β-Amino- and Alkoxy-Substituted Disilanides

Istvan Balatoni, Johann Hlina, Rainer Zitz, Alexander Pöcheim, Judith Baumgartner* and Christoph Marschner*

Institut für Anorganische Chemie, Technische Universität Graz, Stremayrgasse 9, A-8010 Graz, Austria; istvan.balatoni@yahoo.com (I.B.); johann.hlina@tugraz.at (J.H.); Rainer_Zitz@hotmail.com (R.Z.); alexander.poecheim@tugraz.at (A.P.)

* Correspondence: baumgartner@tugraz.at (J.B.); christoph.marschner@tugraz.at (C.M.);
Tel.: +43-316-873-32107 (J.B.); +43-316-873-32112 (C.M.)

Academic Editor: Masafumi Unno
Received: 27 September 2019; Accepted: 20 October 2019; Published: 23 October 2019

Abstract: Our recent study on formal halide adducts of disilenes led to the investigation of the synthesis and properties of β-fluoro- and chlorodisilanides. The reaction of the functionalized neopentasilanes (Me₃Si)₃SiSiPh₂NEt₂ and (Me₃Si)₃SiSiMe₂OMe with KOᵗBu in the presence of 18-crown-6 provided access to structurally related β-alkoxy- and amino-substituted disilanides. The obtained Et₂NPh₂Si(Me₃Si)₂SiK·18-crown-6 was converted to a magnesium silanide and further on to Et₂NPh₂Si(Me₃Si)₂Si-substituted zirconocene and hafnocene chlorides. In addition, an example of a silanide containing both Et₂NPh₂Si and FPh₂Si groups was prepared with moderate selectivity. Also, the analogous germanide Et₂NPh₂Si(Me₃Si)₂GeK·18-crown-6 could be obtained.

Keywords: silanide; disilene adduct; germanide

1. Introduction

The development of silanide chemistry [1–5] has advanced the progress of organosilicon chemistry over the last decades. Being the silicon analogs of carbanions, these compounds are invaluable for the construction of Si-X bonds. Especially, the formation of Si-Si bonds, which has long been restricted to Wurtz-type coupling of halosilanes, has been facilitated by the use of silanides, which allow much easier access to inherently asymmetric di- and oligosilanes [6]. In addition, these compounds also allow a much more flexible access to transition-metal silyl complexes and silylated organic compounds. Typically, silanides are highly reactive species which are easily hydrolyzed to hydrosilanes. They need to be prepared, stored, and handled under strict exclusion of moisture. Initially, the chemistry of silanides was mainly restricted to alkyl-, aryl-, and silyl-substituted compounds. The introduction of functional groups to silanides represented a logical advance to allow further transformations of the formed di- and oligosilanes. Examples of hydrogen-substituted silanides date back to Gilman’s cleavage of HPh₂SiSiPh₂H with lithium [7], and related compounds have been used also later [8,9]. The attachment of Lewis basic heteroatoms to silanides was pioneered by Kawachi and Tamao, who introduced α-aminosilanides in the early 1990s [10,11] and could demonstrate their use as hydroxy anion equivalent in organic synthesis [11]. Later on, α-alkoxy- [12–14] and fluoroasilanides [15–17] were introduced, and these compounds (silylenoids) turned out to be amphiphil with a tendency to self-condensation. This was not observed for aminosilanides, although by NMR spectroscopy they clearly showed a relationship to those more reactive compounds [18].

Recently, we have reported a study on β-halodisilanides XPh₂SiSi(SiMe₃)₂K (X = F, Cl) [19], which we not obtained by self-condensation of halosilylenoids but by reaction of XPh₂SiSi(SiMe₃)₃ with potassium tert-butoxide. These compounds were found to possess distinctly different properties compared to the self-condensation product F(Me₃Si)₂SiSi(SiMe₃)₂K [15,16].

Molecules 2019, 24, 3823; doi:10.3390/molecules24213823 www.mdpi.com/journal/molecules
2. Results and Discussion

After investigating the chemistry of \(\alpha\)-aminooligosilanides some time ago \[20\], we now wish to extend our studies to \(\beta\)-aminooligidisilanides, which can be considered the formal condensation products of \(\alpha\)-aminooligosilanides. As the latter do not undergo facile dimerization, a straightforward way to obtain \(\beta\)-aminooligidisilanides is the reaction of aminosilylchlorides with oligosilanides followed by further silanide formation via a reaction with potassium tert-butoxide. The synthesis of \((\text{Me}_3\text{Si})_3\text{SiSiPh}_2\text{NEt}_2\) (1) was thus achieved by reaction of \((\text{Me}_3\text{Si})_3\text{SiK}\) \[21,22\] with \(\text{Et}_2\text{NPh}_2\text{SiCl}\) \[23,24\]. Single-crystal XRD analysis of the obtained compound (Figure 1) showed that it crystallized in the orthorhombic space group P2(1)2(1)2(1) (Table S1). An observed Si-N distance of 1.717(3) Å reflects the diminished steric demand of the diphenylsilylene unit compared to the respective Si(SiMe\(_3\))\(_2\) element of \([\text{Et}_2\text{N(SiMe}_3)_2\text{SiSiMe}_2\text{}]_2\) \[20\], where the Si-N bond length is increased to 1.741(7) Å. A Si-Si bond length of 2.3744(14) Å for the \(\text{Et}_2\text{NPh}_2\text{Si–Si}\) bond and other Si-Si lengths between 2.3540(15) and 2.3706(14) Å (Table 1) as well as Si-Si bond angles close to the ideal tetrahedral angle, characterized compound 1 as a rather typical neopentasilane. The same conclusion could be drawn from the \(^{29}\text{Si}\) NMR chemical shifts of 1 (Table 2). Resonances at \(-10.1\) and \(-133.4\) ppm for the trimethylsilyl groups and the central silicon are close to that of tetrakis(trimethylsilyl)silane. The shift of +2.0 ppm found for the \(\text{Et}_2\text{NPh}_2\text{Si}\) group is more unusual. Comparable compounds such as \((\text{Et}_2\text{N})\text{Ph}_2\text{Si–SiMe}_3\) \((-15.3\) ppm), \((\text{Et}_2\text{N})\text{Ph}_2\text{Si–SiMe}_2\text{SiPh}_2\text{NEt}_2\) \((-15.7\) ppm) \[25\], and \((\text{Et}_2\text{N})\text{Ph}_2\text{Si–Si}^i\text{Bu}_2\text{H}\) \((-8.7\) ppm) \[26\] featured the respective resonances more up-field.

The reaction of compound 1 with potassium tert-butoxide in the presence of 18-crown-6 \[22\] led to the formation of silanide 1a (Scheme 1). Crystal structure analysis of 1a (Figure 2), which crystallizes in the triclinic space group P-1, showed a silanide with shortened Si-Si bond lengths close to 2.33 Å (Table 1). A sum of Si-Si bond angles of 319.85 deg showed a fairly pyramidalized silanide atom. The potassium ion appeared coordinated by the crown ether, and the Si-K distance of 3.5064(19) Å was within the range usually observed for this type of compounds. No intramolecular N⋯K interaction could be observed, but a weak interaction of the NEt\(_2\) group with a neighboring molecule might be possible. The Si-N distance 1.743(2) of 1a is clearly large compared to that of 1.717(3) Å for 1, which likely reflects a repulsive interaction between the lone pairs on nitrogen and silicon.

Figure 1. Molecular structure of compound 1 (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in degrees). Si(1)-N(1) 1.717(3), Si(1)-C(1) 1.903(4), Si(1)-Si(2) 2.3744(14), Si(2)-Si(3) 2.3540(15), Si(2)-Si(4) 2.3657(15), Si(2)-Si(5) 2.3706(14), Si(3)-C(18) 1.870(5), N(1)-C(15) 1.458(5), N(1)-Si(1)-Si(2) 110.76(11), N(1)-Si(1)-Si(2) 110.76(11), Si(3)-Si(2)-Si(4) 107.04(6).

