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Preparation, Structure and Reactivity of $Et_2N(Me_3Si)_2SiK$

Michaela Zirngast,[a] Judith Baumgartner,[a] and Christoph Marschner*[a]

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Reaction of $Et_2NSi(SiMe_3)_3$ with potassium *tert*-butoxide gives the silylenoid $Et_2N(Me_3Si)_2SiK$. Structural characterisation and reactivity of this compound was studied. It was found that while $Et_2N(Me_3Si)_2SiK$ exhibits the typical NMR spectroscopic properties for a silylenoid species it does not undergo self-condensation under ambient conditions. Its reaction with zirconocene and hafnocene dichlorides gave the expected silyl metallocene chloride. However, there seems to be no strong interaction between the amino nitrogen atom and the group-4 metal. Besides the synthesis of $Et_2N(Me_3Si)_2SiK$ also the preparation of the related silylenoid compound $(Et_2N)_2(Me_3Si)SiK$ and was accomplished.

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Introduction

Aminosilanes are an interesting class of compounds because they can be regarded as protected silyl halides. They can easily be obtained from the respective silyl halides by reaction with either two equivalents of amine or alternatively one equivalent of an amide. In a similar facile reaction with HX, RCOX or SiX_4 the Si–X functionality can be regenerated under very mild conditions.

As part of their studies on hydroxy anion equivalents, Tamao and co-workers have developed the chemistry of diethylamino-substituted silyl anions.[1,2,3] Their preparation was achieved by reaction of amino-substituted silyl chlorides with lithium. In order to obtain charge stabilization the presence of phenyl groups was required for these compounds, whereas use of silyl groups for the same task was not explored to much extent.[4] Popowski et al.[5] could prove that the introduction of bis(trimethylsilyl)amino instead of diethylamino groups to silyl anions forces the silylenoid character. Therefore self-condensation occurs, a process which is also known for alkoxy-[6,7] and halogen-substituted[8] silyl anions. The condensation products: silyl-substituted α-aminosilyl anions were detected indirectly by derivatisation with silyl chlorides.[5] Roewer and co-workers[9] showed that a diethylamino-substituted chlorodisilane could be converted into the first α-aminooligosilanyllithium compound. Related compound were obtained later by Gehrhus and co-workers by addition of oligosilyl anions to amino-stabilized silylenes.[10]

Over the past few years our group has also studied various aspects of the chemistry of silyl anions.[11,12] In particular we have concentrated on the use of potassium alkoxides as reagents for their generation. Methoxy-[7] and halogen-substituted[8] oligosilanes react to give products of selfcondensation, which in the case of the halides leads to the formation of disilenes;[8] the amino-substituted anions behave much more regular.

Results and Discussion

Synthesis and Reactions of (Diethylamino)bis(trimethylsilyl)silyl Potassium

For the synthesis of aminooligosilyl anions we decided to start from (diethylamino)tris(trimethylsilyl)silane (**1**).[13] As for most aminosilanes the diethylamino group can be introduced conveniently by reaction with a silyl halide. This way we achieved the synthesis of **1** by reaction with bromotris(trimethylsilyl)silane. Alternatively, the compound can be synthesized following a procedure, consisting of reaction of diethylamine with tetrachlorosilane and subsequent Wurtz-type coupling of the thus formed trichloro(diethylamino)silane with three equivalents of chlorotrimethylsilane and lithium.[13]

The conversion of (diethylamino)tris(trimethylsilyl)silane (**1**) with potassium *tert*-butoxide proceeded completely selective (Scheme 1) either in THF or alternatively in toluene in the presence of 18-crown-6 to yield (diethylamino)bis(trimethylsilyl)silyl potassium (**2**).[14] In contrast to similar reactions with alkoxy or halide substituents no self condensation tendency of **2** was observed (Scheme 1). This is in agreement with Tamao's results on lithium (diethylamino)silyls.[1]

As compound **2** is a strong nucleophile it can undergo a number of reactions with electrophiles. Reaction of two equivalents of **2** with 1,2-dichlorotetramethyldisilane resulted in the clean formation of **3** (Scheme 2).[15] In a similar way the oxidative coupling of **2** with 1,2-dibromoethane was accomplished to give 1,2-bis(diethylamino)tetrakis(tri-

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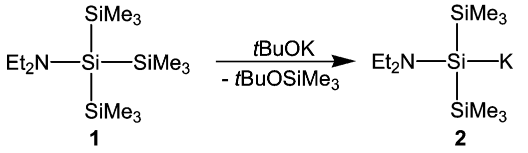
[a] Institut für Anorganische Chemie, Technische Universität Graz,
Stremayrgasse 16, 8010 Graz, Austria
Fax: +43-316-873-8701
E-mail: christoph.marschner@tugraz.at

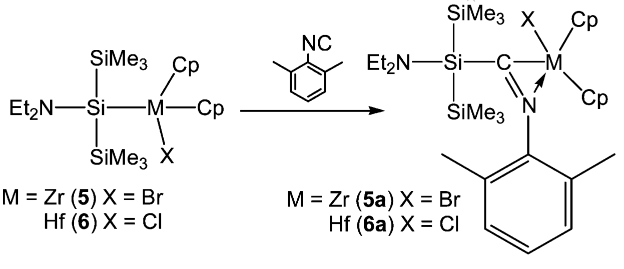


Scheme 1. Synthesis of (diethylamino)bis(trimethylsilyl)silyl potassium (**2**).

methylsilyl)disilane (**4**) (Scheme 2).[14,16] Reactions of **2** with zirconocene and hafnocene dichlorides[17–19] were of interest as aminosilyl-substituted group-4 metallocenes have not been reported yet. Analogous aminoalkyl-substituted compounds[20] have been shown to exhibit coordination of the amino group to the metallocene. This coordination can change the reactivity of the complex dramatically as it reduces the Lewis acidic character of the compound. Reactions such as carbonylations are thus inhibited.

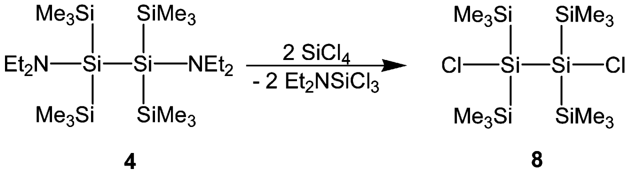
In some cases oligosilylpotassium compounds can be too reactive for certain reactions so that metathesis with magnesium bromide[21] is required in order to obtain clean conversion. This was found for instance for reactions of oligosilyl anions with zirconocene and hafnocene dichlorides.[21,34] Also for the reaction of **2** with zirconocene dichloride this procedure was required. As a consequence of the introduction of bromide into the reaction mixture the exchange of the chloride against bromide on the zirconium was observed in the final product **5** (Scheme 2). The color of the deep-blue **5** was unexpected as the oligosilyl zirconocene chlorides so far obtained by us[14,15b,21] were usually yellow, orange or red. The reaction of hafnocene dichloride to the red colored (diethylamino)bis(trimethylsilyl)silylhafnocene chloride (**6**) was possible directly from **2** (Scheme 2). The fact that both silylmetallocenes reacted with 2,6-dimethylphenylisonitrile to give the insertion products[17,22] very easily (Scheme 3) indicates that the amino nitrogen on the silyl group does not block the coordination site on the metal. This assumption was verified by a crystal structure analysis of zirconocene **5**, which does not show any interaction between the Zr and N atoms (distance 3.8 Å) (Figure 4).

