

Tuning the Si–N Interaction in Metalated Oligosilanylsilatrane

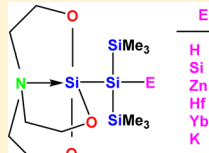
Mohammad Aghazadeh Meshgi,[†] Rainer Zitz,[†] Małgorzata Walewska,[†] Judith Baumgartner,^{*,‡} and Christoph Marschner^{*,†}

[†]Institut für Anorganische Chemie, Technische Universität Graz, Stremayrgasse 9, 8010 Graz, Austria

[‡]Institut für Chemie, Universität Graz, Stremayrgasse 9, 8010 Graz, Austria

Supporting Information

ABSTRACT: Most known silatrane chemistry is concerned with examples where the attached silatrane substituent atom is that of an element more electronegative than silicon. The current study features silylated silatrane with a range of electropositive elements attached to the silyl group. The resulting compounds show different degrees of electron density on the silatrane-substituted silicon atom. This directly affects the Si–N interaction of the silatrane which can be monitored either by ²⁹Si NMR spectroscopy or directly by single crystal XRD analysis of the Si–N distance. Within the sample of study the Si–N distance is increased from 2.153 to 3.13 Å. Moreover, the bis(trimethylsilyl)silatranyl silyl unit was studied as a substituent for disilylated germylene adducts.

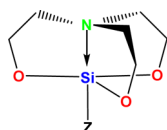


E	d _{Si–N} [Å]
H	2.15
Si	2.16–2.29
Zn	2.26
Hf	2.37
Yb	2.74
K	3.13

INTRODUCTION

Silatrane^{1–4} (Chart 1) and the related germatranes⁵ are hypercoordinated main group compounds. One of the defining

Chart 1. Silatrane Structure



properties of this class of compounds is that the heavy group 14 atom which is coordinated by a triethanolamine ligand is experiencing a transannular interaction with the nitrogen moiety of the ligand.⁶

The bonding interaction between the substituent Z occupying silicon's remaining valence is typically strongly coupled to the relationship between Si and N. Longer Si–Z bond lengths (suggesting weaker interaction) usually result in shorter Si–N distances (suggesting stronger Si–N bonding interaction) and vice versa.² X-ray diffraction studies of silatrane with comparably electronegative halogen, aryl, alkyl, and O substituents indicate a range of Si–N distances from 2.05 to 2.20 Å,² which is significantly shorter than the sum of the van der Waals radii of silicon and nitrogen but slightly longer than the typical covalent Si–N single bond distance.² Not much is known about silatrane with more electropositive substituents, and examples of metalated silatrane are restricted to a single platinum⁷ and a small number of osmium^{8–10} complexes.

Recent studies of silylated silatrane^{11–13} and germatranes¹⁴ have shown that these more electron-donating substituents increase the Si–N distance, and in cases when a silanide unit is attached to the silatrane, they even turn off this interaction. In the current account we are outlining the influence of successively increasing electron-donating silyl groups on the

Si–N interaction of the silatrane. To accomplish this, we decided to use substituted silanes with the attached elements covering Pauling's electronegativity (EN) range χ_P from 0.82 (K) to 1.10 (Yb), 1.30 (Zr), 1.33 (Hf), 1.65 (Zn), 1.90 (Si), and 2.20 (H).¹⁵

RESULTS AND DISCUSSION

Silyl zinc compounds are a fairly established class of compounds. (Ph₃Si)₂Zn, as a first example of a disilylated zinc compound, was reported as early as 1963 by E. Wiberg et al.¹⁶ to form by reaction of Ph₃SiK with ZnCl₂ in liquid ammonia. Only in 1979 did Rösch and Altnau¹⁷ describe synthesis of (Me₃Si)₂Zn by reaction of Li[(Me₃Si)₄Al] with ZnCl₂, which was then followed by Tilley et al.'s synthesis of [(Me₃Si)₃Si]₂Zn from (Me₃Si)₃SiLi and ZnCl₂ in 1987.¹⁸

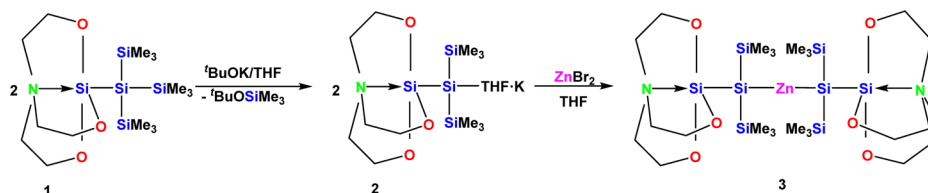
Most of the following synthetic approaches utilized the simple salt metathesis concept. Thus, [(^tBu₃Si)₂(H)Si]Zn,¹⁹ [(Me₃Si)₃SiZnCl]₂,²⁰ [(Me₂HSi)₃Si]₂Zn,²¹ a number of bis-(oligosilanyl)zinc compounds,^{22,23} and trisilyl zincates^{22,24} were all obtained from reactions of the respective alkali silanides with ZnX₂ (X = Cl, Br). A notable exception of this scheme was reported by Apeloig and co-workers who discovered the facile reaction of dialkylzinc reagents with silyl hydrides.²⁵ Most of the described silylzinc reagents were found to be fairly Lewis acidic, and frequently solvent molecules, bases, or even halide ions were found to coordinate to the zinc atoms.

Reacting bis(trimethylsilyl)silatranyl silanide 2,¹² which is easily accessible from tris(trimethylsilyl)silylsilatrane 1, with ZnBr₂ gave disilylzinc compound 3 (Scheme 1). Given the mentioned susceptibility of organozinc compounds to coordinate Lewis bases, we expected at least some interaction between the silatranyl oxygen atoms and the central zinc atom.

