Bulky Phenyl Modifications of the Silanide Ligand Si(SiMe₃)₃ – **Synthesis and Reactivity**

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Dedicated to Professor Dieter Fenske on the Occasion of his 75th Birthday

Abstract. The synthesis and structural characterization of bulkier variations of the very common organometallic compound $MSi(SiMe_3)_3$, namely $MSi(SiMe_3)(SiPh_3)_2$ **3** and $MSi(SiPh_3)_3$ [M = Li (1), K (5)] are presented, which can be synthesized via a step by step exchange of SiMe₃ groups by bulkier SiPh₃ groups. This synthetic route is high selective and is performed in good yields via the silanes

Introduction

Protecting ligands and protecting groups are of fundamental interest in almost all parts of organic and inorganic chemistry, e.g. giving access to compounds that are not stable without a protecting ligand.^[1] Due to their high reactivity and availability of the precursors, anionic silanide ligands used to be ideal protecting compounds. For example the TMS group (TMS = SiMe₃) is a common protecting group for alcohols and hydroxyl groups in organic synthesis.^[2] Starting from TMS, which is sterically less demanding, a huge variety of second sphere silvlated compounds could be invented, e.g. the amide N(SiMe₃)₂,^[3] the methanides CH_n(SiMe₃)_{3-n},^[4] or the silylated silanide Si(SiMe₃)₃ (Hypersilyl, Hyp) exhibiting a triply silvlated central silicon atom.^[5] Even ligands with modifications in the outer sphere were synthesized, e.g. the mixed amide $N(SiMe_3)Dipp$ (Dipp = 2,6-diisopropylphenyl).^[6] In the 1980s, a quite simple synthetic procedure of the lithium compound LiHyp was developed by Gutekunst and Brook by the reaction of MeLi with the fully substituted silane Si(SiMe₃)₄.^[7] However, Marschner et al. found a simpler way to synthesize a potassium silanide in very high yield above 90% by mixing the silane $Si(SiMe_3)_4$ with KOtBu in THF or DME (DME = 1,2-Dimethoxy-ethane).^[8] The big advantage of this route is, that all precursors are air stable compounds. As the potassium silanide can easily react with R_3 SiCl (R = Ph, iPr, etc.),^[9] it is possible to introduce different silvl groups, like SiPh₃, Si*i*Pr₃, etc. As the cleavage of the Si-Si bond to the TMS group is strongly favored in Si(SiMe₃)₃(SiPh₃)^[10] either the classical

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Si(SiMe₃)₂(SiPh₃)₂ (2) and Si(SiMe₃)(SiPh₃)₃ (4). Additionally, the corresponding silanes $HSi(SiMe_3)(SiPh_3)_2$ (6_H) and $HSi(SiPh_3)_3$ (7_H) are obtained via the reaction of 3 and 5 with aqueous HCl, respectively. Oxidation of $6_{\rm H}$ with CCl₄ gives the chlorsilane Cl-Si(SiMe₃)(SiPh₃)₂ (6_{CI}) . The bulkiest chlorsilane Cl-Si(SiPh₃)₃ (7) is obtained by the reaction of **5** with ECl_2 (E = Sn, Pb).

MeLi or Marschner's route can lead to novel modified silanide compounds $MSi(SiMe_3)_2SiPh_3$ (M = Li, K), which were already used in our group as protecting ligands in group 14 chemistry.^[11] Herein we report on further substitution of the SiMe₃ groups in Si(SiMe₃)₃ by SiPh₃ groups, leading thus to bigger, sterically more demanding silanides.

Results and Discussion

Silanide Modification

The first higher modified silanide compound was formed by accident as a side product of approx. 20 small red crystals during the recrystallization process of freshly prepared LiSi(SiMe₃)₂(SiPh₃) (LiHyp^{Ph3}). From time to time, these red crystals could be observed and X-ray crystallography showed,



Figure 1. Molecular structure of 1_{Li} in the solid state. The atoms are presented as thermal ellipsoids with 50% probability (Li, Si) or as wire model (C, O). Hydrogen atoms are omitted for clarity. Selected bond lengths /pm and angles /º: Si12-Si1 235.71(7), Si13-Si1 235.56(7), Si1-Si11 235.77(7); Si12-Si1-Si11 103.18(3), Si13-Si1-Si12 104.01(3), Si13-Si1-Si11 104.38(3).