Reaction of the magnesium derivative of **2** with pivaldehyde gave the expected addition product **7**. This compound is of interest with respect to the generation of amino-substituted silenes via sila-Peterson reaction. Amino groups as internal Lewis bases have been studied to some extent.[23] However, the preparation of a silene with direct nitrogen substitution has still not been achieved so far.



Scheme 3. Derivatization reactions of silylmetallocenes **5** and **6**.

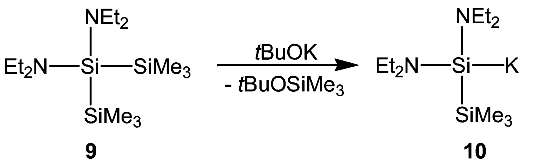
Reaction of **4** with $SiCl_4$[24] gave the 1,2-dichlorotetrakis(trimethylsilyl)disilane[25] (**8**) in a clean reaction (Scheme 4).



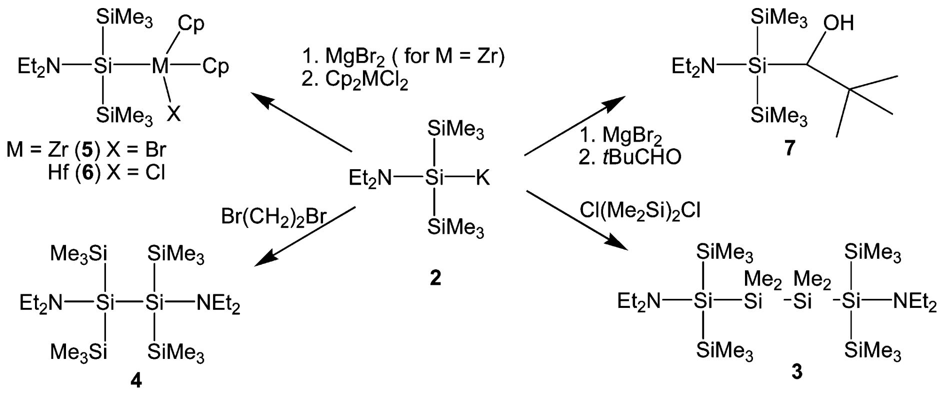
Scheme 4. Chlorination of 1,2-diaminodisilane **4**.

Attempted reactions of **3** and **4** with 2 equiv. potassium *tert*-butoxide in the presence of crown ether in order to obtain the expected 1,4- and 1,2-dipotassium compounds[15b,26] did not lead to clean conversions.

As it is known from Tamao's work that also diamino-substituted lithium silyls can be synthesized, we carried out the reaction of bis(diethylamino)bis(trimethylsilyl)silane (**9**)[13] with potassium *tert*-butoxide to obtain the expected compound **10** in good yield (Scheme 5).



Scheme 5. Synthesis of bis(diethylamino)(trimethylsilyl)silyl potassium (**10**).



Scheme 2. Reactions of **2** with various electrophiles.

NMR Spectroscopy

One of the interesting properties of silylenoids which has been raised initially by Tamao[1d] and was investigated in some detail by Kaupp and Strohmann,[27] is their unusual low-field shifting behaviour. This is in contrast to trialkyl-, trihydro- or trisilyl-substituted silyl anions, which exhibit a shift to higher field compared to the respective silyl chlorides. Similarly, a substantial shift to higher field was also observed in our studies upon metalation of neopenta- and isotetrasilanes with potassium alkoxides. The transformation of $(R_3Si)_4Si$ to $(R_3Si)_3SiK$ is accompanied by a large high-field shift of about 60 ppm for the α-silicon and a slight shift of about 2–3 ppm in the opposite direction for the β-silicon.[14] Comparison of the central ^{29}Si-NMR resonances of **2** [–25.2 (18-crown-6) and –20.1 (THF) ppm] and **1** (δ = –29.0 ppm) shows the typical silylenoid type shift to lower field (Table 1). For the more electronegative methoxy group in $MeO(Me_3Si)_2SiK$ a $\Delta\delta$ value of + 28.4 ppm was observed.[7] The shift behaviour of the trimethylsilyl groups of **2** though is still characterized by a slight move to lower field (Table 1). The attachment of the $(Me_3Si)_3Si$ group to zirconocene or hafnocene halide fragments compared to $(Me_3Si)_4Si$ causes a shift of the resonances for the central silicon atom of about 50–55 ppm to lower field.[18] The strongly deshielded resonances of **5** (+41.8 ppm) and **6** (+48.7 ppm) indicate a very similar behaviour. The spectroscopic behaviour of **10** exhibits a rather large shift of resonance of almost 50 ppm to lower field (from –3.2 ppm for **9** to +43.6 ppm for **10**). Nevertheless, no signs of self-condensation were observed in solution.

Table 1. ^{29}Si NMR resonances (δ values, ppm) of $RR'(Me_3Si)SiNEt_2$.

R	R′	δ SiR	δ SiMe$_3$
Me_3Si	Me_3Si	–29.0	–16.8
K·2THF	Me_3Si	–20.1	–15.4
K·18-crown-6	Me_3Si	–25.2	–15.5
$Cp_2Zr(Br)$	Me_3Si	+41.8	–13.9
$Cp_2Hf(Cl)$	Me_3Si	+48.7	–10.2
$Si(SiMe_3)_2NEt_2$	Me_3Si	–25.1	–15.8
$(SiMe_2)_2Si(SiMe_3)_2NEt_2$	Me_3Si	–23.3	–16.0
$C(OH)CMe_3$	Me_3Si	–21.7	–16.8
$C(N\text{-}2,6\text{-}Me_2C_6H_4)Zr(Br)Cp_2$	Me_3Si	–19.8	–16.7
$C(N\text{-}2,6\text{-}Me_2C_6H_4)Hf(Cl)Cp_2$	Me_3Si	–19.1	–16.6
Me_3Si	Et_2N	–3.2	–23.1
K·18-crown-6	Et_2N	+43.6	–28.6