Received: February 3, 2017

Published: March 21, 2017

Scheme 1. Synthesis of Bis[bis(trimethylsilyl)silatranysilyl]zinc (3)



Single crystal XRD analysis of **3** (Figure 1) showed it to crystallize in the monoclinic space group $C2/c$. Despite the

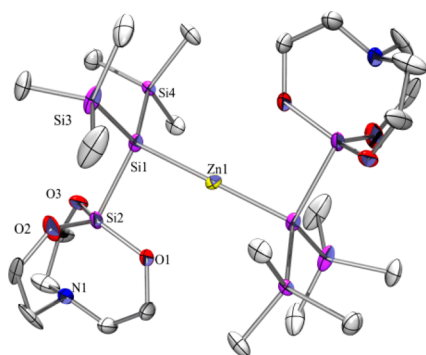


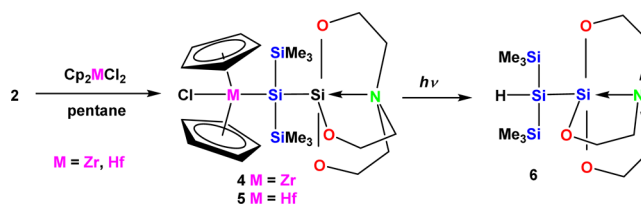
Figure 1. Molecular structure of **3** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in deg). C(2)–N(1) 1.465(2), C(2)–C(1) 1.484(2), C(3)–O(2) 1.424(2), Zn(1)–Si(1) 2.350(12), Si(1)–Si(4) 2.3172(15), Si(1)–Si(2) 2.3489(18), Si(2)–O(1) 1.679(3), Si(2)–N(1) 2.265(4), Si(4)–C(11) 1.865(5), Si(1)–Zn(1)–Si(1A) 180.0, Si(4)–Si(1)–Si(3) 112.58(6), Si(2)–Si(1)–Zn(1) 97.18(5), O(2)–Si(2)–O(1) 118.00(19).

completely linear Si–Zn–Si (180°) arrangement which can be observed frequently in donor-free bis-silylated zinc compounds,^{18,19,22,26} a small Zn–Si–Si_a angle of 97.2° and an almost coplanar arrangement of the Zn–Si–Si–O substructure (dihedral angle: 7.6°) indicate at least some interaction between the closest silatran oxygen atoms and the Zn-atom. The Zn–O distance of 2.877 Å is somewhat smaller than the sum of the van der Waals radii (2.91 Å).²⁷

The silatranyl units engage in a trans conformation with respect to each other, and one of the ethylene units in both silatranes shows disorder. The Zn–Si bond length of 2.350(1) Å (Table 1) is comparable to that of $[(\text{Me}_3\text{Si})_3\text{Si}]_2\text{Zn}$ ¹⁸ and does not show any elongation which otherwise can be observed when larger oligosilyl groups with higher steric demand are bonded to the zinc atom.²²

Synthetic methods for preparing group 4 silyl complexes are quite similar to those for the formation of silyl zinc compounds. Therefore, it is not surprising that the protagonists in these

fields are also largely the same. $\text{Cp}_2\text{Ti}(\text{Cl})\text{SiMe}_3$ was obtained by Rösch and co-workers²⁸ by reaction of $\text{Na}[(\text{Me}_3\text{Si})_4\text{Al}]$ with Cp_2TiCl_2 . Later, Tilley and co-workers prepared $\text{Cp}_2\text{M}(\text{Cl})\text{SiMe}_3$ ($\text{M} = \text{Zr}$ and Hf)²⁹ reacting Cp_2MCl_2 with $\text{Al}(\text{SiMe}_3)_3$ and $\text{Cp}_2\text{M}(\text{Cl})\text{Si}(\text{SiMe}_3)_3$ ³⁰ ($\text{M} = \text{Zr}$ and Hf) utilizing $(\text{Me}_3\text{Si})_3\text{SiLi}$ as nucleophile. A number of mono- and dioligosilylated group 4 metallocenes were obtained employing various potassium oligosilanides.^{31–33} Therefore, not unexpectedly, reaction of silatranysilanide **2** with Cp_2MCl_2 ($\text{M} = \text{Zr}$ and Hf) provided access to respective silylated metallocenes **4** ($\text{M} = \text{Zr}$) and **5** ($\text{M} = \text{Hf}$) (Scheme 2). These

Scheme 2. Synthesis of Silatranysilylzircono- and Hafnocene Chlorides **4** and **5** Followed by Photolysis to the Respective Hydrosilane **6**

two were found to be rather light-sensitive, and exposure to daylight over 2 days resulted in complete photolysis to give silatranylhydrosilane **6** (Scheme 2). Formation of **6** is noteworthy since it was not possible to obtain it cleanly by the more obvious protonation reaction of silanide **2**. The source of the proton in **6** is unclear as is the fate of the Cp_2MCl fragment. Attempts to obtain an analogous silatranysilyl titanocene were not undertaken as it is known that oligosilylated $\text{Cp}_2\text{Ti}(\text{IV})$ compounds are not stable and undergo reductive elimination of silanes to $\text{Cp}_2\text{Ti}(\text{II})$.^{34,35}

Single crystal XRD analysis of hafnocene complex **5** revealed it to crystallize in the monoclinic space group $P2(1)/c$ (Figure 2). The silatranyl unit engages in a trans conformation with respect to the chlorine atom. Interestingly, the number of crystallographically characterized silylated hafnocenes is rather small, and **5** constitutes the first example containing the $\text{Cp}_2\text{Hf}(\text{Cl})\text{Si}$ substructure to be listed in the CCDC. However,