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that it is the fully modified silanide $Li(THF)_3(Et_2O)Si(SiPh_3)_3$ (LiHyp^{Ph9}) (1_{Li}) (Figure 1).

The compound crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell. In $\mathbf{1}_{Li}$ an ion separation is present, where the Li cation is fully coordinated by four solvent molecules. This is in contrast to the previously reported LiHyp^{Ph3}, where the lithium cation is coordinated by the silanide and three solvent molecules, leading to an overall non-charged molecule. This difference might be a consequence of the higher steric influence of the phenyl rings. Even if these crystals are formed by accident, a rational synthesis via a step by step modification of Si(SiMe₃)₄ should be possible, as outlined in Scheme 1 and discussed in the following.

$$\begin{split} &\text{Si}(\text{SiMe}_3)_n(\text{SiPh}_3)_m + \text{KO}t\text{Bu} \rightarrow \text{KSi}(\text{SiMe}_3)_{n-1}(\text{SiPh}_3)_m + \text{Me}_3\text{Si}Ot\text{Bu}\\ &\text{KSi}(\text{SiMe}_3)_{n-1}(\text{SiPh}_3)_m + \text{ClSiPh}_3 \rightarrow \text{Si}(\text{SiMe}_3)_{n-1}(\text{SiPh}_3)_{m+1} + \text{KCl} \end{split}$$

Scheme 1. General concept of the step by step modification of the Hyp ligand (n = 2, 3, 4; m = 4 - n).

Rational Synthesis of Silanides

Starting from KHyp^{Ph3}, which is available in good yield, the second modification could be achieved by the reaction with Ph₃SiCl, to give after work-up procedures small colorless plate-like single crystals of Si(SiMe₃)₂(SiPh₃)₂ (**2**), suitable for X-ray crystallography (Figure 2). **2** crystallizes in a monoclinic unit cell in space group $P2_1/n$ and is stable against air and moisture and is available in good yield of 75%. The sterically more demanding SiPh₃ groups with respect to the SiMe₃ groups lead to a distortion of the tetrahedral arrangement of the central silicon atom Si1. Thereby the Si–Si–Si angles including both silicon atoms from the SiPh₃ groups are 113.8°. Beside this, the angle including the Si atoms from the SiMe₃ groups amounts to 103.0°.



Figure 2. Molecular structure of **2** in the solid state. The atoms are presented as thermal ellipsoids with 50% probability (K, Si) or as wire model (C, O). Hydrogen atoms are omitted for clarity. Selected bond lengths /pm and angles /°: Si4–Si1 238.76(5), Si2–Si1 238.55(5), Si1–Si5 239.39(5), Si1–Si3 237.54(5); Si4–Si1–Si5 112.657(19), Si2–Si1–Si4 113.850(18), Si2–Si1–Si5 110.322(19), Si3–Si1–Si4 107.024(19), Si3–Si1–Si2 109.305(19), Si3–Si1–Si5 103.018(18).

Starting from **2** we tried a further modification by changing one of the remaining SiMe₃ groups by a SiPh₃ group. Therefore we started working on Marschner's route of preparing a potassium silanide by reaction with KO*t*Bu, which shows an ongoing reaction in monitoring NMR experiments. From the crude reaction solution, single crystals of the expected KSi(SiMe₃)(SiPh₃)₂ (**3**) (KHyp^{Ph6}) are obtained after adding the complexing reagent 18-crown-6 and layering the solution with pentane.

 $\mathbf{3}_{crown}$ crystallizes in the triclinic space group $P\bar{1}$ with one ion pair in the unit cell. Therefore, all K atoms are located on crystallographic inversion centers leading to half a K(18crown-6)⁺ cation and half a [HypPh6-K(18-crown-6)-HypPh6]⁻ anion in the asymmetric unit. Interestingly, 3 crystallizes as an ion separated dimer [K(18-crown-6)]⁺ [Hyp^{Ph6}-K(18-crown-6)-Hyp^{Ph6}]⁻ ($\mathbf{3}_{crown}$) (Figure 3). This is in contrast to the less bulky derivative K(18-crown-6)Hyp^{Ph3}, which crystallizes as a monomeric compound, where the potassium cation is coordinated to the silanide and to a crown ether molecule.^[11] The K-Si distances of the potassium cation K1 in 3crown is with 356.4 pm similar to the Si-K distance found in K(18-crown-6)Hyp^{Ph3} (356.3 pm), indicating that a similar interaction is present being mostly electrostatic in nature. Consequently, the most probable explanation of the structural differences between 3_{crown} and K(18-crown-6)Hyp^{Ph3} are packing effects in the solid state.^[12]