The reaction of compound 1 with potassium tert-butoxide in the presence of 18-crown-6 \[22\] led to the formation of silanide 1a (Scheme 1). Crystal structure analysis of 1a (Figure 2), which crystallizes in the triclinic space group P-1, showed a silanide with shortened Si-Si bond lengths close to 2.33 Å (Table 1). A sum of Si-Si bond angles of 319.85 deg showed a fairly pyramidalized silanide atom. The potassium ion appeared coordinated by the crown ether, and the Si-K distance of 3.5064(19) Å was within the range usually observed for this type of compounds. No intramolecular N⋯K interaction could be observed, but a weak interaction of the NEt\(_2\) group with a neighboring molecule might be possible. The Si-N distance 1.743(2) of 1a is clearly large compared to that of 1.717(3) Å for 1, which likely reflects a repulsive interaction between the lone pairs on nitrogen and silicon.
Table 1. Structural data of starting material 1, metallated compounds 1a, 1b, 2a, 3a, and 3b, coupling product 4, and reference compounds XPh₂Si(Me₃Si)₃SiK (X = F, Cl).

| Compound | Si¹-X  | Si¹-Si²  | Si²-SiMe₃ | Si²-M |
|----------|--------|----------|-----------|-------|
| 1        | 1.717(3) | 2.3744(14) | 2.3540(15), 2.3657(15), 2.3706(14) | n.a. |
| 1a       | 1.743(2) | 2.3293(10) | 2.335(2), 2.345(2), 2.3510(9) | 3.4990(10) (K) |
| 1b       | 1.730(7) | 2.338(3) | 2.331(2) | 2.6014(4) (Mg) |
| 2a       | 1.678(5) (X = O) | 2.329(2) | 2.335(2) | 3.5609(14) (K) |
| 2b       | 1.639(2) (X = F) | 2.2970(15) | 2.347(1) | 2.347(1) |
| 3a       | 1.7315(19) | 2.3937(9) | 2.8339(8) | 2.8339(8) (Hf) |
| 3b       | 1.727(3) | 2.464(4) | 2.394(3), 2.410(3) | n.a. |
| 4        | 1.63(2) | 2.30(4) | 2.39(4), 2.40(4) | n.a. |

[a] Data taken from reference [19].

Table 2. ²⁹Si-NMR chemical shift data for 1, 1a, 1b, 2, 2a, 3a, 3b, 4, 5, 5a, 6, 6a and the reference substances XPh₂Si(Me₃Si)₃SiK (X = F, Cl).

| Compound | δ ²⁹Si¹-X (NEt₂) | δ ²⁹Si² | δ ²⁹SiMe₃ | δ ²⁹Si Other |
|----------|-----------------|--------|-----------|-------------|
| 1        | +2.0 | -133.4 | -10.1 |
| 1a       | +16.3 | -186.6 | -6.3 |
| 1b       | +8.7 | -165.5 | -8.3 |
| 2        | +24.5 (Ome) | -136.5 | -10.4 |
| 2a       | +40.0 (Ome) | -201.8 | -4.5 |
| FPh₂Si(Me₃Si)₃SiK[a] | +41.4 (F) | -201.6 | -4.4 |
| ClPh₂Si(Me₃Si)₃SiK[a] | +39.7 (Cl) | -195.7 | -5.7 |
| 3a       | +7.6 | -89.5 | -6.7 |
| 3b       | +9.5 | -83.1 | -5.8 |
| 4        | +4.8 | -115.4 | -7.9 |
| 5        | +0.3 (d, J₅₋₆ = 6 Hz) | -131.2 | -9.2 |
| 5a       | +14.9 (d, J₅₋₆ = 19 Hz) | -198.9 (SiK) | -6.6 (d, J₅₋₆ = 5 Hz) | +20.1 (SiPh₂F) |
| 6        | +4.4 | n.a. | -5.4 |
| 6a       | +17.6 | n.a. | -5.0 |

[a] Data taken from reference [19].

Scheme 1. Reactions of aminosilane 1 and alkoxysilane 2 with potassium tert-butoxide in C₆H₆ in the presence of 18-crown-6 to give β-hetero-substituted oligosilanides 1a and 2a. For 1a, transmetallation with MgBr₂ to magnesium silanide 1b was carried out.
Figure 2. Molecular structure of 1a (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in degrees). Si(2)-Si(1) 2.3293(10), Si(2)-Si(4) 2.3345(10), Si(2)-Si(3) 2.3510(9), Si(2)-K(1) 3.4990(10), Si(4)-C(1) 1.892(3), Si(1)-N(1) 1.743(2), K(1)-O(1) 3.044(5), N(1)-C(21) 1.454(3), C(7)-C(8) 1.394(3), Si(1)-Si(2)-Si(4) 107.14(4), Si(1)-Si(2)-Si(3) 108.28(4), Si(4)-Si(2)-Si(3) 104.42(4), Si(1)-Si(2)-K(1) 123.29(3), Si(4)-Si(2)-K(1) 98.59(3), Si(3)-Si(2)-K(1) 112.87(3), N(1)-Si(1)-Si(2) 121.46(8).

When comparing the structural parameters of 1a to those of FPh₂Si(Me₃Si)₂SiK·18-crown-6 [19], we found that the contraction of the central Si-Si bond was not so pronounced. This can be due to the fact that the disilene adduct character of 1a is smaller than that of FPh₂Si(Me₃Si)₂SiK·18-crown-6. Further comparison with the recently reported Ph₃Si(Me₃Si)₂SiK·18-crown-6 [27] showed a high degree of similarity, which was further emphasized by the ²⁹Si-NMR characterization of 1a (Table 2), featuring the silanide resonance at −186.6 ppm and the signal for SiMe₃ at −6.3 ppm (δ for Ph₃Si(Me₃Si)₂SiK: −189.0 and −5.8 ppm [27]). The expected down-field shift for the SiPh₂NEt₂ caused the respective signal to appear at +16.3 ppm.

Frequently, in reactions with redox labile metal salts, potassium silanides turn out to be too reducing. To moderate the reactivity of these compounds, we found it convenient to transmetallate them to magnesium by metathesis reaction with MgBr₂·Et₂O [28,29]. The application of this method on 1a caused the formation of 1b (Scheme 1). Usually, we prepare silyl magnesium compounds in situ from the respective potassium compounds. Assuming quantitative conversion both for silanide formation and for transmetallation reactions, the stoichiometry of the magnesium silanide is determined by the amount of oligosilane starting material. Typically, we use an excess of MgBr₂·Et₂O for reasons of convenience. While more MgBr₂ has no effect on reactivity, single-crystal XRD analysis of 1b provided us with an example where an additional equivalent of MgBr₂ co-crystallized with two molecules of Et₂NPh₂Si(Me₃Si)₂SiMgBr (Figure 3).

The slightly less anionic character of 1b, compared to 1a, is nicely reflected by its crystal structure. The central Si–Si bond distance of 2.338(3) Å is slightly longer than in 1a, conversely, the Si-N distance of 1.730(7) is somewhat shortened, and the sum of bond angles (328.6(1) deg) is larger, indicating diminished pyramidalization. This is consistent with ²⁹Si-NMR shifts of −165.5 ppm for the silanide atom and of +8.7 ppm for the SiPh₂NEt₂ group (Table 2). Again, this is caused by the increased covalent character of the Si-Mg bond compared to the Si-K interaction of 1a.