Table 1. Some Structural Data Derived by Single Crystal XRD Analysis of **3**, **5–7** and the Related Compounds **1** and **2**

	$d_{\text{Si-M}}$ [Å]	$d_{\text{Si-N}}$ [Å]	$d_{\text{Si-SiO}_3}$ [Å]	$d_{\text{Si-SiMe}_3}$ [Å]	$\Sigma \angle_{\text{CNC}}$
1 ^a	2.351(3)	2.292(3)	2.351(2)	2.341(1)–2.346(1)	344.1
2 ^a	3.363(2)	3.134(4)	2.308(2)	2.312(2)/2.318(2)	358.5
3	2.350(1)	2.265(4)	2.349(2)	2.323(2)/2.317(1)	338.1
5	2.777(1)	2.374(5)	2.361(2)	2.367(2)/2.370(2)	344.8
6	1.44(4)	2.153(3)	2.357(2)	2.327(2)/2.333(2)	340.1
7	3.018(3)/ 3.032(3)	2.736(8) 2.824(8)	2.319(4) 2.329(4)	2.334(4)/2.345(4) 2.326(4)/2.339(4)	354.7/357.3

^aData taken from ref 12.

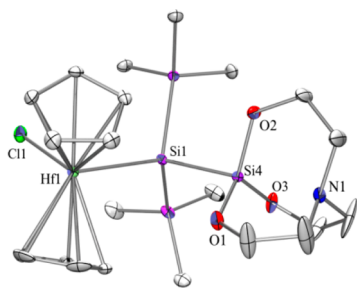


Figure 2. Molecular structure of **5** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in deg). Hf(1)–Cl(1) 2.4114(15), Hf(1)–Si(1) 2.7774(14), O(1)–C(17) 1.394(7), O(1)–Si(4) 1.662(4), Si(1)–Si(4) 2.361(2), Si(1)–Si(2) 2.367(2), Si(2)–C(12) 1.886(7), C(17)–C(18) 1.407(10), Cl(1)–Hf(1)–Si(1) 96.36(4), Si(4)–Si(1)–Si(2) 104.88(7), O(3)–Si(4)–O(1) 116.7(2).

$\text{Cp}_2\text{Hf}(\text{Me})\text{Si}^i\text{BuPh}_2$ ³⁶ and three examples with two silyl ligands are known.

In two of these three examples, the Si–Hf–Si units are part of a cyclic system with Si–Hf bond lengths of 2.791³² and 2.783²³ Å comparable to the 2.777(1) Å length observed for compound **5** (Table 1). The third compound is $\text{Cp}_2\text{Hf}[\text{Si}(\text{SiMe}_3)_3]_2$ ³³ where the Si–Hf bond length is elongated to 2.850 Å, nearly the same value as that observed for $\text{Cp}_2\text{Hf}(\text{Me})\text{Si}^i\text{BuPh}_2$ ³⁶ (2.835 Å). For $\text{CpCp}^*\text{Hf}(\text{Cl})\text{Si}(\text{SiMe}_3)_3$ ³⁷ an even longer Si–Hf distance of 2.888 Å was reported, probably caused by increased steric interactions, because the distance for the analogous complex with a small phenylsilyl ligand: $\text{CpCp}^*\text{Hf}(\text{Cl})\text{SiH}_2\text{Ph}$ amounted only to 2.729 Å.³⁷

²⁹Si NMR spectroscopic analysis of oligosilylated group 4 metallocenes is not completely straightforward. Usually, the chemical shift of the central silicon atom of the tris(trimethylsilyl)silyl group provides a fairly good measure of silanide character. However, reported values for $\text{Cp}_2\text{Zr}(\text{Cl})\text{Si}(\text{SiMe}_3)_3$ and $\text{Cp}_2\text{Hf}(\text{Cl})\text{Si}(\text{SiMe}_3)_3$ are –85.5 and –79.7 ppm, respectively,³¹ which does not reflect the comparably electropositive character of the group 4 metals. Nevertheless, downfield shifts of the SiMe₃ groups attached to the metalated silicon atom are also indicative of silanide character, and the –6.1 and –5.3 ppm observed for $\text{Cp}_2\text{Zr}(\text{Cl})\text{Si}(\text{SiMe}_3)_3$ and $\text{Cp}_2\text{Hf}(\text{Cl})\text{Si}(\text{SiMe}_3)_3$ can be interpreted as to exhibit a silanide character similar to a magnesium silanide. In essence, compounds **4** and **5** exhibit ²⁹Si NMR resonances (Table 2)

very comparable to those of $\text{Cp}_2\text{Zr}(\text{Cl})\text{Si}(\text{SiMe}_3)_3$ and $\text{Cp}_2\text{Hf}(\text{Cl})\text{Si}(\text{SiMe}_3)_3$.³¹

Silatranylhydrosilane **6** was found to crystallize in the triclinic space group *P* $\bar{1}$ (Figure 3). Again, a disorder in one of the ethylene bridges of the silatranyl unit is observed. The position of the hydrogen atom at the silicon was located in the difference Fourier map.

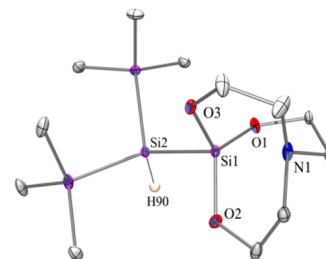


Figure 3. Molecular structure of **6** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms except H90 are omitted for clarity (bond lengths in Å, angles in deg). C(2)–N(1) 1.448(7), C(2)–C(1) 1.584(7), Si(1)–O(1) 1.674(3), Si(1)–N(1) 2.153(3), Si(1)–Si(2) 2.3568(16), Si(2)–Si(4) 2.3268(16), Si(4)–C(11) 1.880(4), O(1)–C(1) 1.429(4), O(1)–Si(1)–O(2) 120.43(15), O(1)–Si(1)–N(1) 83.07(13), N(1)–Si(1)–Si(2) 178.64(10).