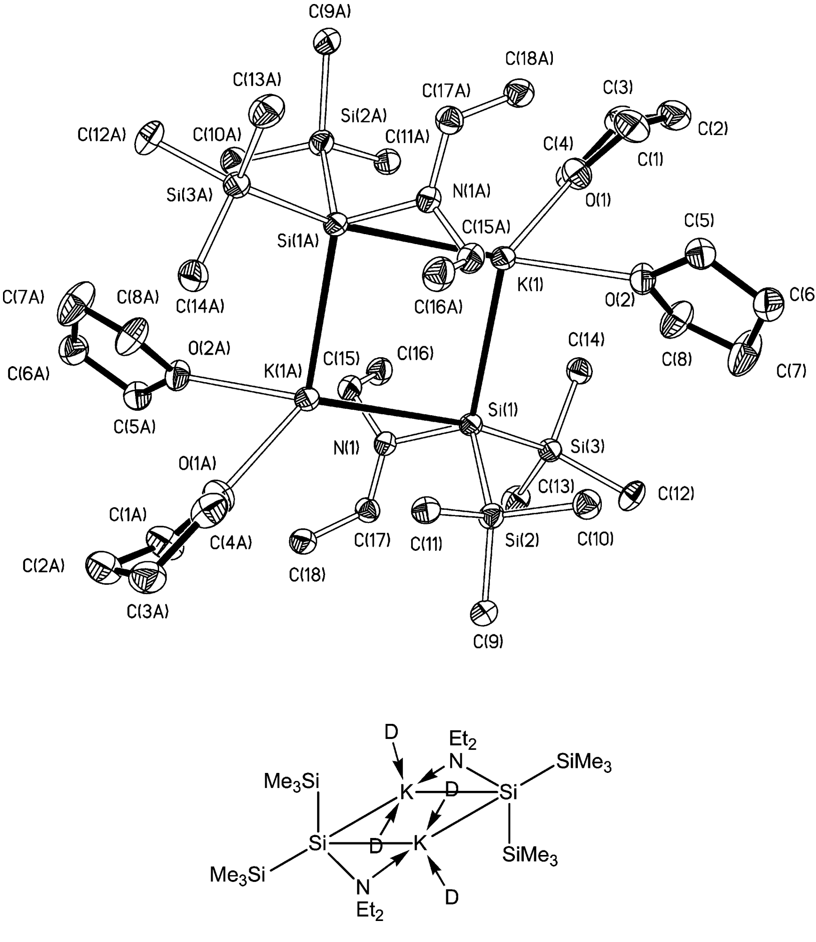


Figure 1. Top: molecular structure and numbering of compound **2**. Selected bond lengths [Å] and bond angles [°] with s.u. values: K(1)–O(2) 2.718(5), K(1)–Si(1) 3.419(2), K(1)–Si(1A) 3.537(3), K(1)–K(1A) 4.512(4), O(1)–C(1) 1.444(10), Si(1)–N(1) 1.829(6), Si(1)–Si(2) 2.357(3), Si(1)–Si(3) 2.394(3), Si(2)–C(9) 1.885(7), N(1)–C(17) 1.467(8), O(2)–K(1)–O(1) 77.89(18), O(2)–K(1)–Si(1) 97.94(11), O(1)–K(1)–Si(1) 118.55(13), N(1A)–K(1)–Si(1) 119.85(13), O(2)–K(1)–Si(1A) 130.57(13), Si(1)–K(1)–Si(1A) 99.14(7), O(1)–K(1)–K(1A) 150.08(15), N(1A)–K(1)–K(1A) 72.87(12). Bottom: schematic representation of **2** in the solid state (D = coordinated THF).

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X-ray Crystallography

Although it was possible to obtain crystal structures of several compounds containing the (diethylamino)bis(trimethylsilyl)silyl group the overall quality of these crystals was not very good as reflected by relatively high *R* factors. The discussion of these structures therefore is mainly focused on general structural features.

The crystal structure analysis of the THF adduct of **2** showed it to be dimeric in the solid state (Figure 1). The structural motif that two silyl anions form dimers via a four-membered ring is quite common[28] and also known for tris(trimethylsilyl)silyl potassium.[29] For the structure of **2**, however, we see additional features. The two potassium atoms are coordinated by two THF molecules and in addition experience internal coordination from the nitrogen atom.[30] This arrangement has an interesting consequence for the trimethylsilyl groups. As the equatorial (with respect to the SiKSiK plane) positions around silicon are occupied by the amino group and one trimethylsilyl group the second trimethylsilyl group adopts an axial position with a significantly elongated bond [2.394(3) Å] compared to the second Si–Si distance [2.357(3) Å]. The Si–N bond is also fairly elongated to 1.829(6) Å compared to the values for the same distance in **3** [1.741(7) Å] and 4 [1.736(6) Å]. A similar extension of this bond is also known for related phenyl(diethylamino)silyllithium compounds[3,31] compared to neutral analogues.[32] The degree of pyramidalization corresponding to angle Si(2)–Si(1)–Si(3) is with a value of 103° in the typical range for a silyl anion (Figure 1).

The structure of compound **3** is similar to related compounds prepared earlier. The Si-main chain of the molecule