In a related way, tris(trimethylsilyl)dimethylmethoxysilylsilane (2) [30] was treated in C₆H₆ with potassium tert-butoxide in the presence of 18-crown-6 (Scheme 1). The fact that the respective methoxylated silane 2a was formed at all is somewhat surprising, as we previously observed that in the reaction of either chloro- or fluorodimethylsilyltris(trimethylsilyl)silane with potassium tert-butoxide, the attack of the alkoxide occurred exclusively at the halodimethylsilyl group. It seems likely that the selectivity in the reaction of 2 does not depend on a stronger steric shielding of the methoxylmethyldimethylsilyl versus the halodimethylsilyl group but rather is due to the fact that the formation of a tert-butoxydimethylsilyl group seems thermodynamically not feasible. The same way
as $\text{FPh}_2\text{Si}([\text{SiMe}_3])_2\text{K}$ is structurally related to $\text{F}([\text{Me}_3\text{Si}])_2\text{Si}([\text{SiMe}_3])_2\text{K}$, compound $2a$ is related to $\text{MeO}([\text{Me}_3\text{Si}])_2\text{Si}([\text{SiMe}_3])_2\text{K}$, which we obtained from the self-condensation of $\text{MeO}([\text{Me}_3\text{Si}])_2\text{SiK}$ [13].

**Figure 3.** Molecular structure of $1b$ (thermal ellipsoid plot drawn at the 30% probability level). Only the anion part of the molecule is shown. All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in degrees). The right silanide part of the structure (Si(5)-Si(7) part) is disordered, and therefore no data on this part are listed. Si(1)-Si(2) 2.338(3), Si(2)-Mg(1) 2.601(4), Si(1)-N(1) 1.730(7), Mg(1)-O(4) 2.009(6), Mg(1)-Br(3) 2.531(3), Mg(1)-Br(2) 2.569(3), Mg(2)-Br(1) 2.569(3), Mg(2)-Br(2) 2.533(3), Mg(2)-Br(3) 2.531(3), Mg(2)-Br(4) 2.533(3), Mg(2)-Mg(3) 3.696(4), Mg(3)-O(2) 2.067(6), Mg(3)-O(1) 2.082(6), Mg(3)-Br(4) 2.665(3), Mg(3)-Br(3) 2.723(3), Si(1)-Si(2)-Si(3) 112.69(12), Si(1)-Si(2)-Mg(1) 113.57(12), N(1)-Si(1)-Si(2) 114.4(3), Br(4)-Mg(1)-Br(3) 94.94(10), O(4)-Mg(1)-Si(2) 112.9(2), Br(4)-Mg(1)-Si(2) 121.50(12), Br(3)-Mg(1)-Si(2) 119.85(12), Br(2)-Mg(2)-Br(1) 93.28(10).

Single-crystal XRD analysis of $2a$ (Figure 4) revealed it to be a typical isotetrasilaneide with a high degree of pyramidalization (sum of bond angles: 305.46(8) deg), a short Si–SiOMe bond distance of 2.329(2) Å (2.3361(13) Å was found for $\text{MeO}([\text{Me}_3\text{Si}])_2\text{Si}([\text{SiMe}_3])_2\text{K}$), and a somewhat longer Si–O distance of 1.678(5) Å. Compared to $1a$, the stronger pyramidalization is consistent with a more shielded $^{29}\text{Si}$ NMR resonance at $-201.8$ ppm (Table 2). Judging the fact that the silanide resonance of $\text{MeO}([\text{Me}_3\text{Si}])_2\text{Si}([\text{SiMe}_3])_2\text{K}$ was observed at $-170.4$ ppm, it can be concluded that $\text{MeO}([\text{Me}_3\text{Si}])_2\text{Si}([\text{SiMe}_3])_2\text{K}$ can be regarded as a methoxide adduct of a disilene [13], whereas $2a$ is better described as a $\beta$-methoxydisilaneide.

Over the last years, we have prepared numerous oligosilylated zirconocenes and hafnocenes, mostly by reaction of either potassium or magnesium oligosilanes with the respective group 4 metallocene dichlorides [31–36]. Reactions of $1b$ with zirconocene and hafnocene dichlorides proceeded analogously and provided access to complexes $3a$ and $3b$ (Scheme 2).
Figure 4. Molecular structure of 2a (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in degrees). Si(1)-Si(2) 2.329(2), Si(2)-Si(4) 2.331(2), Si(2)-K(1) 3.5064(19), Si(1)-O(7) 1.678(5), O(7)-C(1) 1.320(8), Si(1)-Si(2)-Si(4) 101.85(8), Si(1)-Si(2)-Si(3) 101.19(8), Si(4)-Si(2)-Si(3) 102.42(7), Si(1)-Si(2)-K(1) 122.17(7).

Scheme 2. Reactions of 1a with Cp₂MCl₂ (M = Zr, Hf) producing the respective β-aminodisilanyl metallocene chlorides 3a and 3b. Reaction of 1a with Cp₂TiCl₂ causes oxidative coupling, yielding 4.

In the course of the reaction between 1b (prepared in situ by addition of MgBr₂·Et₂O to a solution of 1a) and Cp₂ZrCl₂ (Scheme 2), the formed compound 3a reacted by about 20% with the formed MgClBr to yield Cp₂Zr(Br)Si(SiMe₃)₂SiPh₂NEt₂ as a side product. The presence of the latter was recognized in the crystal structure of 3a (Figure 5). Both the fairly covalent interaction between Si and Zr as well as the steric demand of the Cp₂Zr(Cl) unit caused an elongation of the central Si-Si distance of the Si(SiMe₃)₂SiPh₂NEt₂ moiety to 2.387(3) Å. The observed Si-Zr bond length of 2.863(2) Å is close to those found previously for Cp₂Zr(Cl)Si(SiMe₃)₂SiMe₂Thex (2.853 Å) and Cp₂Zr[Si(SiMe₃)₃]₂ (2.878 Å) [32]. However, compared to the structurally related complex Cp₂Zr(Cl)Si(SiMe₃)₂SiPh₂F (d_{Si-Zr} = 2.799(1)/2.803(1) Å) [19], the bond is significantly longer. As expected, complex 3b (Figure 6) was found to be isostructural to 3a, with the Si-Hf bond (2.8339(8) Å) being slightly shorter than the Si-Zr bond of 3a. The ²⁹Si NMR resonances of the metallated silicon atoms of 3a and 3b were observed at −89.5 and −83.1 ppm, respectively. These values are close to those found for the structurally related compounds Cp₂Zr(Cl)Si(SiMe₃)₃ (−89.5 ppm) and Cp₂Hf(Cl)Si(SiMe₃)₃ (−79.7 ppm) [32]. The recently reported Cp₂Zr(Cl)Si(SiMe₃)₂SiPh₂F exhibited a very similar value of −90.9 ppm [19].
Figure 5. Molecular structure of 3a (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity. About 20% of the chloride position is occupied by bromide (bond lengths in Å, angles in degrees). Cl(1)-Zr(1) 2.4565(19), Zr(1)-Si(2) 2.863(2), Si(1)-Si(2) 2.387(3), Si(1)-N(1) 1.741(6), Si(1)-C(15) 1.881(8), N(1)-C(11) 1.438(10), C(1)-C(2) 1.392(13), Si(3)-Si(2)-Si(1) 104.05(12), Si(3)-Si(2)-Zr(1) 116.95(10), Si(1)-Si(2)-Zr(1) 119.45(10), N(1)-Si(1)-Si(2) 113.2(2).

