Again, we hat solubility issues, which we were not able to solve with filtration unlike for **MeISO** (6), since the layer thickness was highly influenced by the filtration and also visible to the naked eye. Therefore, 10 wt% of cyclooctane were additionally added to the solution of 50 wt% of **7** in toluene. Again, the oligomer needed to be cooled down to -30 °C to achieve a thin coating on the glass substrate. In comparison to **NPO**, a thin layer of **TMSISO** (7) was not achievable with the same spin coating parameters. In fact, the optimized solution of **7** needed way lower rotations per minutes (3000 rpm) and a shorter spin coating time (10 s) to obtain a homogeneous surface layer. With a speed of 9000 rpm no visible layer was obtained. However, the deposition time and temperature remained the same as in previous experiments (**NPO** and **MeISO** (6)). Figure 8 shows the obtained thin layer material of **TMSISO** (7) with optimized solvent and spin coating conditions, as well as the taken picture of the thin layer itself.



**Figure 8.** Picture of the successfully formed thin layer of 50 wt% **TMSISO** (7) in 40 wt% toluene and 10 wt% cyclooctane and light microscopy images of the optimized SiC layer at 200x magnification.

The same solvent and spin coating conditions of **TMSISO** (7) were used for **PhISO** (8). The only difference for those layer materials was the slightly higher rotations per minutes (4000 rpm)

compared to 7. No layers were achievable with the optimized conditions of **NPO**. Figure 9 illustrates the surface in 200x magnification of the optimized thin layer of a solution of 50 wt% of 8 in 40 wt% toluene and 10 wt% cyclooctane (spin coating parameters: 4000 rpm; 10 s), as well as the taken picture of the successfully formed thin layer.



**Figure 9.** Picture of the successfully formed thin layer of 50 wt% **PhISO** (8) in 40 wt% toluene and 10 wt% cyclooctane and light microscopy images of an optimized SiC layer at 200x magnification

The next target was the deposition of oligomeric mixture **9** (**CHSO**). For **9** we found that the solubility in our standard solvents (toluene, cyclooctane, THF) is very low. We were only able to solve 15 wt% of **9** in THF and performed spin coating with this solution. Similar spin coating parameters than those for **TMSISO** were applied for **CHSO**. The only difference was that spin coating at room temperature is possible. However, even at this low concentrations, we were not able to obtain homogenous films. Therefore, microscopic images (Figure 10) show the inhomogeneous surface of the thin layer material, which was also visible without the help of a microscope.



Figure 10. Picture of the formed layer of 15 wt% CHSO (9) in THF and light microscopy images of 200x magnification (homogenous (top right) and inhomogeneous (bottom right) parts of the thin layer material).

Table 1 summarizes the optimized conditions for the spin coating process for compound **6-9**, whereas Table 2 shows the optimized LPD process conditions for each oligomeric mixture.

	Table 1.	Optimized	conditions	for the	prepared	spin	coating	solutions.
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	Concentration [wt%]	Solvent	Temperature [°C]
NPO	50	toluene	RT
6	50	toluene	-30
7	50	toluene + 10 wt% CO	-30

Table 2. Optimized spin coating parameters of the different solutions.

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	Volume [mL]	Speed [rpm]	Time [s]	Depositing temperature [°C]
NPO	0.20	9000	20	500
6	0.20	9000	20	500
7	0.24	3000	10	500
8	0.24	4000	10	500
9	0.24	4000	10	500

The optical properties of the deposited thin layer materials of **NPO** and **6-9** were then further characterized. Therefore, UV/Vis spectra were recorded. All layer materials show a similar trend. The absorptions took place in the range of 300-700 nm (see Figure 11).



Figure 11. UV/Vis spectra of the optimized thin layer material of NPO and 6-9.

Compared to **NPO**, the other layer materials **6-9** show a less broad absorption band and no absorption in the region between 600 to 700 nm. Additionally, there was a trend in aspect to layer thickness detectable. The higher the absorbance of the thin layer materials, the thicker the layer, which can be compared in the ellipsometry and SEM part. By comparing the absorption of the layer of material **9** to the other thin layer materials (Figure 11), the absorbance is significant lower (almost zero). This can be explained because of the low concentrations (15 wt% in THF) and the lack of solubility of **CHSO** (**9**). Therefore, only very thin inhomogeneous layers were obtained and could not be further optimized.