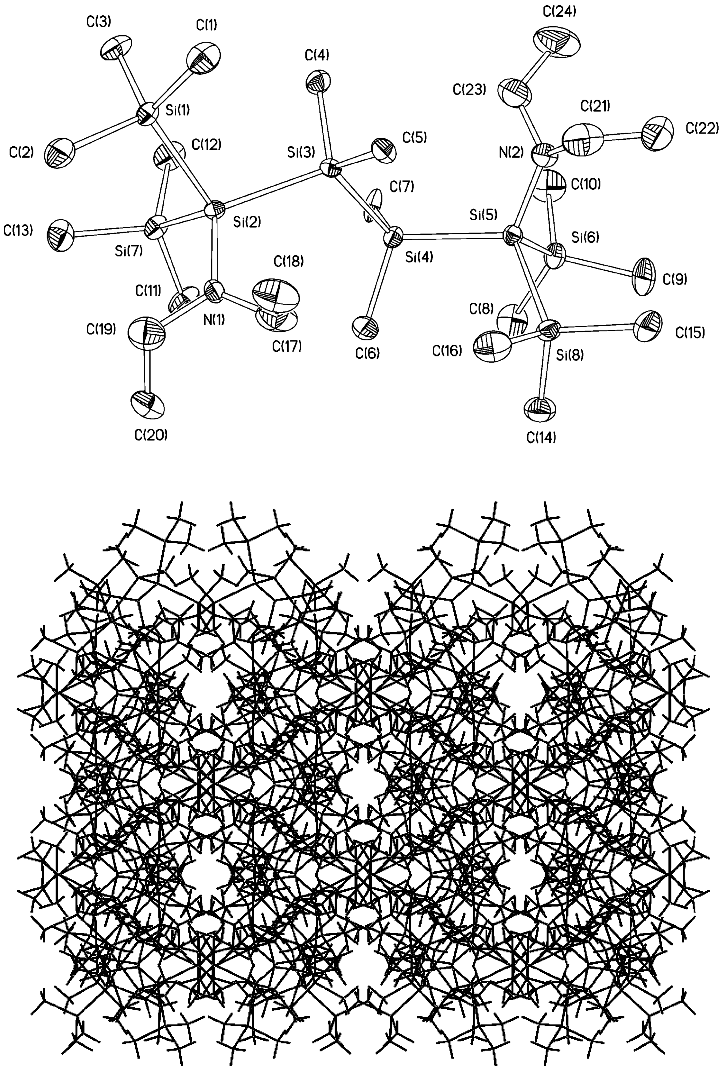

Figure 2. Top: molecular structure and numbering of **3**. Selected bond lengths [Å] and bond angles [°] with s.u. values: Si(1)–C(1) 1.869(9), Si(2)–N(1) 1.741(7), Si(2)–Si(3) 2.364(3), Si(2)–Si(7) 2.368(3), Si(3)–Si(4) 2.360(3), Si(5)–N(2) 1.755(7), N(1)–Si(2)–Si(3) 111.1(2), N(1)–Si(2)–Si(7) 109.2(3), Si(3)–Si(2)–Si(7) 113.05(11), N(1)–Si(2)–Si(1) 111.7(3), Si(3)–Si(2)–Si(1) 106.92(11), Si(7)–Si(2)–Si(1) 104.69(11). Bottom: view of the packing plot of **3** along *c* axis.

adopts an all *transoid* conformation with Si–Si bond lengths around 2.37 Å (Figure 2). The related compound **4** adopts a *trans*-diamino conformation (Figure 3). The central Si–Si bond is elongated in similar way as for $[(Me_3Si)_3Si]_2$.[33] For both compounds **3** and **4** the decrease in pyramidalization which is typical for silylated amines can be observed. The sums of angles around the nitrogen atoms range from 355.5° to 359.1°. Compounds **3** and **4** show interesting packing patterns within the crystal with channels along the *c* axis. The walls of the channels are formed by an alternative arrangement of CH_3 units from the diethylamino and trimethylsilyl groups.

As already mentioned, the structure of **5** (Figure 4) shows no obvious interaction between the zirconium and nitrogen atoms. The nitrogen atom is not even near the equatorial plane. The Si–Zr distance of 2.82 Å is exactly in the range of what has been found previously.[15b,18,34]

Considering the lack of interaction between Zr and the diethylamino group in **5** it is somewhat surprising to find that the amino N atom in the insertion product **5a** (Figure 5) lies in the equatorial plane of the metallocene together with the Br, C and N and Si(1) atoms.

Crystallographic data for compounds **2**, **3**, **4**, **5**, and **5a** are summarized in Table 2.

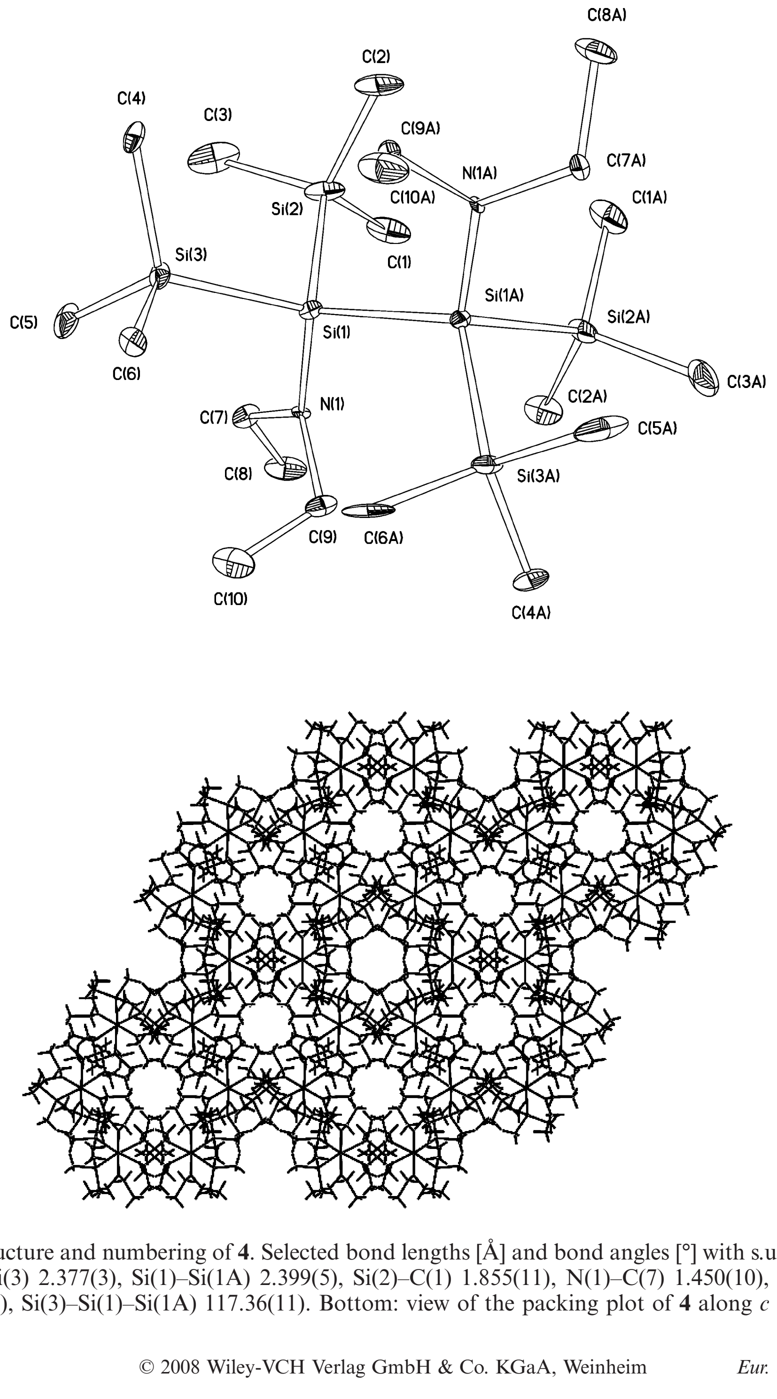

Figure 3. Top: molecular structure and numbering of **4**. Selected bond lengths [Å] and bond angles [°] with s.u. values: Si(1)–N(1) 1.736(6), Si(1)–Si(2) 2.372(4), Si(1)–Si(3) 2.377(3), Si(1)–Si(1A) 2.399(5), Si(2)–C(1) 1.855(11), N(1)–C(7) 1.450(10), Si(2)–Si(1)–Si(3) 104.62(13), Si(2)–Si(1)–Si(1A) 108.89(11), Si(3)–Si(1)–Si(1A) 117.36(11). Bottom: view of the packing plot of **4** along *c* axis.