Figure 6. Molecular structure of 3b (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in degrees). Hf(1)-Cl(1) 2.3998(8), Hf(1)-Si(2) 2.8339(8), Si(1)-Si(2) 2.3937(9), Si(1)-N(1) 1.7315(19), Si(1)-C(17) 1.891(2), Cl(1)-Hf(1)-Si(2) 93.12(3), Si(3)-Si(2)-Si(1) 103.81(4), Si(3)-Si(2)-Hf(1) 117.25(3), Si(1)-Si(2)-Hf(1) 119.29(3), N(1)-Si(1)-Si(2) 113.67(7).

An analogous reaction of 1a with Cp₂TiCl₂ did not give the respective isotetrasilanyl titanocene chloride but the oxidative coupling product 4 (Scheme 2). This is not entirely surprising, as we found out earlier that disilylated titanocenes in the oxidation state +4 tend to undergo reductive elimination of disilanes [34,35]. The crystal structure of 4 (Figure 7) featured a rather long central Si-Si bond distance of 2.464(4) Å. Comparable hexasilylated disilanes such as (Me₃Si)₂SiSi(SiMe₃)₃ (2.403(2) Å) [37,38], (Et₃Si)₂SiSi(SiEt₃)₃ (2.417(1) Å) [39], and PhMe₂Si(SiMe₃)₂SiSi(SiMe₃)₂SiMe₂Ph (2.4166(9) Å) [40] exhibit substantially shorter central bonds. Of all acyclic compounds of this type, only H'Bu₂Si(Me₃Si)₂SiSi(SiMe₃)₂Si'Bu₂H (2.4896(8) Å) [41] was reported to exhibit a longer bond. For the tetrasilane unit, a trans-conformation was found, with a torsional angle of 180 deg and diethylamino
substituents on different sides of the plane defined by the main chain. The $^{29}\text{Si}$-NMR resonance (−115.4 ppm, Table 2) of the central silicon atoms of 4 reflects its extended branched octasilane framework [42].

Since compound 1a appeared somewhat different from FPh$_2$Si(Me$_3$Si)$_2$SiK [19], we wondered if it was possible to prepare a silanide containing both the Et$_2$NPh$_2$Si and the FPh$_2$Si groups. For this reason, we reacted 1a with Ph$_2$SiF$_2$, obtaining neopentasilane 5 in good yield (Scheme 3). The reaction of the latter with KO'Bu in the presence of 18-crown-6 gave access to the respective silanide 5a (Scheme 3) at low temperature (−30 °C). Unfortunately, single-crystal XRD analysis of 5a was not possible, but its NMR spectroscopic properties, in particular the $^{1}J_{\text{SiF}}$ coupling constant and the SiK and SiPh$_2$F chemical shifts, were very similar to those of FPh$_2$Si(Me$_3$Si)$_2$SiK [19].

As tris(trimethylsilyl)germyl potassium is a readily available compound [43], we decided to extend the chemistry of β-aminooligosilanides to that of aminosilyl-substituted germanides. For this reason, we reacted tris(trimethylsilyl)germyl potassium with Et$_2$NPh$_2$SiCl to obtain diethylaminodiphenylsilyltrimethylgermane (6), which in a subsequent step, was converted to potassium diethylaminodiphenylsilylsilb(trimethylsilyl)germanide 6a by reaction with KO'Bu (Scheme 4). The compound can be regarded as the diethylamide adduct of a silagermene.
Scheme 4. Two-step synthesis of 6a starting from tetrakis(trimethylsilyl)germane.

As could be expected, $^1$H and $^{13}$C-NMR spectroscopic properties of 6 and 6a were fairly close to those of 1 and 1a. The $^{29}$Si-NMR spectra of 6 and 6a displayed the typical behavior of silylated germanes, where the silyl resonances were shifted a few ppm towards a lower field [43].

3. Materials and Methods

3.1. General Remarks

All reactions involving air-sensitive compounds were carried out under an atmosphere of dry nitrogen or argon using either Schlenk techniques or a glove box. All solvents were dried using a column-based solvent purification system [44]. Chemicals were obtained from different suppliers and used without further purification.

$^1$H (300 MHz), $^{13}$C (75.4 MHz), $^{19}$F (282.2 MHz), and $^{29}$Si (59.3 MHz) NMR spectra were recorded on a Varian INOVA 300 spectrometer. If not noted otherwise, all samples were measured in C$_6$D$_6$.

To compensate for the low isotopic abundance of $^{29}$Si, the INEPT pulse sequence was used for the amplification of the signal [45,46]. Frequently, this did not allow observing diphenylsilyl Si signals; therefore, a simple inverse-gated single pulse experiment was used for those cases. Elementary analyses were carried out using a Heraeus VARIO ELEMENTAR instrument. As potassium and magnesium silanides usually give poor analysis data, the purity of these compounds was confirmed by $^1$H, $^{13}$C and $^{29}$Si-NMR spectra.

3.2. X-Ray Structure Determination

For X-ray structure analyses, the crystals were mounted onto the tip of a glass fiber, and data collection was performed with a BRUKER-AXS SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (0.71073 Å). The data were reduced to F$^2_o$ and corrected for absorption effects with SAINT [47] and SADABS [48,49], respectively. The structures were solved by direct methods and refined by a full-matrix least-squares method (SHELXL97) [50]. If not noted otherwise, all non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles. All diagrams were drawn with 30% probability thermal ellipsoids, and all hydrogen atoms were omitted for clarity. Crystallographic data (excluding structure factors) for the structures of compounds 1, 2a, 1a, 1b, 3a, 3b, and 4 reported in this paper are deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1952884 (1), 1952880 (2a), 1952885 (1a), 1952883 (1b), 1952881 (3a), 1952886 (3b), and 1952882 (4). Copies of data can be obtained free of charge at: http://www.ccdc.cam.ac.uk/products/csd/request/. The figures of solid-state molecular structures were generated using Ortep-3 as implemented in WINGX [51] and rendered using POV-Ray 3.6 [52].

Tetrakis(trimethylsilyl)silane [53], N,N-diethylaminodiphenylsilane [23,24], MgBr$_2$·OEt$_2$ [54], titanocene dichloride [55], and tetrakis(trimethylsilyl)germane [56] were prepared following published procedures.

3.2.1. N,N-Diethylaminodiphenylsilanyltris(trimethylsilyl)silane (1)

A solution of tris(trimethylsilyl)silyl potassium (freshly prepared from tetrakis(trimethylsilyl)silane (1.50 g, 4.68 mmol) and KO'Bu (0.54 g, 4.81 mmol) in THF (10 mL)) was added dropwise to a vigorously stirred solution of N,N-diethylaminodiphenylsilane (1.36 g, 4.71 mmol) in THF (10 mL). After the
addition, the yellow reaction mixture was stirred for 1 d at ambient temperature, after which all volatiles were evaporated under reduced pressure. The slightly yellow residue was extracted with pentane, and the concentrated extracts were stored at −50 °C to yield colorless crystals of 1 (1.45 g, 62%). NMR (δ in ppm): 1H: 7.77 (m, 4H), 7.22 (m, 6H), 2.11 (q, 4H, J = 7.1 Hz and 14.3 Hz, CH2CH3), 0.73 (t, 6H, J = 7.2 Hz, CH2CH3), 0.30 (s, 27H, SiMe3). 13C: 141.2, 134.7, 129.5, 127.9, 43.4, 14.6, 3.1. 29Si: 2.0 (SiPh2NEt2), −10.1 (SiMe3), −133.4 (Siq). Anal. calcd. for C28H42NSi5 (502.08): C 59.81, H 9.44, N 2.79. Found: C 59.61, H 9.45, N 2.76.