From the above illustrated absorption onsets, the optical band gap was obtained and can be seen in Table 3. The band gap of **9** was not determined since the layer itself offered no homogeneous surface and therefore, no high absorbance values could be detected.

	Wavelength [nm]	Optical bandgap [eV]
NPO	680	1.82
6	457	2.71
7	495	2,50
8	482	2.57

Table 3. Obtained optical bandgap values of NPO and 6-8.

The bandgap of **NPO** offers a value of 1.82 eV which is in the range of literature observed value for this material.<sup>37</sup> All obtained values for the carbon doped amorphous silicon layers are also in the range of literature known optical bandgaps.<sup>510</sup> The highest bandgap was obtained from thin layers of compound **6** (2.71 eV).

Furthermore, Raman spectroscopy was performed, which is the ideal method to determine the nature of the silicon film. Consequently, we measured the Raman spectrum of **6-8**. All films show the typical phonon bands of a-Si:H between 150 and 480 cm<sup>-1</sup> (Figure 12). These spectra are comparable to the Raman spectra of vacuum-processed a-Si:H<sup>522,523</sup> and amorphous silicon layers from cyclic silanes<sup>506,524</sup> and branched silanes<sup>37,477</sup>. For the thin film derived from **8** we also found bands of a-C (only amorphous carbon) between 1250 and 1750 cm<sup>-1</sup> indicating the formation of amorphous carbon during the thermal treatment.



Figure 12. Raman spectra of the solution processed a-Si:H films formed from 6-8.

Additionally, the layer thickness is an important key parameter for the applicability. Therefore, we analyzed the layer thickness of all different optimized thin layers (**NPO** and **6-8**) via spectroscopic ellipsometry. A good fit of the ellipsometric parameters extrapolated with the model to the measured values was achieved for all four layers studied. Again we used the thin film for **NPO** as benchmark. The dielectric function or the optical constants of the investigated thin films were described with a model using a pole site in the UV outside the measured spectral range, a DC offset, a small (symmetric) Gaussian broadened- as well as a large (asymmetric)

Cody-Lorentz oscillator in the UV-VIS-NIR range. Moreover, a Drude term for the longwavelength absorption in the IR was applied, if necessary. The Cody-Lorentz-formula typically is used for the description of the optical properties of pure amorphous silicon in the UV-VIS range. Three of the thin films (**TMSISO**, **MeISO**, and **NPO** exhibit strong absorption extending from the UV into the visible region, coupled with the corresponding refractive index profile. It can be seen that these thin films are not completely optically homogeneous in the normal direction of the layer; adding a (linear) gradient of the optical constant into the model of about 10% could significantly improve the goodness of fit to the measured values. For the **TMSISO** and **NPO** layers, the *n* and *k* values decrease from the top to the bottom of the layer, while for **MeISO** they increase (see Figure 13).



Figure 13. Optical constants n and k of the investigated thin films determined by spectroscopic ellipsometry.

These coatings also optically exhibit low surface roughness of about 12 nm for **TMSISO** and **MeISO** and about 3 nm for **NPO**. The ellipsometrically determined layer thicknesses are 73 and 70 nm for **TMSISO** and **MeISO**, respectively, and - distinctly larger - 159 nm for **NPO**. The optical properties of **PhISO** are significantly different. Here, no absorption can be detected within the ellipsometric sensitivity and the optical model gets by with one pole in the UV and a DC offset component. The layer thickness here is only about 31 nm, and the refractive index is much lower than for the other three layers (see Table 4). Due to the small layer thickness, the statement about further non-idealities such as surface roughness and index gradients is not possible (rather, the simultaneous determination of thickness and refractive index must already be judged as clearly borderline). Further experimental details can be found in the *Supporting Information* (Figure S12).

**Table 4.** Measured layer thicknesses of the layers obtained for NPO and **6-8**. For 6 and **7** a thickness variation within the measuring spot could be determined.

Layer Thickness [nm] Surface Roughness [nm]

NPO	159	3
MeISO (6)	70 ±2%	12
TMSISO (7)	$73\pm8\%$	13
PhISO (8)	31	0

In order to conform the obtained thickness via ellipsometry, scanning electron microscopy (SEM) was carried out for thin layers of **6** and an overall thickness of 96 nm was obtained (Figure 14).