The number of known silylated lanthanides is still small.³⁸ In order to follow reactions easily by NMR spectroscopy, the use of diamagnetic lanthanide ions is advisable. Ytterbium(II) complexes have proven useful in this respect. A few previously reported silylated Yb(II) complexes contained oligosilyl ligands.^{39–41}

Recently we reported the reaction of tris(trimethylsilyl)silyl potassium and YbI₂ to give a disilylated Yb-complex with three additional THF molecules coordinated to the Yb ion.⁴¹ Repeating this reaction with silatranylsilanide **2** led to clean product **7** with two silatranylsilyl ligands attached to Yb(II) in addition to two THF molecules (Scheme 3).

Scheme 3. Synthesis of Bis(silatranylsilyl)ytterbium Complex **7**

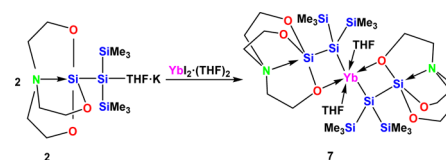


Table 2. NMR Spectroscopic Data of Oligosilylanyl Silatranes (ppm)

	²⁹ Si (SiMe ₃)	²⁹ Si (SiO ₃)	²⁹ Si (Si _q)	other ²⁹ Si shifts	¹³ C (OCH ₂ /CH ₂ N)	¹ H (OCH ₂ /CH ₂ N)
1 ^d	–9.9	–52.6	–133.9		58.6/52.2 ^a 58.6/51.5 ^b	3.65/2.72 ^a 3.30/1.83 ^b
2 ^d	–3.2	–11.8	–210.5		61.0./ 54.3 ^b	3.86/2.84 ^b
3	–7.2	–48.1	–133.8		59.1/51.5	3.41/1.93
4	–5.7	–39.3	–82.9		60.0/52.3	3.44/2.12
5	–4.5	–35.9	–79.0		60.1/52.4	3.42/2.12
6	–12.0	–60.9	–117.4		58.1/51.0	3.28/1.80
7	–2.5	–25.9	–177.0		61.0/52.2	3.69/2.40
8 ^b	–8.1/–8.4	–43.7	–125.7		59.5/51.5	3.37/2.10
9 ^b	–6.5	–53.1	–168.6	–0.6 (GeSiMe ₃)	n.d.	3.38/1.93
10 ^c	–8.3/–8.5	–41.9	–130.6		60.5/53.1	3.49/2.66

^aMeasured in CDCl₃. ^bMeasured in C₆D₆. ^cMeasured in THF-*d*₈. ^dData taken from ref 12.

Single crystal XRD analysis of **7** shows it to crystallize in the triclinic space group $P\bar{1}$ (Figure 4). In addition to the expected

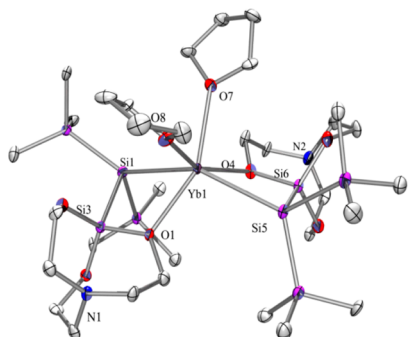


Figure 4. Molecular structure of **7** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in deg). Yb(1)–O(8) 2.410(7), Yb(1)–O(1) 2.436(6), Yb(1)–O(7) 2.454(7), Yb(1)–O(4) 2.510(6), Yb(1)–Si(1) 3.018(3), Yb(1)–Si(5) 3.032(3), Si(1)–Si(3) 2.329(4), Si(1)–Si(4) 2.339(4), Si(3)–O(3) 1.642(7), Si(4)–C(5) 1.879(10), N(1)–C(14) 1.467(12), O(1)–C(13) 1.452(11), C(13)–C(14) 1.508(14), O(8)–Yb(1)–O(7) 78.7(2), Si(1)–Yb(1)–Si(5) 150.60(8), Si(2)–Si(1)–Si(3) 98.28(14), Si(2)–Si(1)–Si(4) 106.49(14), O(3)–Si(3)–O(2) 112.2(4).

Si–Yb interaction, coordination of one silatrane oxygen atom of each ligand to Yb was also observed. The two thus-formed four-membered rings are almost planar with Si(6) 0.281 Å and Si(3) 0.444 Å out of planarity. Furthermore, the two rings are engaging an angle of 121.6° and thus provide space for the coordinated THF molecules. The Si–Yb (Table 1) and the O–Yb distances are in the expected ranges.⁴¹ The inter- and intramolecular Yb–O distances are very much alike.⁴²

The ²⁹Si NMR spectrum of **7** (Table 2) shows signals at $\delta = -2.5$, -25.9 , and -177.0 ppm for the SiMe₃, SiO₃, and SiYb silicon atoms. The peak at -177.0 ppm indicates a strong silanide character more pronounced than what we observed before for other ytterbium oligosilanyl complexes,⁴¹ which is likely caused by the bidentate nature of the silanide ligand.