3.2.2. N,N-Diethylaminodiphenylsilylsilyl Potassium 18-Crown-6 (1a)

Compound 1 (500 mg, 0.996 mmol), KOtBu (117 mg, 1.05 mmol), and 18-crown-6 (276 mg, 1.05 mmol) were dissolved in a minimum amount of benzene. The color of the mixture immediately turned to orange. After a few minutes, the reaction was finished as could be determined by 29Si-NMR spectroscopy of an aliquot sample. The solvent was removed in vacuum, and pentane was added to the residue. Product 1a (171 mg, 32%) was crystallized as deep-orange crystals from pentane. NMR (δ in ppm): 1H: 8.14 (m, 4H, Ph), 7.12-7.18 (m, 3H, Ph), 3.61 (br s, 8H, OCH3), 1.04 (t, JHH = 7 Hz, 6H, NCH2CH3), 0.54 (s, 18H, SiMe3). 13C: 148.1, 136.6, 126.9, 126.8, 70.0 (18cr6), 41.4 (NCH2CH3), 15.1 (NCH2CH3), 7.7 (SiMe3). 29Si: 16.3 (SiPh2NEt2), −6.3 (SiMe3), −186.6 (Siq).

3.2.3. N,N-Diethylaminodiphenylsilylsilyl Magnesium Bromide (1b)

Compound 1b was prepared according to 1a, with 1 (200 mg, 0.40 mmol) and KOtBu (47 mg, 0.42 mmol). Instead of work-up after 3 h, the mixture was dropped to MgBr2·OEt2 (108 mg, 0.42 mmol) in THF (1 mL) and stirred for 3 h. Then, all volatiles were evaporated under reduced pressure, and the yellowish residue was extracted with benzene/pentane (3:1). The combined extracts were concentrated to a volume of about 0.5 mL, and addition of pentane (10 mL) afforded the precipitation of 1b as a colorless microcrystalline solid (231 mg, 34%). NMR (δ in ppm): 1H: 7.90 (m, 4H, Ph), 7.26 (t, JHH = 7 Hz, 3H, Ph), 7.14-7.18 (m, 3H, Ph), 3.61 (br s, 8H, OCH2CH3), 3.27 (q, JHH = 7 Hz, 4H, NCH2CH3), 1.25 (br s, 8H, OCH2CH3), 1.04 (t, JHH = 7 Hz, 6H, NCH2CH3), 0.44 (s, 18H, SiMe3). 13C: 143.8, 136.2, 128.3, 127.8, 69.8 (OCH2CH3), 41.7 (NCH2CH3), 25.1 (OCH2CH3), 15.0 (NCH2CH3), 5.6 (SiMe3). 29Si (inverse-gated): 8.7 (SiPh2NEt2), −8.3 (SiMe3), −165.5 (SiMe3).

3.2.4. Methoxydimethylsilylethyltrimethylsilylsilane (2)

Procedure according to 1, using: tetrakis(trimethylsilyl)silane (1000 mg, 3.12 mmol), KOtBu (367 mg, 3.27 mmol), MgBr2·OEt2 (845 mg, 3.27), and Me2SiCl2 (422 mg, 3.27 mmol) which was added at 0 °C. After 12 h, the solvent was removed, and the residue was treated with pentane. The solvent was again removed, and the obtained slight-yellow oil dissolved in DME (10 mL) and dropped to a cooled (0 °C) solution of DME (50 mL), MeOH (105 mg, 3.27 mmol), and Et3N (331 mg, 3.27 mmol). After 12 h, the solvent was removed, and the residue was treated with pentane. Compound 2 (787 mg, 75%) was obtained as a colorless oil. NMR (δ in ppm): 1H: 3.28 (s, 3H), 0.37 (s, 6H), 0.30 (s, 27H). 13C: 50.5, 3.9, 2.9. 29Si: 24.5 (SiMe3OMe), −10.44 (SiMe3), −136.5 (Siq). Anal. calcd. for C12H34OSi5 (336.84): C 42.79, H 10.77. Found: C 42.58, H 10.80.

3.2.5. 2-Methoxydimethylsilylethyltrimethylsilyl Potassium 18-Crown-6 (2a)

Same procedure as for 1a, using: 2 (200 mg, 0.59 mmol), KOtBu (70 mg, 0.62 mmol), and 18-crown-6 (165 mg, 0.62 mmol). Product 2a (128 mg, 38%) was crystallized as deep-orange crystals from pentane. NMR (δ in ppm): 1H: 3.42 (s, 3H, OMe), 3.12 (s, 24H, 18-c-6) 0.26 (s, 18H, SiMe3), 0.21 (s, 6H, SiMe2). 13C: 70.1 (18-c-6), 50.4 (OMe), 7.6 (SiMe2), 7.5 (SiMe3). 29Si: 40.0 (SiMe3OMe), −4.5 (SiMe3), −201.8 (Siq).
3.2.6. N,N-Diethylaminodiphenylsilyl bis(trimethylsilyl) silyl Zirconocene Chloride (3a)

A cold solution of 1b (449 mg, 1.00 mmol) (stored at −35 °C prior to the reaction) in THF (2 mL) was added dropwise to a cold solution of Cp₂ZrCl₂ (350 mg, 1.10 mmol) in THF (5 mL) under vigorous stirring. After the addition, the orange reaction mixture was kept at −35 °C for another 1 h, followed by evaporation of all volatiles under reduced pressure. The orange residue was extracted with benzene/pentane (1:2 ratio), the solutions were combined and evaporated to dryness, and the solid residue was washed with pentane (3 × 3 mL). The remaining solid was taken up in benzene (3 mL), and the solution was layered with pentane, which afforded red crystalline 3a (520 mg, 73%). NMR (δ in ppm): 1H: 7.90 (m, 4H, Ph), 7.22-7.28 (m, 4H, Ph), 7.14-7.19 (m, 2H, Ph), 5.92 (s, 10H, Cp), 3.19 (q, J = 6 Hz, 4H, NEt₂), 0.24 (s, 18H, SiMe₃). 13C: 142.2, 136.4, 129.0, 127.8, 112.1 ( Cp), 41.7 (NCH₂CH₃), 14.0 (NCH₂CH₃), 5.7 (SiMe₃). 29Si (inverse-gated): −7.6 (SiPh₂NEt₂), −6.7 (SiMe₃), −89.5 (SiZr). Anal. calcd. for C₅₂H₄₈Br₀.₂Cl₀.₈NSi₄Zr (694.65): C 55.33, H 6.96, N 2.02. Found: C 55.15, H 7.18, N 1.96.

3.2.7. N,N-Diethylaminodiphenylsilyl bis(trimethylsilyl) silyl Hafnocene Chloride (3b)

Reaction was done according to 3a, using 1b (1.00 mmol) and Cp₂HfCl₂ (449 mg, 1.10 mmol). Recrystallization with pentane afforded orange crystalline 3b (552 mg, 69%). NMR (δ in ppm, C₆D₆): 1H: 7.91 (m, 4H, Ph), 7.23-7.28 (m, 4H, Ph), 7.16-7.18 (m, 2H, Ph), 5.82 (s, 10H, Cp), 3.20 (q, J = 6 Hz, 4H, NEt₂), 0.47 (s, 18H, SiMe₃). 13C: 142.5, 136.5, 128.9, 127.7, 111.1 ( Cp), 41.7 (NCH₂CH₃), 14.0 (NCH₂CH₃), 5.9 (SiMe₃). 29Si (inverse-gated): −9.5 (SiPh₂NEt₂), −5.7 (SiMe₃), −83.1 (SiHf). Anal. calcd. for C₅₂H₄₈ClHfNSi₄ (773.02): C 49.72, H 6.26, N 1.81. Found: C 50.08, H 6.08, N 1.84.