Figure 14. SEM images of MeISO (6) (left: 80,000x magnification; right: 10,000x magnification).

The layer thickness of compound **6** varies because of floating particles in the glovebox atmosphere, as well as dust particles. To our delight, the overall thickness of this particular layer material offered values which we anticipated. Additionally, since the determination of the layer thickness of all materials was successful and offered great values, the elemental composition of those compounds was also analyzed. This characterization method was achieved via SEM/EDX. The amount of oxygen was omitted since the layer materials were stored outside of the glovebox. (See Supporting Information Table S4 for the values of carbon, oxygen and silicon). Additionally, small contaminations during the measurement of the elemental composition were also omitted. The measured and theoretical silicon and carbon content can be found in Table 5.

Table 5. Elemental analysis of three different layers of oligomeric mixtures 6-8 and NPO (les	ft:
measured values by EDX; right: theoretical values).	

	Meassure	ed		Theoreti	cal
	C [wt%]	Si [wt%]		C [wt%]	Si [wt%]
	0.00	100.00	NPS	0.00	100.00
NPO	0.00	100.00	2	9.66	90.34
	0.00	100.00	3	20.42	79.58
	9.92	90.07	4	39.08	60.92
6	9.26	90.75			
	9.16	90.84			
7	6.10	93.90	_		

5.68	94.33
5.26	94.74
19.12	80.88
21.06	78.95
21.56	78.44
	5.68 5.26 19.12 21.06 21.56

As expected, for thin layer materials of **NPO** no carbon was detected, whereas the oligomeric mixtures **6-8**, offered carbon values. The amount of C varies in the different thin layers due to the different carbon groups of each starting material (**2-4**). When compared to the theoretical carbon content, a lower carbon content can be spotted for the thin layer materials of **7** and **8**. To our delight we found that the carbon content for the different layers of **MeISO** (**6**) is almost identical to the theoretical value. We assume that during the oligomerization process the incooperation of carbon in the amorphous silicon films of **6** is better than compared to **7** and **8**. Additionally, some of the smaller oligomers from the oligomeric mixtures **7** and **8** evaporate during the deposition process at 500 °C, which further explains the decreased carbon content compared to the theoretical amount.

Microscopic images of the different layer materials at different magnifications can be seen in Figure 15-19. Those images were obtained during the SEM/EDX measurement to further analyze the surface of each thin layer material at higher magnitudes (200x - 5.02 kx) than for light microscopy (200x magnification).



Figure 15. SEM images of thin layers of NPO in different magnifications (left: 220x; right: 2.20 kx).



Figure 16. SEM images of thin layers of MeISO (6) in different magnifications (left: 200x; right: 2.01 kx).



Figure 17. SEM images of thin layers of TMSISO (7) in different magnifications (left: 459x; right: 1.00 kx).



**Figure 18.** SEM images of thin layers of **PhISO (8)** in different magnifications (left: 220x; right: 1.00 kx). For the different thin layer materials (**NPO** and **6-8**), homogenous surfaces were detectable via SEM/EDX measurements. No holes, cracks or other impurities were visible throughout the layers surfaces. Therefore, high quality amorphous silicon layers of **NPO**, as well as the carbon doped amorphous silicon layers (**6-8**) were successfully deposited on glass substrates. In contrast to the thin layers of the oligomeric mixtures **6-8**, no homogeneous surface layer for **CHSO (9**) was found (Figure 19). The oligomeric mixture **9** rather formed aggregates on the glass substrate after deposition, than an actual thin layer, thus confirm that bigger precursor materials, such as cyclic compound **5**, can be used for oligomerization, but are not quite suitable for liquid phase deposition of thin layer materials.



**Figure 19.** SEM images of thin layers of **CHSO (9)** in different magnifications (top left: 200 x; top right: 2.00 kx; bottom left: 4.98 kx; bottom right: 5.02 kx).