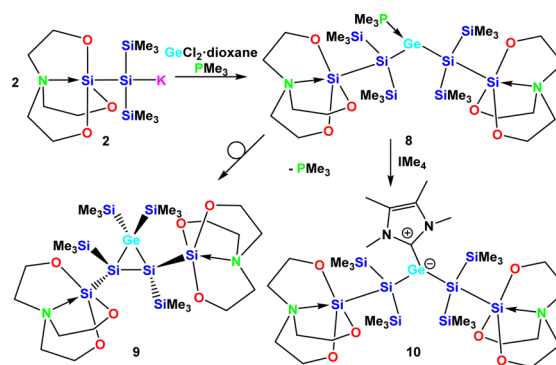
The availability of a number of metalated silylsilatrane with different extent of silanide character provides a unique opportunity to study the influence of the electron density of the substituent on the degree of Si–N interaction. The latter can be judged either by Si–N distance in the solid state or by the upfield shift of the ²⁹Si SiO₃ resonance. For compound **1** with the largely neutral tris(trimethylsilyl)silyl substituent, we observed a SiN distance of 2.292(3) Å accompanied by a chemical shift for the SiO₃ resonance of -52.6 ppm. For silanide **2** with the strongly anionic substituent (Me₃Si)₂KSi, these values change to 3.134(4) Å and -11.8 ppm, respectively, indicating almost no Si–N interaction. Now, the (Me₃Si)₂MSi substituents of compounds **3–5**, **7**, and **2** can be considered to be increasingly anionic; therefore, the associated ²⁹Si SiO₃ resonances should be shifting downfield and the respective Si–N distances should increase. As can be seen in Tables 1 and 2, this expected trend is indeed observed for all compounds.

Together with the dimethylphenylsilylated and methylphenylsilylated silatrane,¹¹ hydrosilanyl silane **6** which features a Si–N distance of 2.153 Å displays the shortest value observed so far for all silylated silatrane. This is also consistent with a more shielded ²⁹Si resonance for the silatrane silicon of -60.9 ppm, which is substantially upfield-shifted compared to the

-52.6 ppm observed for **1**, but it is still short of Yorimitsu's monosilylated silatrane which display the respective resonances in a range between -64 and -69 ppm.¹¹

We wanted to test whether the bis(trimethylsilyl)silatranyl group can be of use as an alternative to the tris(trimethylsilyl)silyl group. In a recent study we have described synthesis and reactivity of a bis[tris(trimethylsilyl)silyl]germylene-PMe₃ adduct.⁴³ While this is a very interesting compound, it is also very reactive, and it was not possible to isolate the compound in solid state since it easily loses PMe₃ and the resulting bis[tris(trimethylsilyl)silyl]germylene rearranges to hexakis-(trimethylsilyl)disilagermirane.⁴³ Attempts to attach either less or substantially more bulky oligosilanyl groups to the germanium atom accompanied by stabilization with PMe₃ were unsuccessful. However, reacting silanide **2** with GeCl₂·dioxane in the presence of PMe₃ proceeded cleanly and gave the respective germylene PMe₃ adduct, **8** (Scheme 4).

Scheme 4. Synthesis of **8** and Its Rearrangement to **9** upon Loss of PMe₃



Compound **8** is slightly more stable than the PMe₃ adduct of bis[tris(trimethylsilyl)silyl]germylene. It precipitates well from pentane or toluene at -30 °C and from a pentane/ether mixture (1:1) at room temperature.

Unfortunately, the obtained pale yellow crystals were not suitable for X-ray diffraction analysis. Applying vacuum to **8** led to the removal of the weakly bound PMe₃ and rearrangement of the resulting germylene to disilagermirane **9** occurred (Scheme 4). The latter was formed exclusively as the 1,2-trans-isomer.

Addition of the N-heterocyclic carbene IMe₄ to a solution of **8** in THF at room temperature led to immediate replacement of PMe₃ by the carbene and formation of germylene adduct **10** (Scheme 4). As was observed before for other NHC-stabilized germylenes,^{44–48} adduct **10** is stable and does not show any tendency to rearrange to **9**.

²⁹Si NMR spectra of germylene adducts **8** and **10** feature the silatranyl silicon shifts at -43.7 and -41.9 ppm. This suggests a diminished degree of hypercoordination. A silatranyl chemical shift of -53.1 for disilagermirane **9**, however, corresponds to a perfectly normal silatranyl unit such as that found for **1**. The Ge(II) atoms of **8** and **10** thus can be considered to be more electropositive than the Ge(IV) atom in **9**. The ²⁹Si resonance at -168.6 ppm found for **9** exhibits the typical upfield shift common for three-membered rings.^{49,50} In the ¹H, ¹³C, and ²⁹Si spectra, only one signal for the trimethylsilyl groups at germanium was observed, which indicates magnetic equivalence of these groups and suggests that the silatranyl groups are located trans to each other.

CONCLUSION

Most silatrane chemistry is concerned with examples where the attached substituent atom is that of an element more electronegative than silicon. Electron withdrawal from silicon renders it more electrophilic and thus susceptible to interaction with the triethanol amine nitrogen atom. If the substituent atom is a metal or another electron rich group, then a higher degree of electron density is shifted toward the silatrane silicon atom and the interaction with the nitrogen atom is diminished. This was previously observed for silatranyl platinum and osmium complexes, with Si–N distances of 2.89(1) Å for the Pt complex⁷ and between 3.000(7) and 3.242(3) Å for the respective Os compounds.^{8–10} Comparable Si–N distances (3.10 to 3.18 Å) were observed recently for potassium silatranyl silanides such as **2**.¹² In addition to the Si–N distance, the ²⁹Si NMR shift of the silatranyl silicon atom reflects the degree of hypercoordination with chemical shifts in a range between $\delta = -65$ ppm (Z = Me) and -100 ppm (Z = F).² These values are clearly upfield-shifted compared to those of related compounds without hypercoordination such as (MeO)₃SiX ($\delta = -38.4$ ppm for X = Me⁵¹ and -84.9 ppm for X = F⁵²). A similar upfield shift is observed when comparing (MeO)₃SiSi(SiMe₃)₃ ($\delta = -32.2$ ppm) to silatrane **1** ($\delta = -52.6$ ppm).¹²