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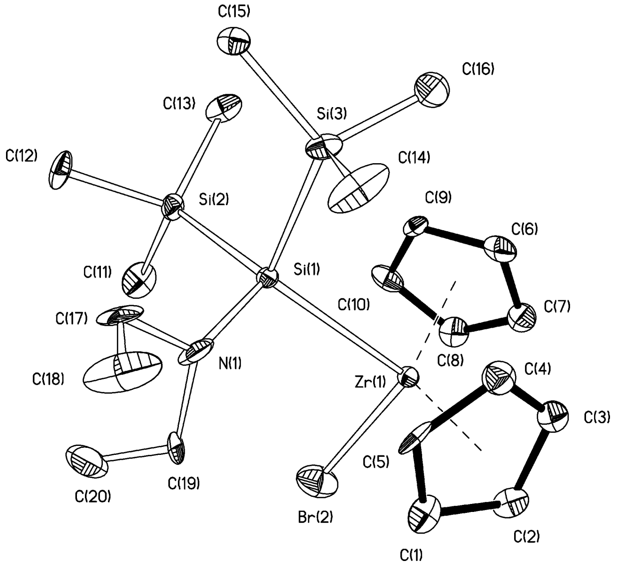

Figure 4. Molecular structure and numbering of compound **5** (two crystallographically independent molecules of **5** are in the asymmetric cell, only one is shown). Selected bond lengths [Å] and bond angles [°] with s.u. values: Zr(1)–C(4) 2.45(2), Zr(1)–Br(2) 2.528(3), Zr(1)–Si(1) 2.818(5), Si(1)–N(1) 1.765(19), Si(1)–Si(2) 2.361(8), Si(1)–Si(3) 2.392(8), N(1)–C(19) 1.43(3), C(6)–Zr(1)–Br(2) 135.6(6), C(6)–Zr(1)–Si(1) 96.9(5), C(2)–Zr(1)–Si(1) 128.7(5), Br(1)–Zr(2)–Si(4) 94.81(13), N(1)–Si(1)–Si(2) 108.1(7), Si(2)–Si(1)–Si(3) 104.3(3), N(1)–Si(1)–Zr(1) 110.8(6).

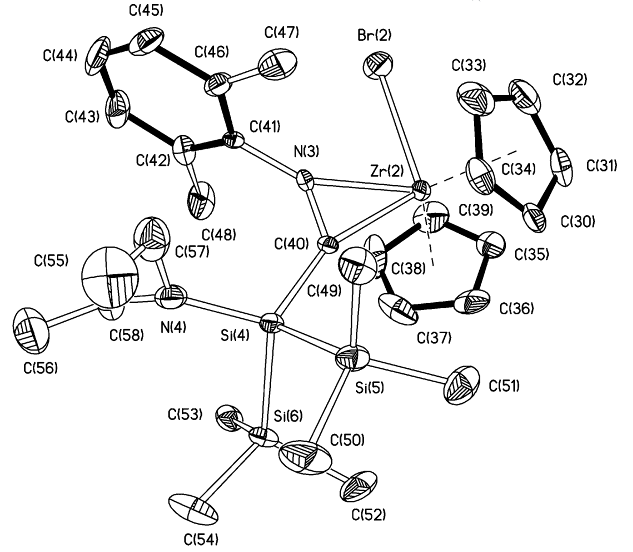

Figure 5. Molecular structure and numbering of compound **5a** (two toluene molecules and two crystallographically independent molecules of **5a** were found in the asymmetric cell, only one is shown). Selected bond lengths [Å] and bond angles [°] with s.u. values: Br(2)–Zr(2) 2.722(2), Zr(2)–N(3) 2.206(6), Zr(2)–C(40) 2.282(8), Zr(2)–C(38) 2.483(11), Si(4)–N(4) 1.773(9), Si(4)–C(40) 1.928(8), Si(4)–Si(5) 2.366(4), Si(4)–Si(6) 2.374(3), Si(5)–C(51) 1.865(11), N(3)–Zr(2)–C(36) 125.3(3), N(4)–Si(4)–C(40) 116.0(4), N(4)–Si(4)–Si(5) 109.4(3), C(40)–Si(4)–Si(5) 107.5(3), N(4)–Si(4)–Si(6) 107.4(3), Si(5)–Si(4)–Si(6) 106.67(13).

Table 2. Crystallographic data for compounds **2**, **3**, **4**, **5**, and **5a**.

	2	**3**	**4**	**5**	**5a**
Empirical formula	$C_{36}H_{88}KN_2O_4Si_6$	$C_{24}H_{68}N_2Si_8$	$C_{20}H_{56}N_2Si_6$	$C_{40}H_{76}Br_2N_2Si_6Zr_2$	$C_{72}H_{110}Br_2N_4Si_6Zr_2$
M_w	859.82	609.52	493.21	1095.83	1542.44
Temperature [K]	100(2)	200(2)	100(2)	100(2)	100(2)
Size [mm]	0.32 × 0.20 × 0.18	0.32 × 0.22 × 0.15	0.30 × 0.26 × 0.20	0.35 × 0.28 × 0.22	0.36 × 0.28 × 0.24
Crystal system	triclinic	monoclinic	hexagonal	monoclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$	$P\bar{3}c1$	$P2_1/c$	$P2_1/c$
a [Å]	9.6909(2)	16.376(3)	17.011(3)	30.279(6)	14.402(3)
b [Å]	11.952(2)	9.3652(2)	17.011(3)	10.693(2)	17.923(4)
c [Å]	13.274(3)	51.929(4)	19.032(4)	15.904(3)	30.042(6)
α [°]	89.24(3)	90	90	90	90
β [°]	70.01(3)	98.58(3)	90	94.30(3)	97.99(3)
γ [°]	69.23(3)	90	120	90	90
V [Å^3]	1341(5)	7875(3)	4770(2)	5135(2)	7679(2)
Z	1	8	6	4	4
$\rho_{calcd.}$ [g cm^{-3}]	1.065	1.288	1.030	1.418	1.3340
Absorption coefficient [mm^{-1}]	0.343	0.294	0.272	2.130	1.447
F(000)	472	2704	1644	2256	3216
θ range [°]	$2.31 < \theta < 25.00$	$0.79 < \theta < 23.00$	$1.38 < \theta < 22.50$	$0.67 < \theta < 22.50$	$1.78 < \theta < 24.00$
Reflections collected/unique	6465/4533	23053/5493	25896/2090	28216/6707	49907/12060
% completeness to θ	96.0	100	100	99.7	100
Data/restraints/parameters	4533/0/232	5493/0/327	2090/12/135	6707/30/485	12060/6/807
Goodness of fit on F^2	0.90	1.283	1.41	1.18	1.03
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.088 wR_2 = 0.207	R_1 = 0.117 wR_2 = 0.221	R_1 = 0.138 wR_2 = 0.251	R_1 = 0.135 wR_2 = 0.321	R_1 = 0.090 wR_2 = 0.193
R indices (all data)	R_1 = 0.186 wR_2 = 0.262	R_1 = 0.140 wR_2 = 0.232	R_1 = 0.139 wR_2 = 0.252	R_1 = 0.150 wR_2 = 0.329	R_1 = 0.133 wR_2 = 0.218
Largest diff. Peak/hole [e$^-$/Å^3]	0.62/–0.65	0.87/–0.40	0.97/–0.57	3.31/–1.51	2.94/–1.45