#### Conclusion

In summary we have successfully synthesized a variety of single source precursor (2-5) for Si/C thin film deposition. Moreover, these compounds were photochemical oligomerized at  $\lambda = 365$  nm. The so obtained five different oligomeric silicon mixtures (6-9) were used for liquid phase deposition (LPD). The optimum conditions for the LPD process in aspect to solution and spin coating parameters were developed. Subsequently thin layer materials of the oligomeric mixtures 6-9 were successfully deposited on 25x25 mm pre-cleaned glass substrates at 500 °C. All thin layer materials were characterized via light microscopy, SEM, SEM/EDX, spectroscopic ellipsometry, as well as UV/Vis spectroscopy. Optical bandgaps of thin layers of compound 6-9 were determined and compared to literature known values for amorphous Si and SiC layers. Layer thicknesses of 31-73 nm were achieved. Elemental analyses were carried out and the obtained values were compared to theoretical ones. Therefore, thin amorphous carbon doped silicon layers were successfully achieved. No homogenous thin layer was obtained by using the oligomeric mixture 9. Further investigation according to the possibility of the usage for solar cells will be done in future.

#### ASSOCIATED CONTENT

#### **Experimental Section**

#### **General Procedures**

All experiments were performed under a nitrogen atmosphere using standard Schlenk techniques. Additionally, all deposition processes were performed in a Glove-Box. Solvents were dried using a column solvent purification system.<sup>453</sup> MeLi (1.6 M in Et<sub>2</sub>O), KOtBu and  $C_6D_6$  (99.5 atom%, D) were used without any further purification. For the measurement of air sensitive samples C<sub>6</sub>D<sub>6</sub> was additionally dried by 24-hour reflux above a sodium/potassium (Si(OMe)<sub>3</sub>)<sub>4</sub>Si<sup>497,526</sup>,  $Me(SiH_3)_3Si^{525}$ (2), $Me_3Si(SiH_3)_3Si^{520}$ (3), alloy. and  $K[(MeO)_3Si]_2Si(SiMe_2)_2Si[(MeO)_3Si]_2K^{527}$  were synthesized according to published procedures. Other commercial reagents were used as purchased unless otherwise noted. <sup>1</sup>H (200 MHz) <sup>13</sup>C (50 MHz and <sup>29</sup>Si (40 MHz) NMR spectra were also recorded on a 200 MHz Bruker AVANCE DPX spectrometer in  $C_6D_6$  solution (99.5 atom%, D) using the internal <sup>2</sup>H-lock signal of the solvent. Infrared spectra were obtained on a Bruker Alpha-P Diamond ATR Spectrometer from the solid sample. Elemental analyses were carried out on a Hanau Vario Elementar EL apparatus. UV absorption spectra were recorded on a Perkin Elmer Lambda 5 spectrometer. The ellipsometric measurements were performed on a J. A. Woollam VASE Ellipsometer in the spectral range from 300 nm to 1500 nm with a step size of 10 nm and angles of incidence 65°,  $70^{\circ}$  and  $75^{\circ}$ .

# Synthesis of 2.

A solution of  $(Si(OMe)_3)_3SiK$  in 40 mL THF was prepared from 3.00 g of  $Si(Si(OMe)_3)_4$ (5.85 mmol) and 0.69 g KOtBu (6.14 mmol) and slowly added to a solution of 0.38 mL MeI (6.14 mmol) in 40 mL THF at 0 °C. The reaction mixture was stirred for one hour at RT. The solvent was then removed via vacuum. 50 mL *n*-pentane were added and the remaining salts were filtered off. Recrystallization in *n*-pentane at – 70 °C afforded 2.02 g of Me(Si(OMe)\_3)\_3Si (85%) as a white solid precipitates. As next step, 8.06 mL DIBAL-H (45.2 mmol) are slowly added to 2.02 g of MeSi(Si(OMe)\_3)\_3 (4.97 mmol) at 0 °C. The solution was allowed to stir at RT overnight. Recondensation at room temperature and 0.01 mbar afforded 0.49 g (72%) of **2** as a viscous liquid. <sup>1</sup>**H NMR** (200 MHz, C<sub>6</sub>D<sub>6</sub>, ppm)  $\delta = 3.41$  (s, 9H, SiH<sub>3</sub>), 0.17 (s, 3H, CH<sub>3</sub>). **UV/Vis** measured in *n*-hexane (nm, [L mol<sup>-1</sup> cm<sup>-1</sup>]): 210 [4317].