Figure 3.: Molecular structure of 3_{crown} in the solid state. The atoms are presented as thermal ellipsoids with 50% probability (K, Si, O) or as wire model (C). Hydrogen atoms are omitted for clarity. Selected bond lengths /pm and angles /°: K1–Si1 356.43(6), K2–O101 276.90(14), K2–O104 282.49(14), K2–O1072 280.31(15), Si1–Si2 234.38(8), Si1–Si3 235.47(8), Si1–Si4 233.51(8); Si4–Si1–Si3 106.82(3), O101–K2–O107 118.51(4), Si4–Si1–Si2 107.82(3).

Having the potassium salt **3** in hand, a further salt metathesis reaction to introduce a third SiPh₃ group is possible to get the highly phenylated silane Si(SiMe₃)(SiPh₃)₃ (**4**). Thereby compound **4** has a decreased solubility in aliphatic or aromatic solvents with respect to the lower modified derivative **2**. Single crystals suitable for X-ray measurements could only be obtained from ether, THF, or hot ethanol (Figure 4).



Figure 4. Molecular structure of **4** in the solid state. The atoms are presented as thermal ellipsoids with 50% probability (K, Si) or as wire model (C). Hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles (°): Si1–Si2 240.14(11), Si1–Si3 240.68(11), Si1–Si4 241.80(11), Si1–Si5 242.39(10); Si2–Si1–Si3 106.34(4), Si2–Si1–Si4 104.19(4), Si2–Si1–Si5 110.18(4), Si3–Si1–Si4 115.18(4), Si3–Si1–Si5 106.11(4), Si4–Si1–Si5 114.55(4).

The sterically highly demanding silane 4 crystallizes in a monoclinic crystal system in space group $P2_1/c$. Due to the steric overload at the central silicon atom, the Si-Si bond lengths in 4 are increased to an average value of 241 pm with respect to the less crowded compound 2, where average Si-Si distances of 238 pm are found. By obtaining 4 via this rational synthesis there should be only one more step to obtain the previously accidentally formed silanide [Si(SiPh₃)₃]⁻ (Hyp^{Ph9}). However, we were not able to get a crystalline product of LiHyp^{Ph9} from a reaction of **4** with MeLi because of the very low reaction speed, i.e. after two weeks, only 5% conversion could be observed in monitoring NMR experiments. However, reaction of 4 with KOtBu is possible by increasing the reaction time from a few hours up to three days. Single crystalline KHyp^{Ph9} (5) (Figure 5) could be achieved by layering the THF mother liquor with pentane.



Figure 5. Molecular structure of **5** in the solid state. The atoms are presented as thermal ellipsoids with 50% probability (K, Si) or as wire model (C, O). Hydrogens are omitted for clarity. Selected bond lengths /pm and angles /°: Si1–Si2 235.53(4), Si1–Si4 235.02(4), Si1–Si3 236.28(4); Si2–Si1–Si3 103.544(16), Si4–Si1–Si2 102.419(16), Si4–Si1–Si3 101.998(16).

In the silanide **5**, the maximum steric overload in the Hyp^{Phx} system (x = 3, 6, 9) is reached. The molecule crystallizes in a monoclinic lattice in space group $P2_1/c$. Interestingly we found a new structural motif for the cation coordination in the Hyp^{Phx} system. In all previously presented examples, the potassium cation is either attached to the central Si atom of the silanide or completely surrounded by chelating agents or solvent molecules. Within **5**, the potassium cation is now attached to the silanide at the phenyl rings and not to the central Si atom. This circumstance might be caused by the steric demand of Hyp^{Phy} and by the better interaction of the phenyl π -system with the soft Lewis acid K⁺.