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UV Spectroscopy

Electronic spectra of compounds **1**, **4**, and especially **3** were quite unexpected. Isotetrasilane **1** exhibits the expected absorption around 220 nm for the trisilane unit. An additional shoulder is found around 250 nm which must be the result of interaction of the nitrogen with the oligosilane framework. The UV spectrum of **4** is similar but another shoulder can be observed around 270 nm. The spectrum of **3** is again similar in the region from 220 to 270 but it shows two discrete bands at 278 and 306 nm. The lowest energy absorption of the related 1,1,1,4,4,4-hexakis(trimethylsilyl)-2,2,3,3-tetramethyltetrasilane is at 253 nm. A red shift of about 50 nm is surprising and indicates a profound influence of the nitrogen onto the frontier orbitals of the oligosilane. This is in accordance with the high degree of planarization of the nitrogen atoms in the crystal structures.

Tris(trimethylsilyl)silyl derivatives of zirconocene and hafnocene chlorides have been found to absorb light around 460 (Zr) and 400 (Hf) nm.[35] The nature of these transitions has been described as ligand to metal charge transfer. The fact that compound **5** displays a maximum at 602 nm again indicates a profound influence of the nitrogen on the oligosilyl ligand. As expected the absorption maximum for the hafnium compound **6** is shifted to higher energy compared to **5** but still some 100 nm at lower energy compared to a corresponding $Si(SiMe_3)_3$ derivative.[35]

Conclusions

The synthesis of $Et_2N(Me_3Si)_2SiK$ (**2**) from $Et_2NSi(SiMe_3)_3$ (**1**) and potassium *tert*-butoxide proceeds smoothly. Despite its silylenoid character **2** behaves much like an "ordinary" silyl anion and does not show self condensation tendencies. Reactions with several electrophiles were carried out. The conversion of the magnesium derivative of **2** with zirconocene dichloride gave the expected compound **5**, which in the solid state does not exhibit direct interaction between the nitrogen of the silyl substituent and the zirconium atom.

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 glove box. Solvents were dried by means of a column for solvent purification.[36] Potassium *tert*-butoxide (*t*BuOK) was purchased exclusively from Merck and was used without further purification. All other chemicals were bought from different suppliers and were used without further purification.

^1H (300 MHz), ^{13}C (75.4 MHz), and ^{29}Si (59.3 MHz) NMR spectra were recorded on a Varian INOVA 300 spectrometer. For all samples C_6D_6 was used as solvent. To compensate for the low isotopic abundance of ^{29}Si the INEPT pulse sequence was used for the amplification of the signal.[37] Elementary analysis was carried out using a Heraeus VARIO ELEMENTAR.

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_o^2 and corrected for absorption effects with SAINT[38] and SADABS,[39] respectively. The structures were solved by direct methods and refined by full-matrix least-squares method (SHELXL97).[40] 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. Unfortunately, the obtained crystal quality of some substances was poor. This fact is reflected by quite high R and low theta values.

CCDC-661716 (for **2**), -661720 (for **3**), -661717 (for **4**), -661719 (for **5**), and -661718 (for **5a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(Diethylamino)tris(trimethylsilyl)silane (**1**),[13] bromotris(trimethylsilyl)silane,[41] dibromobis(trimethylsilyl)silane,[13,41] bis(diethylamino)bis(trimethylsilyl)silane (**9**),[13] and $MgBr_2{\cdot}Et_2O$[42] were prepared according to literature procedures.

(Diethylamino)tris(trimethylsilyl)silane (1): To a solution of tris(trimethylsilyl)silyl bromide (12.00 g, 36.6 mmol) in toluene (20 mL) diethylamine (25.0 g, ca. 35 mL; 342 mmol) was added. Immediately a white precipitation occurred. After stirring for 4 d at room temp. the solvent was removed in vacuo and to the remaining residue pentane was added. After filtration and removal of the pentane the residue was purified by sublimation to give **1** (9.83 g, 85%) as a colorless crystalline solid with spectroscopic properties in accordance with published values.[13] UV (pentane): λ_{max} (ε) = 210 (7.5×10^3), 251 nm (shoulder).

(Diethylamino)bis(trimethylsilyl)silyl Potassium (2): To a solution of **1** (150 mg, 0.50 mmol) in toluene (2 mL) 18-crown-6 (55 mg, 1.05 equiv.) and *t*BuOK (130 mg, 1.05 equiv.) were added. The solution turned immediately orange and was stirred for 2 h at room temp. until the conversion was complete (determined by ^{29}Si NMR spectroscopy). After removal of the solvent compound **2** was obtained as a yellow-green crystalline solid (250 mg, 98%) which was used without further purification. ^{29}Si NMR: δ = –15.5 (*Si*Me$_3$), –25.2 (*Si*N) ppm. ^1H NMR: δ = 3.45 (q, *J* = 7.0 Hz, 4 H, CH_2N), 3.18 (s, 24 H, CH_2O), 1.31 (t, *J* = 7.0 Hz, 6 H, CH_3CH_2), 0.61 (s, 18 H, Me_3Si) ppm. ^{13}C NMR: δ = 69.9 (CH_2O), 50.9 (CH_2N), 16.5 (CH_3CH_2), 5.1 (H_3CSi) ppm.

Alternatively the reaction can also be carried out in THF. Orange brown crystals suitable for crystal structure analysis were obtained from a solution in pentane at –30 °C. ^{29}Si NMR: δ = –15.4 (*Si*Me$_3$), –20.1 (*Si*N) ppm. ^1H NMR: δ = 3.52 (m, 8 H, CH_2O), 3.04 (q, *J* = 7.0 Hz, 4 H, CH_2N), 1.44 (m, 8 H, CH_2CH_2O), 1.06 (t, *J* = 7.0 Hz, 6 H, CH_3CH_2), 0.43 (s, 18 H, Me_3Si) ppm. ^{13}C NMR: δ = 67.7 (CH_2O), 49.6 (CH_2N), 25.5 (CH_2CH_2O), 15.1 (CH_3CH_2), 4.7 (H_3CSi) ppm.