# Synthesis of 3.

A solution of  $(Si(OMe)_3)_3SiK$  in 40 mL THF was prepared from 3.00 g of  $Si(Si(OMe)_3)_4$ (5.85 mmol) and 0.69 g KOtBu (6.14 mmol) and slowly added to a solution of 0.78 mL ClSiMe<sub>3</sub> (6.14 mmol) in 40 mL THF at -30 °C. The reaction mixture was stirred for one hour at RT. The solvent was then removed via vacuum. 50 mL *n*-pentane were added and the remaining salts were filtered off. Recrystallization in *n*-pentane at -70 °C afforded 2.15 g of (SiMe<sub>3</sub>)Si(Si(OMe)<sub>3</sub>)<sub>3</sub> (79%) as a white solid. As next step, 7.50 mL DIBAL-H (42.1 mmol) are slowly added to 2.15 g of (SiMe<sub>3</sub>)Si(Si(OMe)<sub>3</sub>)<sub>3</sub> (4.63 mmol) at 0 °C. The solution was allowed to stir at RT overnight. Recondensation at 40 °C and 0.01 mbar afforded 0.61 g (68%) of **3** as white solid. <sup>1</sup>**H NMR** (200 MHz, C<sub>6</sub>D<sub>6</sub>, ppm)  $\delta = 3.52$  (s, 9H, SiH<sub>3</sub>), 0.13 (s, 9H, CH<sub>3</sub>). **UV/Vis** measured in *n*-hexane (nm, [L mol<sup>-1</sup> cm<sup>-1</sup>]): 213 [9426].

## Synthesis of 4.

A solution of (Si(OMe)<sub>3</sub>)<sub>3</sub>SiK in 40 mL THF was prepared from 3.00 g of Si(Si(OMe)<sub>3</sub>)<sub>4</sub> (5.85 mmol) and 0.69 g KOtBu (6.14 mmol) and slowly added to a solution of 1.46 mL PhI (6.14 mmol) in 40 mL toluene at -70 °C. The reaction mixture was stirred for one hour at RT. The solvent was then removed via vacuum. 50 mL n-pentane were added and the remaining salts were filtered off. Again, the solvent was removed via vacuum and recondensation at 180 °C and 0.01 mbar afforded 2.06 g of PhSi(Si(OMe)<sub>3</sub>)<sub>3</sub> as a gelatinous oil (75%). As next step, 7.13 mL DIBAL-H (39.99 mmol) are slowly added to 2.06 g (4.39 mmol) of PhSi(Si(OMe)<sub>3</sub>)<sub>3</sub> at 0 °C. The solution was allowed to stir at RT for another 3 h. Acidic aqueous workup was achieved by pouring the reaction mixture onto 120 mL ice-cold H<sub>2</sub>SO<sub>4</sub> (1 M, degassed) and allowing the suspension to meet RT while adding 60 mL of heptane under continuous stirring. The organic layer is dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered off and the solvent is removed under reduced pressure. Purification by fractional distillation at 0.01 mbar at 50 °C resulted in 0.64 g (73%) of a viscous colorless liquid (4). Anal. Calcd of  $C_6H_{14}Si_4$ : C, 36.30%; H, 7.11%. Found: C, 36.41%; H, 7.25. <sup>1</sup>**H** NMR (200 MHz,  $C_6D_6$ )  $\delta = 7.47$  (m, 2H, aryl *H*), 7.05 (m, 3H, aryl *H*), 3.54 (s, 9H, Si*H*<sub>3</sub>). <sup>13</sup>C-NMR (50 MHz, C<sub>6</sub>D<sub>6</sub>, TMS, ppm): δ = 136.34 (Aryl-*C*), 130.17 (Aryl-*C*), 129.61 (Aryl-*C*), 128.89 (Aryl-*C*). <sup>29</sup>Si-NMR (40 MHz, C<sub>6</sub>D<sub>6</sub>, TMS, ppm):  $\delta = -90.01$  (*Si*(SiH<sub>3</sub>)<sub>3</sub>Ph); -93.12 (*Si*H<sub>3</sub>). **UV/Vis** measured in *n*-hexane (nm, [L mol<sup>-1</sup> cm<sup>-1</sup>]): 209 [223180], 231, [127700]. **IR** (v [cm–1]): 2128 (s, SiH).