Compounds presented in the current study can be considered to be variations of potassium silanide **2** with gradually diminished silanide character. A Pauling electronegativity of 1.65 makes the Zn–Si bond of silatranyl silyl zinc compound **3** relatively nonpolar. The associated ²⁹Si NMR chemical shift of the SiO₃ unit of $\delta = -48.1$ ppm is therefore close to that of **1** (Table 2), and the respective Si–N distance of 2.265(4) Å is even smaller than that of **1** indicating that the local steric demand of the bis(trimethylsilyl)silatranyl silyl zinc-bis(trimethylsilyl)silyl unit is likely smaller than that of the tris(trimethylsilyl)silyl group.

For compounds **4** and **5**, the electronegativity difference between silicon (EN: 1.9) and zirconium (EN: 1.33) and hafnium (EN: 1.3) is more pronounced going along with an enhanced silanide character. This is nicely reflected by the ²⁹Si NMR chemical shifts of the SiO₃ units being -39.3 ppm (**4**) and -35.9 ppm (**5**) (Table 2). Along with these signs of diminished hypercoordination, the Si–N distance of **5** is elongated to 2.374(5) Å (Table 1). Compound **7** with the more electropositive Yb (EN: 1.1) continues this trend with a ²⁹Si NMR chemical shift of the SiO₃ units of -25.9 ppm and Si–N distances of 2.736(8) and 2.824(8) Å for the two crystallographically inequivalent silatranyl units of **7**. Potassium silanide **2** is at the end point of the series with a Si–N distance of 3.134(4) Å and a SiO₃ ²⁹Si NMR resonance of -11.8 ppm. The local geometry of the nitrogen atom in **2** is almost trigonal with even a slight pyramidalization toward the outside of the silatrane (exo-isomer). For compound **6**, on the other side with hydrogen (EN: 2.2) attached to the bis(trimethylsilyl)silyl unit, a ²⁹Si NMR shift of the silatranyl silicon atom of -60.9 ppm indicates enhanced hypercoordination compared to that of **1**, which is also reflected by a diminished Si–N distance of 2.153(3) Å.

Introduction of the bis(trimethylsilyl)silatranyl silyl unit as a substituent for a disilylated germylene adduct was accomplished by reaction of potassium silatranyl silanide **2** with GeCl₂·dioxane in the presence of PMe₃. While the resulting germylene PMe₃ adduct **8** is reasonable stable, removal of the phosphane base

caused rearrangement to disilagermirane **9**. Exchanging PMe₃ as a base by an N-heterocyclic carbene caused formation of stable NHC-adduct **10**.

EXPERIMENTAL SECTION

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 glovebox. Solvents were dried using column based solvent purification system.⁵⁴ Tris(trimethylsilyl)silatranyl silane (**1**),¹² bis(trimethylsilyl)silatranyl silyl potassium (**2**),¹² 1,3,4,5-tetramethylimidazol-2-ylidene (IMe₄),⁵⁵ and ytterbium diiodide⁵⁶ were prepared according to previously published procedures. All other chemicals were obtained from different suppliers and used without further purification.

¹H (300 MHz), ¹³C (75.4 MHz), ²⁹Si (59.3 MHz), and ³¹P (124.4 MHz) NMR spectra were recorded on a Varian INOVA 300 spectrometer and are referenced to tetramethylsilane (TMS) for ¹H, ¹³C, and ²⁹Si and to 85% H₃PO₄ for ³¹P. If not otherwise noted, the solvent was C₆D₆ and samples were measured at rt. In the case of reaction samples, a D₂O capillary was used to provide an external lock frequency signal. To compensate for the low isotopic abundance of ²⁹Si, the INEPT pulse sequence^{57,58} was used for the amplification of the signal for some of the spectra. Frequently this does not allow observing the silatranyl Si signal; therefore, the Varian s2pul sequence was used in these cases.

Elementary analyses were carried out using a Heraeus VARIO ELEMENTAR instrument. For a number of compounds, no good elemental analysis values could be obtained, which is a typical problem for these compounds caused primarily by silicon carbide formation during the combustion process. Multinuclear NMR spectra (¹H, ¹³C, and ²⁹Si) of these compounds are presented in the Supporting Information as proof of purity. The IR spectrum of **6** was measured with a Bruker Alpha FT IR ATR instrument.

X-ray Structure Determination. For X-ray structure analyses, the crystals were mounted onto the tip of glass fibers, and data collection was performed with a BRUKER-AXS SMART APEX CCD diffractometer using graphite-monochromated Mo K α radiation (0.71073 Å). The data were reduced to F_o² and corrected for absorption effects with SAINT⁵⁹ and SADABS,^{60,61} respectively. The structures were solved by direct methods and refined by full-matrix least-squares method (SHELXL97).⁶² If not noted otherwise, all non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles. Crystallographic data (excluding structure factors) for the structures of compounds **3** and **5–7** reported in this paper have been deposited with the Cambridge Crystallographic Data Center (CCDC) as supplementary publication no. CCDC-1505646 (**3**), 1505644 (**5**), 1505643 (**6**), and 1505645 (**7**) of data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/products/csd/request/>. Figures of solid-state molecular structures were generated using Ortep-3 as implemented in WINGX⁶³ and rendered using POV-Ray 3.6.⁶⁴