3.2.8. 1,2-Bis(N,N-diethylaminodiphenylsilyl)-1,1,2,2-Tetakis(trimethylsilyl) disilane (4)

To a solution of 1 (400 mg, 0.80 mmol) in THF (3 mL), KO'Bu (94 mg, 0.84 mmol) was added. The color immediately turned to dark reddish. The reaction mixture was stirred for 15 h, whereupon the conversion was quantitative according to NMR measurements, and the solution was cooled to −78 °C. A solution of Cp₂TiCl₂ in THF (1 mL) was added dropwise to the reaction mixture, and stirring was continued at rt for 24 h. The solvent was removed in vacuo, and the residue was dissolved in pentane. The precipitated salts were removed by decantation, and the product was crystallized from pentane by slow evaporation, yielding crystalline colorless 4 (274 mg, 80%). NMR (δ in ppm): 1H: 7.83 (m, 8H, Ph), 7.22 (m, 12H, Ph), 3.06 (q, J = 6 Hz, 8H, NCH₂CH₃), 0.95 (t, J = 6 Hz, 12H, NCH₂CH₃), 0.34 (s, 18H, SiMe₃). 13C: 140.5, 137.4, 129.5, 42.7, 14.3, 6.3. 29Si (inverse-gated): 4.8 (SiPh₂NEt₂), −7.9 (SiMe₃), −115.4 (Si(SiMe₃)₂). Anal. calcd. for C₄₄H₇₈N₂Si₈ (857.79): C 61.61, H 8.93, N 3.27. Found: C 61.37, H 9.01 N 3.23.

3.2.9. N,N-Diethylaminodiphenylsilyl (fluorodiphenylsilyl) bis(trimethylsilyl) silane (5)

A suspension of 1b (freshly prepared from 1 (645 mg, 1.29 mmol), KO'Bu (152 mg, 1.36 mmol), and MgBr₂·OEt₂ (352 mg, 1.36 mmol)) in THF (9 mL) was added dropwise under vigorous stirring to difluorodiphenylsilane at ambient temperature. After the addition, the off-white reaction mixture was stirred for another 21 h, and then all volatiles were evaporated under reduced pressure. The remaining white solid was extracted with toluene/pentane (1:4), and the combined extracts were dried under vacuum, yielding 5 as colorless microcrystals (730 mg, 90%). NMR (δ in ppm): 1H: 7.56-7.62 (m, 8H, Ph), 7.13-7.15 (m, 6H, Ph), 7.06 (m, 6H, Ph), 3.00 (q, J = 6 Hz, 4H, NCH₂CH₃), 0.86 (t, J = 6 Hz, 6H, NCH₂CH₃), 0.24 (s, 18H, SiMe₃). 13C: 139.3, 138.5 (d, J = 13 Hz, Ph), 136.2, 134.3 (d, J = 3 Hz, Ph), 130.0, 129.5, 128.1, 128.0, 14.6 (NCH₂CH₃), 3.4 (SiMe₃). 19F: −168.6 (d, J = 318 Hz). 29Si (inverse-gated): 20.1 (d, J = 318 Hz, Si₂Ph₂F), 0.3 (d, J = 6 Hz, Si₂Ph₂NEt₂), −9.2 (SiMe₃), −131.2 (d, J = 19 Hz, Si₃). Anal. calcd. for C₃₄H₄₈FNSi₅ (630.19): C 64.80, H 7.68, N 2.22. Found: C 64.66, H 7.70, N 2.27.
3.2.10. N,N-Diethylaminodiphenylsilyl(fluorodiphenylsilyl)(trimethylsilyl)silyl Potassium 18-Crown-6 (5a)

The reaction was done according to 1a, using 5 (100 mg, 0.16 mmol), KOt-Bu (19 mg, 0.17 mmol), and 18-crown-6 (44 mg, 0.17 mmol). Recrystallization from pentane at −60 °C afforded orange crystalline 5a (102 mg, 75%). NMR (δ in ppm, D2O capillary, THF, −30 °C, reaction solution): 1H: 7.55 (m, 8H), 7.17-7.45 (m, 12H), 3.03 (q, 3JHH = 7 Hz, 4H, CH2CH3), 0.70 (t, 1JHH = 7 Hz, 6H, CH2CH3), −0.47 (s, 9H, SiMe3). 13C: 148.3 (d, 1JC = 17 Hz, Ph), 146.8, 136.3, 134.5, 126.7, 126.3, 126.2, 71.0, 40.8, 14.6, 6.4. 19F: −165.6 (1JSiF = 357 Hz). 29Si (inverse-gated): 36.0 (d, 1JSiF = 359 Hz, SiPh2F), 14.9 (SiPh2NEt2), −6.6 (d, 3JSiF = 5 Hz, SiMe3), −198.9 (SiK).

3.2.11. N,N-Diethylaminodiphenylsilyltris(trimethylsilyl)germane (6)

A solution of tris(trimethylsilyl)germyl potassium (freshly prepared from tetrakis(trimethylsilyl)germane (1.10 g, 3.00 mmol) and KOt-Bu (354 mg, 3.15 mmol) in THF (6 mL)) was added dropwise to a vigorously stirred solution of chloro(diethylamino)diphenylsilane (273 mg, 0.500 mmol), in THF (6 mL) was added dropwise to a vigorously stirred solution of chloro(diethylamino)diphenylsilane (273 mg, 0.500 mmol), 18-crown-6 (139 mg, 0.16 mmol), and benzene (4 mL). The reaction mixture turned yellow immediately and was left standing for 4 h. Then, all volatiles were evaporated under reduced pressure. The yellow residue was washed with pentane and dried under vacuum, yielding 6 as colorless crystals (230 mg, 14%). NMR (δ in ppm, THF-d8, 60 °C, reaction solution): 1H: 7.17-7.45 (m, 8H, Ph), 3.08 (q, 3JHH = 7 Hz, 4H, NCH2CH3), 0.96 (t, 1JHH = 7 Hz, 6H, NCH2CH3), 0.27 (s, 27H, SiMe3). 13C: 140.3 (Ph), 136.0 (Ph), 129.4 (Ph), 127.9 (Ph), 41.7 (NCH2CH3), 14.8 (NCH2CH3), 3.8 (SiMe3). 29Si (inverse-gated): 4.4 (SiPh2NEt2), −5.4 (SiMe3). Anal. calcd. for C35H47GeNSi4 (546.63): C 54.93, H 8.67, N 2.56. Found: C 54.78, H 8.82, N 2.56.

3.2.12. N,N-Diethylaminodiphenylsilylisis(trimethylsilyl)germyl Potassium 18-Crown-6 (6a)

A vial was charged with 6 (273 mg, 0.500 mmol), KOt-Bu (59 mg, 0.53 mmol), 18-crown-6 (139 mg, 0.525 mmol), and benzene (4 mL). The reaction mixture turned yellow immediately and was left standing for 4 h. Then, all volatiles were evaporated under reduced pressure. The yellow residue was washed with pentane and dried under vacuum, yielding 6a as a yellow microcrystalline solid (241 mg, 31%). NMR (δ in ppm, THF-d8, 60 °C, reaction solution): 1H: 7.17-7.45 (m, 8H, Ph), 3.15 (s, 24H, 18cr6), 1.19 (t, 1JHH = 7 Hz, 6H, NCH2CH3), 0.56 (s, 18H, SiMe3). 13C: 148.4 (Ph), 136.5 (Ph), 126.9 (Ph), 126.7 (Ph), 70.0 (18cr6), 41.6 (NCH2CH3), 15.2 (NCH2CH3), 7.9 (SiMe3). 29Si (inverse-gated): 17.6 (SiPh2NEt2), −5.0 (SiMe3).