# Synthesis of 5.

A solution of 2.45 g of K[(MeO)<sub>3</sub>Si]<sub>2</sub>Si(SiMe<sub>2</sub>)<sub>2</sub>Si[(MeO)<sub>3</sub>Si]<sub>2</sub>K (3.33 mmol) in 20 mL THF was slowly added to a solution of 0.65 mL SiCl<sub>2</sub>Me<sub>4</sub> (3.50 mmol) in 20 mL n-pentane at -70 °C. The mixture was stirred for an hour at RT. The solvent was removed via vacuum. 50 mL of *n*-pentane were added and the salts were removed by filtration. A white solid precipitates in *n*-pentane at -70 °C to obtain 0.97 g of the methoxylated cyclic hexasilane (70%). <sup>1</sup>**H-NMR** (200 MHz, C<sub>6</sub>D<sub>6</sub>,

ppm):  $\delta = 3.59$  (s, 36H, OC*H*<sub>3</sub>), 0.74 (s, 24H, C*H*<sub>3</sub>).<sup>29</sup>**Si-NMR** (40 MHz, C<sub>6</sub>D<sub>6</sub>, ppm):  $\delta = -33.80$  (*Si*(CH<sub>3</sub>)<sub>2</sub>); -35.34 (*Si*(OCH<sub>3</sub>)<sub>3</sub>); -144.09 (*Si*(Si(OCH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>).

2.70 mL DIBAL-H (15.2 mmol) is slowly added to 0.97 g of the methoxylated cyclic hexasilane (1.25 mmol) at 0 °C. The solution was allowed to stir at RT overnight. Acidic aqueous workup was achieved by pouring the reaction mixture onto 60 mL ice-cold H<sub>2</sub>SO<sub>4</sub> (1 M) and allowing the suspension to warm up to RT while adding 30 mL of *n*-pentane under continuous stirring. The organic layer is dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered off and the solvent is removed under reduced pressure, resulting in 0.50 g of **5** (97%). Anal. Calcd of C<sub>8</sub>H<sub>36</sub>Si<sub>10</sub>: C, 23.25%; H, 8.78%; Si, 67.97%. Found: C, 23.39; H, 8.61%; Si, 68.00% <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 3.57 (s, 12H, SiH<sub>3</sub>), 0.31 (s, 24H, CH<sub>3</sub>). <sup>29</sup>Si NMR (40 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  -34.13 (*Si*(CH<sub>3</sub>)<sub>2</sub>), -97.14 (*Si*H<sub>3</sub>), -146.77 (*Si*(SiH<sub>3</sub>)<sub>2</sub>). IR (v [cm–1]): 2123 (s, SiH). UV/Vis measured in *n*-hexane (nm, [L mol<sup>-1</sup> cm<sup>-1</sup>]): 216 [217974], 232 [13682], 356 [7174].

# Photooligomerization of 2,2-disilyltrisilane to NPO.

For the oligomerization 0.41 g (6.56 mmol) of  $(SiH_3)_4Si$  was photolyzed at  $\lambda$ =365 nm to form a yellow viscous liquid (**NPO**) after 24 h. <sup>1</sup>**H-NMR** (200MHz. D<sub>2</sub>O capillary, ppm):  $\delta$  = 3.89 – 3.62 (SiH<sub>3</sub>).

## Photooligomerization of 2-methyl-2-silyltrisilane (2) to MeSIO (6).

For the oligomerization 0.49 g of **2** (8.76 mmol) mixed with 0.01 wt% of **NPO** as initiator was photolyzed at  $\lambda$ =365 nm to form a yellow viscous liquid (6) after 24 h. <sup>1</sup>**H-NMR** (200MHz. C<sub>6</sub>D<sub>6</sub>, TMS, ppm):  $\delta$  = 3.65 – 3.33 (SiH<sub>3</sub>), 0.46 – -0.07 (CH<sub>3</sub>).

## Photooligomerization of 1,1,1-trimethyl-2,2-disilyltrisilane (3) to TMSISO (7).

For the oligomerization 0.61 g of **3** (3.14 mmol) mixed with 0.01 wt% of **NPO** as initiator was photolyzed at  $\lambda$ =365 nm to form a milky yellow viscous liquid (**7**) after 20 h. <sup>1</sup>H-NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>, ppm):  $\delta$  = 3.89-3.44 (Si*H*<sub>3</sub>); 0.29-0.11 (TMS).

## Photooligomerization of 2-phenyl-2-silyltrisilane(4) to PhISO (8)

For the oligomerization 1.0 g (5.04 mmol) of **4** mixed with 0.01 wt% of **NPO** as initiator was photolyzed at  $\lambda$ =365 nm to form a milky yellow viscous liquid (**8**) after 50 h. <sup>1</sup>H-NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>, ppm):  $\delta$  = 7.52 – 7.39 (aryl *H*), 7.09 – 7.01 (m, aryl *H*), 3.62-3.35 (SiH<sub>3</sub>).