Bis[bis(trimethylsilyl)silatranyl silyl]zinc (3**).** To a solution of **2** (0.237 mmol, 134 mg) in THF (1 mL) was added dropwise a solution of ZnBr₂ (0.118 mmol, 27 mg, 0.5 equiv) in THF (2 mL). After 6 h, the volatiles were removed and the residue extracted with pentane and again the solvent removed. Crystallization with diethyl ether and pentane (1:1) at rt afforded pale yellow crystals of **3** (177 mg, 83%). Mp: 74–76 °C. NMR (δ in ppm): ¹H: 3.41 (t, ³J = 5.7 Hz, 12H, OCH₂), 1.93 (t, ³J = 5.7 Hz, 12H, NCH₂), 0.64 (s, 36H, Me₃Si). ¹³C: 59.1 (OCH₂), 51.5 (NCH₂), 4.3 (Me₃Si). ²⁹Si: -7.2 (Me₃Si), -48.1 (SiO₃), -133.8 (Si_q). Elemental analysis calculated for: C₂₄H₆₀N₂O₆Si₈Zn: C 37.79, H 7.93, N 3.67. Found: C 38.63, H 7.88, N 3.80.

Dicyclopentadienyl[bis(trimethylsilyl)silatranyl silyl]zirconocenechloride (4**).** A solution of **2** (0.237 mmol, 134 mg) in benzene (2 mL) was slowly added dropwise to zirconocenedichloride (0.237 mmol, 69 mg) in pentane (3 mL) under strict exclusion of light. After 3 h, the solvent was removed and the residue extracted with

toluene (2 mL). Red crystals of **4** (142 mg, 86%) were obtained after 3 days at $-50\text{ }^{\circ}\text{C}$ under light protection. Mp: 145–168 $^{\circ}\text{C}$. NMR (δ in ppm): ^1H : 6.24 (s, 10H, Cp), 3.44 (t, $^3J = 5.4\text{ Hz}$, 6H, OCH_2), 2.12 (t, $^3J = 5.4\text{ Hz}$, 6H, NCH_2), 0.59 (s, 18H, Me_3Si). ^{13}C : 111.40 (Cp), 59.97 (OCH_2), 52.32 (NCH_2), 4.32 (Me_3Si). ^{29}Si : -5.7 (Me_3Si), -39.3 (SiO_3), -82.9 (Si_q). Elemental analysis calculated for: $\text{C}_{22}\text{H}_{40}\text{ClNO}_3\text{Si}_4\text{Zr}$: C 43.63, H 6.66, N 2.31. Found: C 43.51, H 6.58, N 2.41.

Dicyclopentadienyl[bis(trimethylsilyl)silatranyl-silyl]-hafnocenechloride (5). The same procedure as that for **4** was carried out using **2** (0.189 mmol, 107 mg) and Cp_2HfCl_2 (0.189 mmol, 72 mg). Crystallization with diethyl ether and benzene (20:1) at rt afforded orange crystals of **5** (130 mg, 89%). Mp: 137–172 $^{\circ}\text{C}$. NMR (δ in ppm): ^1H : 6.15 (s, 10H, Cp), 3.42 (t, $^3J = 5.2\text{ Hz}$, 6H, OCH_2), 2.12 (t, $^3J = 5.2\text{ Hz}$, 6H, NCH_2), 0.57 (s, 18H, Me_3Si). ^{13}C : 110.62 (Cp), 60.1 (OCH_2), 52.4 (NCH_2), 4.56 (Me_3Si). ^{29}Si : -4.5 (Me_3Si), -35.9 (SiO_3), -79.0 (Si_q). Elemental analysis calculated for: $\text{C}_{22}\text{H}_{40}\text{ClHfNO}_3\text{Si}_4$: C 38.14, H 5.82, N 2.02. Found: C 37.52, H 5.81, N 2.00.

Bis(trimethylsilyl)silatranyl-silane (6). A solution of **5** (0.106 mmol, 83 mg) in toluene (2 mL) was exposed to daylight over 3 days. Colorless crystals of **6** (53 mg, 64%) were obtained after recrystallization in pentane at $-55\text{ }^{\circ}\text{C}$. Mp: 90–93 $^{\circ}\text{C}$. NMR (δ in ppm): ^1H : 3.28 (t, $^3J = 5.8\text{ Hz}$, 6H, OCH_2), 2.85 (s, 1H, SiH), 1.83 (t, $^3J = 5.8\text{ Hz}$, 6H, NCH_2), 0.52 (s, 18H, Me_3Si). ^{13}C : 58.1 (OCH_2), 51.0 (NCH_2), 2.0 (Me_3Si). ^{29}Si : -12.0 (Me_3Si), -60.9 (SiO_3), -117.4 (Si_q). Elemental analysis calculated for: $\text{C}_{12}\text{H}_{31}\text{NO}_3\text{Si}_4$: C 41.21, H 8.93, N 4.01. Found: C 41.89, H 8.85, N 3.88. IR (ATR, neat) $\nu_{\text{Si-H}} = 2045\text{ cm}^{-1}$.

Bis[bis(trimethylsilyl)silatranyl-silyl]ytterbium-(THF)₂ (7). The same procedure as that for **4** was carried out using **2** (0.170 mmol, 96 mg) and $\text{Yb}_2(\text{THF})_2$ (0.080 mmol, 47 mg). The whole procedure was carried out under strict light exclusion in toluene. Yellow-orange crystals of **7** (34 mg, 40%) were obtained after 2 days at $-37\text{ }^{\circ}\text{C}$. Mp: 157–158 $^{\circ}\text{C}$. NMR (δ in ppm): ^1H : 3.86 (bs, 8H, THF), 3.69 (t, $^3J = 4.9\text{ Hz}$, 12H, OCH_2), 2.40 (t, $^3J = 4.9\text{ Hz}$, 12H, NCH_2), 1.45 (bs, 8H, THF), 0.63 (s, 36H, SiMe_3). ^{13}C : 69.0 (THF), 61.0 (OCH_2), 52.2 (NCH_2), 25.3 (THF), 6.2 (SiMe_3). ^{29}Si : -2.5 (SiMe_3), -25.9 (SiO_3), -177.0 (SiYb).