Silanide Halogenation

During the modification procedure, we were able to isolate the negatively charged silvl compounds 3 and 5 in good yield. These silanides can be easily introduced in organometallic chemistry and even in cluster chemistry applying salt metathesis reactions, what is part of ongoing research in our lab. However, in some cases the introduction via a halogenated compound is also useful, as, for example, shown by Sevov and Li with the rational synthesis of the metalloid cluster $[Ge_{0}(Hyp_{3})]^{-}$ by the reaction of the Zintl phase $K_{4}Ge_{0}$ with Hyp-Cl.^[13] Before this approach, the metalloid cluster $[Ge_9(Hyp_3)]^-$ was only available by a reaction of LiHyp with a metastable emulsion of oily donor stabilized GeBr^[14] in moderate yields.^[15] Sevov's synthetic concept could be also applied to other halides, like $ClSniPr_3^{[16]}$ and smaller $ClSiR_3$ groups (R = Et, *i*Pr, *i*Bu), as used by *Fässler* et al.^[17] and even larger groups like ClHyp^{Ph3}, as introduced by our group^[18] could be used to obtain metalloid $[Ge_0R_3]^-$ clusters.

To get a full library of precursors for the Hyp^{Phx} chemistry, we tried to synthesize and characterize the Hyp^{Phx} halides. Thereby, we used the same reaction pathway previously described for the synthesis of Hyp-Cl^[19] starting from hydrolysis of the lithium or potassium salt of the silanide to give the silane HHyp^{Phx} (Scheme 2).

$$KSiR_3 + HCl(aq) \rightarrow HSiR_3 + KCl$$

 $HSiR_3 + CCl_4 \rightarrow ClSiR_3 + HCCl_3$

Scheme 2. General reaction pathway of the chlorination of silanides $(R = \text{SiMe}_3, \text{SiPh}_3)$.

The so obtained silane should be chlorinated by stirring in CCl_4 to give Cl-Hyp^{Phx} and HCCl₃, which works in the case of the non-modified Hyp-H in almost quantitative yield. Additionally, increasing the number of SiPh₃ groups in the silane leads to an increase of the melting point,^[18] i.e. crystallization of the crude silane should be possible, as well.

In case of Hyp^{Ph6}, hydrolysis and chlorination works as predicted, but an extension of the reaction time for the chlorination from one day to at least one week is necessary as indicated by daily monitoring NMR experiments. The silane HHyp^{Ph6} ($\mathbf{6}_{H}$) (see Supporting Information) and the chlorosilane ClHyp^{Ph6} ($\mathbf{6}_{Cl}$) (Figure 6) could be crystallized and structurally characterized.



Figure 6. Molecular structure of 6_{CI} in the solid state. The atoms are presented as thermal ellipsoids with 50% probability (Cl, Si) or as wire model (C). Hydrogen atoms are omitted for clarity. Selected bond lengths /pm and angles /°: Cl1–Si1 211.94(5), Si1–Si2 237.37(5), Si1–Si3 237.74(5), Si1–Si4 237.89(5); Cl1–Si1–Si2 103.41(2), Cl1–Si1–Si3 102.57(2), Cl1–Si1–Si4 102.99(2), Si2–Si1–Si3 110.86(2), Si2–Si1–Si4 113.34(2), Si3–Si1–Si4 121.04(2).



Figure 7. Molecular structure of 7_{CI} in the solid state. The atoms are presented as thermal ellipsoids with 50% probability (Cl, Si) or as wire model (C). Hydrogen atoms are omitted for clarity. Selected bond lengths /pm and angles /°: Cl1–Si1 213.24(8), Si1–Si2' 239.11(4); Cl1–Si1–Si2 102.118(17); Si2–Si1–Si2' 115.714(12).

The chlorosilane $\mathbf{6}_{Cl}$ crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The Si–Si bond lengths of 237 pm are in line with previously presented Si–Si bonds in tetrasubstituted silanes, like Si(SiMe_3)_2(SiPh_3)_2 (2). The steric influence of the bulky phenyl rings results in a shrinking of all Si–Si–Cl angles from the ideal tetrahedral angle of 109° to 102–103°, whereas all Si–Si–Si angles are widened up to 110–120°.