1,4-Bis(diethylamino)-2,2,3,3-tetramethyl-1,1,4,4-tetrakis(trimethylsilyl)tetrasilane (3): The procedure for the synthesis of **4** was followed starting from 500 mg (1.563 mmol) **1**. Instead of 1,2-dibromoethane, 1,2-dichlorotetramethyldisilane (0.149 mg, 0.797 mmol) was added at –20 °C. **3** was obtained as a colorless crystalline solid (362 mg, 76%) (m.p. 116–132 °C). ^{29}Si NMR: δ = –16.0 (*Si*Me$_3$), –23.3 (*Si*N), –38.0 (*Si*Me$_2$) ppm. ^1H NMR: δ = 2.89 (q, *J* = 7.0 Hz,

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8 H, CH_2N), 0.99 (t, J = 7.0 Hz, 12 H, CH_3CH_2), 0.54 (s, 12 H, Me_2Si), 0.35 (s, 36 H, Me_3Si) ppm. ^{13}C NMR: δ = 44.9 (CH$_2$N), 15.1 (CH$_3$CH$_2$), 2.2 (H$_3$$C$Si), –0.9 (H$_3$$C$Si) ppm. $C_{24}H_{68}N_2Si_8$ (609.49): calcd. C 47.29, H 11.25, N 4.60; found C 47.20, H 11.08, N 3.61. UV (pentane): λ_{max} (ε) = 225 (2.2×10^4), 245 (shoulder), 278 (1.2×10^4), 307 nm (6.2×10^3).

1,2-Bis(diethylamino)-1,1,2,2-tetrakis(trimethylsilyl)disilane (4): Compound **2** was prepared starting from **1** (1.50 g, 4.69 mmol). After complete conversion the mixture was diluted with Et_2O (20 mL), cooled to –70 °C and 1,2-dibromoethane (485 mg, 0.55 equiv.) in Et_2O (20 mL) was added dropwise. After complete addition the mixture was stirred for 20 h at room temp. The solvent was removed and the residue treated with 30 mL of pentane. The obtained precipitate was removed by filtration and the solution was concentrated. A white crystalline product (921 mg, 80%) could be obtained by crystallization from pentane at –70 °C (m.p. 193–208 °C). ^{29}Si NMR: δ = –15.8 (SiMe$_3$), –25.1 (SiN) ppm. ^{1}H NMR: δ = 2.85 (q, J = 7.0 Hz, 8 H, CH_2N), 0.99 (t, J = 7.0 Hz, 12 H, CH_3CH$_2$), 0.38 (s, 36 H, Me_3Si) ppm. ^{13}C NMR: δ = 45.4 (CH$_2$N), 15.1 (CH$_3$CH$_2$), 2.6 (H$_3$$C$Si) ppm. $C_{20}H_{56}N_2Si_6$ (493.22): calcd. C 48.71, H 11.44, N 5.68; found C 46.83, H 11.31, N 4.80. UV (pentane): λ_{max} (ε) = 220 (2.1×10^4), 276 (6.6×10^3), 478 (5.1×10^2), 602 nm (7.4×10^2).

[Diethylaminobis(trimethylsilyl)silyl]zirconocene Bromide (5): To a solution of **2** [prepared from **1** (300 mg, 0.94 mmol), and tBuOK (106 mg, 1.01 equiv.)] $MgBr_2\cdot Et_2O$ (242 mg, 1 equiv.) was added. Zirconocene dichloride (274 mg, 1 equiv.) dissolved in a mixture of pentane (5 mL) and toluene (5 mL) was added dropwise at –20° and stirred for 16 h at room temp. **5** was obtained as a deep blue crystalline solid (293 mg, 62%). ^{29}Si NMR (δ =): 41.8 (SiN), –13.9 (SiMe$_3$) ppm. ^{1}H NMR: δ = 5.94 (s, 10 H, CpH), 3.04 (q, J = 7.0 Hz, 4 H, CH_2N), 1.06 (t, J = 7.0 Hz, 6 H, CH_3CH$_2$), 0.36 (s,18 H, Me_3Si) ppm. ^{13}C NMR: δ = 110.6 (Cp), 45.2 (CH$_2$N), 14.9 (CH$_3$CH$_2$), 3.9 (H$_3$$C$Si) ppm. $C_{20}H_{38}BrNSi_3Zr$ (547.91): calcd. C 43.84, H 6.99, N 2.56; found C 43.25, H 6.99, N 2.46. UV (pentane): λ_{max} (ε) = 223 (1.4×10^4), 245 (shoulder), 270 nm (shoulder).

Reaction of 5 with 1-Isocyano-2,6-dimethylbenzene (5a): To a solution of **5** (642 mg, 1.17 mmol) in toluene (3 mL) 1-isocyano-2,6-dimethylbenzene (154 mg, 1 equiv.) was added. The solution turned deep red and was stirred for 16 h. By cooling the solution to –70 °C pure red crystalline **5a** was obtained (438 mg, 55%). ^{29}Si NMR: δ = –16.7 (SiMe$_3$), –19.8 (SiN) ppm. ^{1}H NMR: δ = 7.12 (m, 2 H, ArH), 7.01 (m, 1 H, ArH), 5.91 (s, 10 H, CpH), 2.54 (q, J = 7.1 Hz, 4 H, CH_2N), 2.08 (s, 6 H, CH_3Ar), 0.79 (t, J = 7.1 Hz, 6 H, CH_3CH$_2$), 0.24 (s,18 H, Me_3Si) ppm. ^{13}C NMR: δ = 270.3 [CSi(SiMe$_3$)], 148.3 (NC_{Ar}), 129.2 (C_{Ar}), 129.1 (C_{Ar}), 128.7 (C_{Ar}), 128.2 (C_{Ar}), 125.5 (C_{Ar}), 109.7 (Cp), 45.4 (CH$_2$N), 20.4 (H$_3$$C$Ar), 16.0 ($CH_3CH_2$), 1.7 (H$_3$$C$Si) ppm. $C_{29}H_{47}BrN_2Si_3Zr$ (679.08): calcd. C 51.29, H 6.98, N 4.13; found C 50.60, H 7.08, N 3.80.