# Photooligomerization of 1,1,2,2,4,4,5,5-octamethyl-3,3,6,6-tetrasilylcyclohexasilinane (5) to CHSO (9)

For the oligomerization 0.5 g (1.2 mmol) of **5** mixed with 0.1 wt% of **NPO** as initiator in benzene was photolyzed at 365 nm for 24 h. The solvent was removed under reduced pressure to form a yellow viscous liquid (**9**). <sup>1</sup>**H-NMR** (200 MHz, C<sub>6</sub>D<sub>6</sub>, ppm):  $\delta$  = 3.58-3.33 (SiH<sub>3</sub>), 0.31 (CH<sub>3</sub>).

# **Thin Layer Materials**

Thin layer materials were spin coated on glass substrates (25 x 25 mm). Prior to the spin coating, the substrates were cleaned with deionized water, acetone and sonication in isopropanol (1-2 h). The spin coating speed for depositing the layers was varied from 3000 rpm to 9000 rpm at 10-20 s. UV/Vis-spectroscopy was recorded with an UV/Vis-spectrometer Lambda 35 from Perkin Elmer (start wavelength: 900 nm; end wavelength: 300 nm; slit width: 1.0 nm; scan speed: 240 nm/min; data interval: 1.0 nm). The absorption spectra were measured in thin films on glass substrates after spin coating and deposition at 500 °C. Images of the layer surfaces with a magnification of 200x were obtained by light microscopy. (Light Microscope BX60 from Olymp

with an attached camera (Olymp)). Layer Thickness was determined by FELMI-ZFE. Broad ion beam technique was used for the preparation for SEM (ESEM 450). Low vac mode was used to obtain images in different magnifications. The layers were measured in high-contrast CBS images using the GMS3 software. Elemental analysis and further images of the surface layer were obtained via SEM/EDX. SEM micrographs and EDX spectra were collected using Tescan VEGA 3 SEM (Oxford Instruments plc, Abingdon, United Kingdom) with tungsten source filament working at 20 kV. For SEM imagines, a resolution of 5  $\mu$ m and a working distance of around 15 mm was used, and the EDX spectra were collected at a 0-10 keV scale. Prior the analysis, the samples were sputter-coated with gold.

## **Author Contributions**

A.S. and T.L. were equally responsible for experimental investigations. A. S. performed formal analysis, visualization, data presentation, and writing the original draft (lead). A.K. and F. G. were responsible for experimental investigations (supportive). H.F. measured and analyzed the Raman Spectra. M. D. and G. K. were responsible for the SEM measurements. M.H. was in charge of methodology and conceptualization, review and editing of the manuscript (lead), project administration, and funding acquisition.

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The authors declare no competing financial interest.

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# 2.4. Outlook

Climate change is an existential threat to Europe and the world. To meet these challenges, the European Union wants to have zero net emissions of greenhouse gases in 2050. To ensure this, there are several technologies under consideration, but a key industry is the photovoltaic industry. Here silicon (mostly in the form of single-crystal wafer silicon (c-Si)) still accounts for the majority of material used in the industry.

However, the modern production technology for c-Si is associated with high energy consumption and waste problems. In this context, solution processing (LPD) of silicon based devices has attracted considerable attention owing to the possibility of low-cost fabrication by printing processes. Here silicon hydrides are ideal precursor molecules as the readily decompose upon heating to  $T \ge 300$  °C to amorphous silicon.

During this habilitation we have provided a deeper understanding of the outcome of chemical transformations involving higher silicon hydrides and to create a synthetic library of previously unknown functional hydrosilanes. Moreover, we could show that these new derivatives are single-source precursors for the manuficatoring of doped amorpous silicon films.

Although liquid phase deposition is a well-established technique, there are still challenges, which have to be mastered. The synthesis of the precursor molecules is a tedious multi step procedure, which require a soffisticated Schlenk technique. Moreover, highly reactive and expensive chemicals are required to syntheizes these molecules. Therefore, their application in industrial applications is still not economical. In order to achieve this, it would be necessary to obtain higher hydropolysilanes starting from monosilanes or disilanes

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