4. Conclusions

Some years ago, we studied the chemistry of α-fluoro- [15,16], alkoxy- [13] and amino-substituted [20] oligosilanides. For fluoro- and alkoxydisilanides, we found a tendency to self-condensation, yielding β-fluoro- and alkoxydisilenes. Unusual spectroscopic and chemical properties suggested that these compounds should be regarded as base adducts of symmetrical disilenes. Recently, we reported the synthesis of some β-halodisilanides with different substituents at the 1- and 2-positions of the disilane unit. NMR spectroscopic, structural, and chemical characterization clearly showed that the disilene adduct character of the novel compounds was much diminished.

The preparation and characterization of β-N,N-diethylaminodisilanes, outlined in the current study, clearly showed that also those compounds should be regarded as oligosilanides and not as amide disilene adducts. The study includes the conversion of the initially obtained potassium silanides to the respective derivatives of magnesium, zirconium, and hafnium. In addition, we extended this chemistry to a β-N,N-diethylaminodiphenylsilylisis(trimethylsilyl)germanide.

Supplementary Materials: The following are available online at http://www.mdpi.com/1420-3049/24/21/3823/s1, Figures S1–S46: 1H, 13C, 19F, and 29Si-NMR spectra of compounds 1, 1a, 1b, 2, 2a, 3a, 3b, 4, 5, 5a, 6, and 6a, Table S1: Crystallographic data for compounds 1, 1a, 1b, 2a, 3a, 3b, and 4.
Author Contributions: Investigation, I.B., J.H., R.P. and A.P.; funding acquisition, C.M. and J.B.; project administration C.M. and J.B.; writing—original draft, C.M. and J.B.

Funding: This research was funded by the Austrian Science Fund (Fonds zur Förderung der wissenschaftlichen Forschung) (FWF) via projects P-30955 (J.B.) and P-19338 (C.M.).

Acknowledgments: The authors gratefully acknowledge support for Open Access Funding by the Austrian Science Fund (FWF).

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

1. Lickiss, P.D.; Smith, C.M. Silicon derivatives of the metals of groups 1 and 2. Coord. Chem. Rev. 1995, 145, 75–124. [CrossRef]
2. Tamao, K.; Kawachi, A. Silyl Anions. Adv. Organomet. Chem. 1995, 38, 1–58.
3. Belzner, J.; Dehnet, U. Alkaline and Alkaline Earth Silyl Compounds—Preparation and Structure. In The Chemistry of Organic Silicon Compounds; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons, Ltd.: Chichester, UK, 2003; pp. 779–825. ISBN 978-0-470-85725-0.
4. Lerner, H.-W. Silicon derivatives of group 1, 2, 11 and 12 elements. Coord. Chem. Rev. 2005, 249, 781–798. [CrossRef]
5. Marschner, C. Silicon Centered Anions. In Organosilicon Compounds: Theory and Experiment (Synthesis); Lee, V.Y., Ed.; Academic Press: London, UK, 2017; Volume 1, ISBN 978-0-12-801991-7.
6. Marschner, C. Preparation and Reactions of Polysilanyl Anions and Dianions. Organometallics 2006, 25, 2110–2125. [CrossRef]
7. Gilman, H.; Steudel, W. Diphenylsilyllithium, a new type of organosilyl-metallic compound. Chem. Ind. 1959, 1094.
8. Gilman, H.; Holmes, J.M.; Smith, C.L. Branched-chain Methylated Polysilanes Containing a Silyl-lithium Group. Chem. Ind. 1965, 848–849.
9. Lampland, N.L.; Pindwal, A.; Yan, K.; Ellern, A.; Sadow, A.D. Rare Earth and Main Group Metal Poly(hydrosilyl) Compounds. Organometallics 2017, 36, 4546–4557. [CrossRef]
10. Tamao, K.; Kawachi, A.; Ito, Y. The first stable functional silyl anions: (aminosilyl)lithiums. J. Am. Chem. Soc. 1992, 114, 3989–3990. [CrossRef]
11. Tamao, K.; Kawachi, A.; Tanaka, Y.; Ohtani, H.; Ito, Y. Synthetic applications of functionalized silyl anions: Aminosilyl anions as hydroxy anion equivalent. Tetrahedron 1996, 52, 5765–5772. [CrossRef]
12. Tamao, K.; Kawachi, A. The Chemistry of Silylenoids: Preparation and Reactivity of (Alkoxysilyl)lithium Compounds. Angew. Chem. Int. Ed. Engl. 1995, 34, 818–820. [CrossRef]
13. Líkhar, P.R.; Zirngast, M.; Baumgartner, J.; Marschner, C. Preparation and structural characterisation of methoxybis(trimethylsilyl)silyl potassium and its condensation product. Chem. Commun. 2004, 1764–1765. [CrossRef] [PubMed]
14. Harloff, J.; Popowsk, E.; Reinke, H. Substituted lithium trimethylsiloxyisilanes LiSiRR'(OSiMe3) - Investigations of their synthesis, stability and reactivity. J. Organomet. Chem. 2007, 692, 1421–1441. [CrossRef]
15. Fischer, R.; Baumgartner, J.; Kickelbick, G.; Marschner, C. The First Stable β-Fluorosilylanion. J. Am. Chem. Soc. 2003, 125, 3414–3415. [CrossRef] [PubMed]
16. Zirngast, M.; Flock, M.; Baumgartner, J.; Marschner, C. Formation of Formal Disilene Fluoride Adducts. J. Am. Chem. Soc. 2008, 130, 17460–17470. [CrossRef]
17. Molev, G.; Bravo-Zhivotovskii, D.; Karni, M.; Tumanski, B.; Botoshansky, M.; Apeloig, Y. Synthesis, Molecular Structure, and Reactivity of the Isolable Silylenoid with a Tricoordinate Silicon. J. Am. Chem. Soc. 2006, 128, 2784–2785. [CrossRef]
18. Auer, D.; Kaupp, M.; Strohmann, C. “Unexpected” 29Si NMR Chemical Shifts in Heteroatom-Substituted Silyllithium Compounds: A Quantum-Chemical Analysis. Organometallics 2004, 23, 3647–3655. [CrossRef]
19. Balatoni, I.; Hína, J.; Zitz, R.; Föchim, A.; Baumgartner, J.; Marschner, C. Disilene Fluoride Adducts versus β-Halooligosilanes. Inorg. Chem. 2019. [CrossRef]
20. Zirngast, M.; Baumgartner, J.; Marschner, C. Preparation, Structure and Reactivity of Et₂N(Me₃Si)₂SiK. *Eur. J. Inorg. Chem.* **2008**, *1078–1087*. [CrossRef]
21. Marschner, C. A New and Easy Route to Polysilanylpotassium Compounds. *Eur. J. Inorg. Chem.* **1998**, *221–226*. [CrossRef]
22. Kayser, C.; Fischer, R.; Baumgartner, J.; Marschner, C. Tailor-made Oligosilyl Potassium Compounds. *Organometallics* **2002**, *21*, 1023–1030. [CrossRef]
23. Barrett, A.G.M.; Head, J.; Smith, M.L.; Stock, N.S.; White, A.J.P.; Williams, D.J. Fleming–Tamao Oxidation and Masked Hydroxyl Functionality: Total Synthesis of (+)-Pramanicin and Structural Elucidation of the Antifungal Natural Product (−)-Pramanicin. *J. Org. Chem.* **1999**, *64*, 6005–6018. [CrossRef]
24. Suji, H.; Fukazawa, A.; Yamaguchi, S.; Toshimitsu, A.; Tamao, K. *All-Anti*-Pentasilane: Conformation Control of Oligosilanes Based on the Bis(tetramethylene)-Tethered Trisilane Unit. *Organometallics* **2004**, *23*, 3375–3377. [CrossRef]
25. Uhlig, W. Tailor-made synthesis of functionally substituted oligosilanes from silyl triflates and (aminosilyl)lithium compounds. *Z. Naturforsch. B Chem. Sci.* **2003**, *58*, 183–190. [CrossRef]
26. Ishida, S.; Otsuka, K.; Toma, Y.; Kyushin, S. An Organosilicon Cluster with an Octasilacuneane Core: A Missing Silicon Cage Motif. *Angew. Chem. Int. Ed.* **2013**, *52*, 2507–2510. [CrossRef]
27. Klink, R.; Schwenk, C.; Schnepp, A. Si(SiMe₃)₂SiPh₃ – a ligand for novel sub-valent tin cluster compounds. *Dalton Trans.* **2014**, *43*, 16097–16104. [CrossRef]
28. Farwell, J.D.; Lappert, M.F.; Marschner, C.; Strissel, C.; Tilley, T.D. The first structurally characterised oligosilylmagnesium compound. *J. Organomet. Chem.* **2000**, *603*, 185–188. [CrossRef]
29. Gaderbauer, W.; Zirngast, M.; Baumgartner, J.; Marschner, C.; Tilley, T.D. Synthesis of PolysilanylMagnesium Compounds. *Organometallics* **2006**, *25*, 2599–2606. [CrossRef]
30. Derouiche, Y.; Lickiss, P.D. Preparation and reactions of tris(trimethylsilyl)silyl silicon derivatives and related tetrasilylsilanes. *J. Organomet. Chem.* **1991**, *407*, 41–49. [CrossRef]
31. Kayser, C.; Marschner, C. Oligosilylaniions and their Reactions with Zirconocene and Hafnocene Dichlorides. *Monatsh. Chem.* **1999**, *130*, 203–206.
32. Kayser, C.; Frank, D.; Baumgartner, J.; Marschner, C. Reactions of oligosilyl potassium compounds with Group 4 metallocon dichlorides. *J. Organomet. Chem.* **2003**, *667*, 149–153. [CrossRef]
33. Kayser, C.; Kickelbick, G.; Marschner, C. Einfache Synthese von Oligosilyl-α,ω-dikaliumverbindungen. *Angew. Chem.* **2002**, *114*, 1031–1034. [CrossRef]
34. Zirngast, M.; Flörke, U.; Baumgartner, J.; Marschner, C. Oligosilylated group 4 titanocenes in the oxidation state +3. *Chem. Commun.* **2009**, *37*, 5538–5540. [CrossRef] [PubMed]
35. Arp, H.; Zirngast, M.; Marschner, C.; Baumgartner, J.; Rasmussen, K.; Zark, P.; Müller, T. Synthesis of Oligosilyl Compounds of Group 4 Metallocenes with the Oxidation State +3. *Organometallics* **2012**, *31*, 4309–4319. [CrossRef] [PubMed]
36. Zirngast, M.; Flock, M.; Baumgartner, J.; Marschner, C. Group 4 Metallocene Complexes of Disilenes, Digermerenes, and a Silagermene. *J. Am. Chem. Soc.* **2009**, *131*, 15952–15962. [CrossRef]
37. Bock, H.; Meuret, J.; Klaus, R. Structures of charge-perturbed or sterically overcrowded molecules. 22. Structures and properties of supersilyl compounds (R₃Si)₂Si(SiR₃)₂ and (R₃Si)₂SiC₆H₄Si(SiR₃)₃. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 414–416. [CrossRef]
38. Fronczek, F.R.; Lickiss, P.D. Structure of the highly crowded alkyne di[(trimethylsilyl)methyl]acetylene and the octasilane hexakis(trimethylsilyldisilane. *Acta Cryst. C* **1993**, *49*, 331–333. [CrossRef]
39. Kyushin, S.; Sakurai, H.; Betsuyaku, T.; Matsumoto, H. Highly Stable Silyl Radicals (Et₃Me₃-n-Si)₃Si⁺ (n = 1–3). *Organometallics* **1997**, *16*, 5386–5388. [CrossRef]
40. Fischer, R.; Konopa, T.; Baumgartner, J.; Marschner, C. Small Cyclosilanes: Syntheses and Reactions toward Mono- and Dianions. *Organometallics* **2004**, *23*, 1899–1907. [CrossRef]
41. Kravchenko, V.; Bravo-Zhivotovskii, D.; Tumanskiy, B.; Botoshansky, M.; Segal, N.; Molev, G.; Kosa, M.; Apeloig, Y. Kinetic stabilization of polysilyl radicals. In *Organosilicon Chemistry VI*; Auner, N., Weis, J., Eds.; Wiley-VCH: Weinheim, Germany, 2005; Volume 1, pp. 48–58.
42. Krempner, C. Polysilane Dendrimers. *Polymers* **2012**, *4*, 408–447. [CrossRef]
43. Fischer, R.; Baumgartner, J.; Marschner, C. Silylgermylpotassium Compounds. *Organometallics* **2005**, *24*, 1263–1268. [CrossRef]
44. Pangborn, A.B.; Giardello, M.A.; Grubbs, R.H.; Rosen, R.K.; Timmers, F.J. Safe and Convenient Procedure for Solvent Purification. *Organometallics* 1996, 15, 1518–1520. [CrossRef]