[(Diethylamino)bis(trimethylsilyl)silyl]hafnocene Chloride (6): Same procedure as described for **5** [150 mg, (0.47 mmol)] of **1**, 58 mg, (1.1 equiv.) tBuOK, and 178 mg (1 equiv.) hafnocene dichloride (added at room temp.). Crystallization from pentane at –70 °C yielded pure red crystalline **6** (246 mg, 89%). ^{29}Si NMR: δ = 48.7 (SiN), –10.2 (SiMe$_3$) ppm. ^{1}H NMR: δ = 5.85 (s, 10 H, CpH), 3.08 (q, J = 7.0 Hz, 4 H, CH_2N), 1.09 (t, J = 7.0 Hz, 6 H, CH_3CH$_2$), 0.41 (s, 18 H, Me_3Si) ppm. ^{13}C NMR: δ = 109.9 (Cp), 45.5 (CH$_2$N), 15.1 (CH$_3$CH$_2$), 4.1 (H$_3$$C$Si) ppm. $C_{20}H_{38}ClHfNSi_3$ (590.72): calcd. C 40.66, H 6.48, N 2.37; found C 40.83, H 6.36, N 2.18. UV (pentane): λ_{max} (ε) = 213 (1.6×10^4), 503 nm (5.5×10^2).

Reaction of 6 with 1-Isocyano-2,6-dimethylbenzene (6a): Same procedure as described for **9** using 184 mg (0.31 mmol) **6** and 41 mg (1 equiv.) 1-isocyano-2,6-dimethylbenzene. By cooling the solution to –70° pure yellow crystalline **6a** was obtained (183 mg, 81%). ^{29}Si NMR: δ = –16.6 (SiMe$_3$), –19.1 (SiN) ppm. ^{1}H NMR: δ = 7.15 (m, 1 H, ArH), 6.85 (m, 2 H, ArH), 5.82 (s, 10 H, CpH), 2.52 (q, J = 7.1 Hz, 4 H, CH_2N), 2.14 (s, 6 H, CH_3Ar), 0.78 (t, J = 7.1 Hz, 6 H, CH_3CH$_2$), 0.28 (s,18 H, Me_3Si) ppm. ^{13}C NMR: δ = 283.6 [CSi(SiMe$_3$)], 148.9 (NC_{Ar}), 129.2 (C_{Ar}), 128.7 (C_{Ar}), 125.3 (C_{Ar}), 109.1 (Cp), 45.2 (CH$_2$N), 19.8 (H$_3$$C$Ar), 15.9 ($CH_3CH_2$), 1.8 (H$_3$$C$Si) ppm. $C_{29}H_{47}ClHfN_2Si_3$ (721.90): calcd. C 48.25, H 6.56, N 3.88; found C 48.21, H 6.59, N 3.68.

[(Diethylamino)bis(trimethylsilyl)silyl]-1-hydroxy-2,2-dimethylpropane (7): Compound **2** was prepared from 250 mg of **1** (0.78 mmol). After 2 h $MgBr_2\cdot Et_2O$ (222 mg, 1.1 equiv.) was added and stirred for additional 15 min. The mixture was diluted with THF (7 mL), cooled to –70 °C and pivaldehyde (67 mg, 1 equiv.) was added. The mixture turned colorless and was warmed up to room temp., stirred for additional 16 h before it was poured onto H_2O/Et_2O. The layers were separated and the aqueous phase washed twice with diethyl ether. The combined organic layers were treated with brine and dried with Na_2SO_4 before the solvent was removed; **7** was obtained as a light yellow oil (198 mg, 76%). ^{29}Si NMR: δ = –16.8 (SiMe$_3$), –21.7 (SiN) ppm. ^{1}H NMR: δ = 3.72 (s, 1 H), 2.88 (dq, J = 7.0 Hz, 4 H, CH_2N), 1.09 (s, 9 H), 0.95 (t, J = 7.0 Hz, 6 H, CH_3CH$_2$), 0.26 (s, 18 H, Me_3Si) ppm. ^{13}C NMR: δ = 67.7 (COH), 44.4 (CH$_2$N), 32.1 (CCH$_3$), 26.1 (CCH$_3$), 15.2 (CH$_3$CH$_2$), –2.1 (H$_3$$C$Si) ppm.

1,2-Dichloro-1,1,2,2-tetrakis(trimethylsilyl)disilane (8): Compound **4** (100 mg, 0.20 mmol) was dissolved in toluene (2 mL) and $SiCl_4$ (70 mg, 2 equiv.) was added. The mixture was stirred for 18 h at room temp. then the solvent and volatile components were removed. The white residue was diluted with pentane and after centrifugation the solvent was removed again yielding a semi-crystalline colorless product (78 mg, 92%). ^{29}Si-NMR resonances are in accordance with reported values.[25] ^{1}H NMR: δ = 0.30 (s, 36 H, Me_3Si) ppm. ^{13}C NMR: δ = –0.2 (H$_3$$C$Si) ppm.

2,2-Bis(diethylamino)-1,1,1,3,3,3-hexamethyltrisilane (9): To a solution of dibromobis(trimethylsilyl)silane (1.50 g, 4.49 mmol) in toluene (10 mL) diethylamine (10 mL) was added. Immediately a white precipitate occurred and the suspension was stirred for 5 d. After removal of the volatiles in vacuo the yellow residue was treated with pentane (20 mL) and filtered. After removal of the pentane from the filtrate **9** (1.05 g, 76%) was obtained as a semi-crystalline solid. ^{29}Si NMR: δ = –3.2 (SiN), –23.1 (SiMe$_3$) ppm. ^{1}H NMR: δ = 2.93 (q, J = 7.0 Hz, 8 H, CH_2N), 1.01 (t, J = 7.0 Hz, 12 H, CH_3CH$_2$), 0.26 (s, 18 H, Me_3Si) ppm. ^{13}C NMR: δ = 41.3 (CH$_2$N), 15.2 (CH$_3$CH$_2$), 0.6 (H$_3$$C$Si) ppm.

Bis(diethylamino)(trimethylsilyl)silyl Potassium·18-Crown-6 (10): For the synthesis of **10** the procedure for **2** was followed using **9** (150 mg, 0.47 mmol), tBuOK (55 mg, 0.48 mmol, 1.03 equiv.) and 18-crown-6 (128 mg, 0.48 mmol, 1.03 equiv.). Compound **10** was obtained as a red oil (250 mg, 98%) ^{29}Si NMR: δ = 43.6 (SiN), –28.6 (SiMe$_3$) ppm. ^{1}H NMR: δ = 3.65 (m, 8 H, CH_2N), 3.21 (s, 24 H, CH_2O), 1.40 (t, J = 7.0 Hz, 12 H, CH_3CH$_2$), 0.53 (s, 9 H, Me_3Si) ppm. ^{13}C NMR: δ = 70.0 (CH$_2$O), 38.9 (CH$_2$N), 15.5 (CH$_3$CH$_2$), –2.1 (H$_3$$C$Si) ppm.

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