An equivalent reaction starting from the hydrolysis of KHyp^{Ph9} (5) was promising at first, as the silane HHyp^{Ph9} (7_H) could be isolated and characterized via NMR spectroscopy (see Supporting Information) but the subsequent chlorination reaction with CCl₄ failed. Monitoring NMR experiments showed that no reaction takes place over three weeks, as only $7_{\rm H}$ could be detected, showing a massively different reactivity with respect to the other silanes. Nevertheless, we were able to synthesize ClHyp^{Ph9} (7_{Cl}), but not via the common way: During the attempt to introduce Hyp^{Ph9} in group 14 chemistry we reacted MCl_2 (M = Sn, Pb) with KHyp^{Ph9} (5) to obtain a compound like $M(\text{Hyp}^{\text{Ph9}})_2$, the modified analogue of $M\text{Hyp}_2^{[20]}$ or at least a KCl adduct of it, like KM(Hyp^{Ph9})₂Cl, as found in similar reactions with KHyp^{Ph3.[11]} However, what we observed in both cases is the precipitation of a gray solid to give a colorless solution. From both solutions, we could isolate colorless crystals of the chlorosilane 7_{Cl} (Figure 7), which crystallizes in contrast to all other presented compounds in a highly symmetric hexagonal crystal lattice in space group $P6_3$.

This result directly shows that in case of **5** a different reaction pathway is opened, which might be due to the steric overload of this silanide ligand. Herein not only a simple metathesis reaction takes place but a redox reaction to give 7_{CI} and a gray solid, which is most probable elemental tin or lead.^[21] The reaction might proceed via two steps, where first a metathesis reaction gives Hyp^{Ph9}MCl, which then reductively eliminates 7_{CI} to give the element Sn or Pb. It has to be proven by further experiments, if this reaction can be used for the synthesis of clusters that are formed on the way to the element. Additionally, a different reaction pathway or different reaction conditions have to be found to introduce the bulkiest ligand of the presented series in group 14 chemistry.

Conclusions

We showed that further modification of the hypersilyl ligand $Si(SiMe_3)_3$ by bulkier phenyl groups is possible leading at the end to the superbulky compound $Si(SiPh_3)_3(Hyp^{Ph9})$, which can be now used in organometallic chemistry as silanide substituents, e.g. via the potassium compound $KHyp^{Ph6}$ (**3**) or via the chlorosilane Cl-Hyp^{Ph6} (**6**_{Cl}). Furthermore, we found a change in reactivity with increasing number of SiPh₃ groups in a way that the silane HHyp^{Ph9} (**7**_H) could not be chlorinated by the reaction with CCl₄ in contrast to the lower modified ClHyp^{Ph6} (**6**_{Cl}) or ClHyp^{Ph3}. However, ClHyp^{Ph9} (**7**_{Cl}) is obtained via a salt metathesis reaction of KHyp^{Ph9} (**5**) with the group 14 halides SnCl₂ and PbCl₂ implying the preference of redox chemistry with increasing number of SiPh₃ groups compared to classical salt metathesis reactions.

Experimental Section

General Considerations: All experiments were done in an inert gas atmosphere by using standard Schlenk techniques. All organic solvents were dried with sodium and purificated via distillation. All solids were stored in a glovebox in an argon atmosphere. NMR measurements were done with a Bruker DRX-250. The chemical shifts are given in ppm against external standard SiMe₄ (¹H, ¹³C, ²⁹Si). C₆D₆ and [D₈]THF were dried with 3 Å molecular sieves. Elemental analyses were performed with a varioMICROcube in the CHNS mode.

General Procedure for the Synthesis of KHyp^{Phx}: One equivalent of Si(SiMe₃)_n(SiPh₃)_m (m = 1, 2, 3; n + m = 4) was mixed with 1.05

equivalents of KOtBu. This mixture was dissolved in THF and stirred at room temperature for at least 10 h. All volatile compounds were evaporated and the yellow to orange residue was recrystallized from Et₂O, if necessary.