45. Morris, G.A.; Freeman, R. Enhancement of Nuclear Magnetic Resonance Signals by Polarization Transfer. *J. Am. Chem. Soc.* 1979, 101, 760–762. [CrossRef]

46. Helmer, B.J.; West, R. Enhancement of $^{29}$Si NMR Signals by Proton Polarization Transfer. *Organometallics* 1982, 1, 877–879. [CrossRef]

47. *SAINTPLUS: Software Reference Manual*; Version 6.45; Bruker-AXS: Madison, WI, USA, 1997–2003.

48. Blessing, R.H. An empirical correction for absorption anisotropy. *Acta Cryst. A* 1995, 51, 33–38. [CrossRef]

49. Sheldrick, G.M. *SADABS*; Version 2.10; Bruker AXS Inc.: Madison, WI, USA, 2003; Available online: [https://xray.chem.tamu.edu/pdf/manuals/bruker_guide.pdf](https://xray.chem.tamu.edu/pdf/manuals/bruker_guide.pdf) (accessed on 9 July 2008).

50. Sheldrick, G.M. A short history of SHELX. *Acta Cryst. A* 2008, 64, 112–122. [CrossRef]

51. Farrugia, L.J. *WinGX and ORTEP for Windows: An Update*. *J. Appl. Cryst.* 2012, 45, 849–854. [CrossRef]

52. *POVRAY 3.6.*; Persistence of Vision Pty Ltd.: Williamstown, VIC, Australia, 2004; Available online: [http://www.povray.org/download/](http://www.povray.org/download/) (accessed on 9 July 2008).

53. Gilman, H.; Smith, C.L. Tetrakis(trimethylsilyl)silane. *J. Organomet. Chem.* 1967, 8, 245–253. [CrossRef]

54. Nützel, K. Methoden zur Herstellung und Umwandlung magnesiumorganischer Verbindungen. In *Houben-Weyl Methoden der Organischen Chemie*; Müller, E., Ed.; Thieme: Stuttgart, Germany, 1973; Volume 13/2a, p. 76. ISBN 978-0-86577-944-0.

55. Heyn, B.; Hipfler, B.; Kreisel, G.; Schreer, H.; Walthier, D. *Anorganische Synthesechemie*; Springer-Lehrbuch: Berlin, Germany, 1990; ISBN 978-3-540-16588-0.

56. Brook, A.G.; Abdessen, F.; Solfradl, H. Synthesis of some tris(trimethylsilyl)germyl compounds. *J. Organomet. Chem.* 1986, 299, 9–13. [CrossRef]

**Sample Availability:** No samples available from the authors.

© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).