Bis[bis(trimethylsilyl)silatranyl-silyl]germylene- PMe_3 (8). A solution of **2** (0.12 mmol) in THF (1 mL) freshly prepared from **1** (50 mg, 0.12 mmol) and KOTu (15 mg, 0.12 mmol) was slowly added dropwise to a stirred solution of $\text{GeCl}_2\cdot\text{dioxane}$ (14 mg, 0.06 mmol) and PMe_3 (5 mg, 0.06 mmol) in THF (1 mL) at $-30\text{ }^{\circ}\text{C}$. After 1 h, the solvent was removed in vacuum, and the residue was extracted with pentane ($3 \times 8\text{ mL}$). Careful evaporation of solvent gave a yellowish solid of **8** (45 mg, 88%). NMR (δ in ppm): ^1H (C_6D_6): 3.37 (t, $^3J = 5.4\text{ Hz}$, 12H, OCH_2), 2.10 (t, $^3J = 5.2\text{ Hz}$, 12H, NCH_2), 1.59 (d, $^2J_{\text{H-P}} = 10.5\text{ Hz}$, 9H, PCH_3), 0.64 (s, 36H, SiMe_3). ^{13}C (C_6D_6): 59.5 (OCH_2), 51.5 (NCH_2), 18.1 (d, $^1J_{\text{C-P}} = 22\text{ Hz}$, PMe_3), 3.8 (SiMe_3), 3.8 (SiMe_3). ^{29}Si (C_6D_6): -8.1 (d, $^3J_{\text{Si-P}} = 9\text{ Hz}$, SiMe_3), -8.4 (s, SiMe_3), -43.7 (d, $^3J_{\text{Si-P}} = 16\text{ Hz}$, SiO_3), -125.7 (d, $^2J_{\text{Si-P}} = 15\text{ Hz}$, $\text{Si}(\text{SiMe}_3)_3$). ^{31}P (C_6D_6): -18.2 (PMe_3).

trans-1,1,2,3-Tetrakis(trimethylsilyl)-2,3-silatranyl-cyclopropane-1-germasilane (9). Application of vacuum to solid **8** (45 mg, 0.05 mmol) for 90 min resulted in quantitative formation of **9** (41 mg, 100%). NMR (δ in ppm): ^1H (C_6D_6): 3.38 (t, $^3J = 5.6\text{ Hz}$, 12H, OCH_2), 1.93 (t, $^3J = 5.6\text{ Hz}$, 12H, NCH_2), 0.73 (s, 18H, SiMe_3), 0.66 (s, 18H, SiMe_3). ^{29}Si (C_6D_6): -0.6 (GeSiMe_3), -6.5 (s, SiSiMe_3), -53.1 (SiO_3), -168.6 ($\text{Si}(\text{SiMe}_3)_3$). No satisfactory ^{13}C NMR spectrum was obtained due to bad solubility of **9**.

Bis[bis(trimethylsilyl)silatranyl-silyl]germylene- IME_4 (10). IME_4 (7 mg, 0.06 mmol) was added to a stirred solution of **8** (50 mg, 0.06 mmol) in THF (10 mL) at rt. After 1 h, the solvent was removed under reduced pressure and the residue extracted with pentane/toluene 1:1 ($3 \times 5\text{ mL}$). Removal of the solvent in vacuum yielded **10** as an orange solid (47 mg, 88%). Mp: 128–129 $^{\circ}\text{C}$. NMR (δ in ppm): ^1H ($\text{THF-}d_8$): 3.97 (s, 3H, NCH_3), 3.94 (s, 3H, NCH_3), 3.49 (t, $^3J = 5.4\text{ Hz}$, 12H, OCH_2), 2.66 (t, $^3J = 5.4\text{ Hz}$, 12H, NCH_2), 2.17 (s, 3H, CCH_3), 2.16 (s, 3H, CCH_3), 0.23 (s, 18H, SiMe_3), 0.02 (s, 18H,

SiMe_3). ^{13}C ($\text{THF-}d_8$): 174.8 (NCN), 125.8 (CMe), 125.7 (CMe), 60.5 (OCH_2), 53.1 (NCH_2), 38.9 (NCH_3), 35.4 (NCH_3), 9.4 (CCH_3), 8.9 (CCH_3), 3.3 (SiMe_3), 2.8 (SiMe_3). ^{29}Si ($\text{THF-}d_8$): -8.3 (SiMe_3), -8.5 (SiMe_3), -41.9 (SiO_3), -130.6 ($\text{Si}(\text{SiMe}_3)_3$).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00084.

Crystallographic information of compounds **3** and **5–7**; ^1H , ^{13}C , ^{29}Si , and ^{31}P NMR spectra of compounds **3** and **5–10** (PDF)

Crystallographic information file of compounds **3** and **5–7** (CIF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: baumgartner@tugraz.at.

*E-mail: christoph.marschner@tugraz.at.

ORCID

Judith Baumgartner: 0000-0002-9938-1813

Christoph Marschner: 0000-0001-8586-2889

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Support for this study was provided by the Austrian Fonds zur Förderung der wissenschaftlichen Forschung (FWF) via the projects P-22678, P-26417 (C. M.) and P-25124 (J. B.).

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