General Procedure for the Synthesis of Si(SiMe₃)_n(SiPh₃)_m (m = 2, 3; n + m = 4): One equivalent of KHyp^{Phx} was dissolved in THF and cooled to -78 °C. A solution of 1.05 equiv. of ClSiPh₃, dissolved in approx. 50 mL toluene was added. The mixture was allowed to warm to room temperature within 10 h, whereby the former yellow color disappeared. When the solution became completely colorless, the reaction was finished. The mixture was quenched with 100 mL of diluted aqueous HCl. The liquid phases were separated and the aqueous phase was extracted three times with 100 mL Et₂O. All organic phases were combined, dried with Na₂SO₄, and all solvents were evaporated. The remaining off-white waxy residue could be recrystallized from hot ethanol leading to single crystals of Si(SiMe₃)_n(SiPh₃)_m (m = 2, 3; n + m = 4)

Synthesis of LiSi(SiPh₃)₃ [LiHyp^{Ph9}] (1): Compound 1 was formed accidentally during the synthesis of LiHyp^{Ph3}, as described in the literature^[11] in very small amounts of approx. 20 crystals per 100 mmol LiHyp^{Ph3}, i.e. further characterization was not possible.

Synthesis of Si(SiMe₃)₂(SiPh₃)₂ (2): Following the general procedure, Si(SiMe₃)₂(SiPh₃)₂ (2) could be obtained as air and moisture stable colorless crystals from hot ethanol in yields of 21 g (75%) starting from KHyp^{Ph3} (20 g, 42 mmol). ¹H NMR (250 MHz, [D₈]THF): $\delta = 0.09$ (s, 18 H, SiMe₃), 7.23 (m, 30H SiPh₃); ¹³C{¹H} NMR (62.5 MHz, [D₈]THF): $\delta = 4.0$ (s, SiMe₃), 128.3 (s), 129.7 (s), 137.3 (s), 137.6 (s, all SiPh₃); ²⁹Si{¹H} NMR (50 MHz, [D₈]THF): $\delta = -9.2$ (s, SiMe₃), -10.0 (s, SiPh₃), -126.7 (s, Si_{central}) C₄₂H₄₈Si₅: found (calcd.): C 72.9 (72.7), H 6.87% (6.98%).

Synthesis of KSi(SiMe₃)(SiPh₃)₂ [KHyp^{Ph6}] (3): Following the general procedure, Si(SiMe₃)₂(SiPh₃)₂ (**2**, 10 g, 14.4 mmol) and KOtBu (1.7 g, 15.1 mmol) were used leading to **3** (yield 9.3 g, 13 mmol, 92%). Single crystals could be obtained by changing the solvent to toluene and adding 1 equiv. of 18-crown-6. Layering the solution with pentane resulted in single crystals of **3**_{crown}. ¹H NMR (250 MHz, C₆D₆): $\delta = -0.29$ (s, 9 H, SiMe₃), 3.59 (s, 18 H, 18-crown-6), 6.93 (m, 18 H, SiPh₃), 7.46 (m, 12 H, SiPh₃); ¹³C[¹H] NMR (62.5 MHz, C₆D₆): $\delta = 7.0$ (s, SiMe₃), 71.1 (s, 18-crown-6), 126.5 (s), 126.7 (s), 137.7 (s), 146.2 (s, all SiPh₃); ²⁹Si[¹H] NMR (50 MHz, C₆D₆): $\delta = 0.8$ (s, SiMe₃), -7.3 (s, SiPh₃), -185.8 (s, Si_{central}). C₄₅H₅₁KO₃Si₄: found (calcd.): C 67.7 (68.3), H 6.42% (5.50%).

Synthesis of Si(SiMe₃)(SiPh₃)₃ (4): Following the general procedure, KHyp^{Ph6} (**3**, 8 g, 12.1 mmol) and ClSiPh₃ (3.8 g, 13 mmol) were used leading to Si(SiMe₃)(SiPh₃)₃ (**4**) (yield 8.1 g, 9.7 mmol, 81%). X-ray suitable single crystals could be obtained via a second recrystallization step from Et₂O at 4 °C.^[22] ¹**H** NMR (250 MHz, [D₈]THF): δ = 0.13 (s, 9H SiMe₃), 7.04 (m, 36 H, SiPh₃), 7.28 (m, 9 H, SiPh₃); ¹³C{¹H} NMR (62.5 MHz, [D₈]THF): δ = 5.3 (s, SiMe₃), 128.0 (s), 129.6 (s), 137.2 (s), 138.1 (s, all SiPh₃); ²⁹Si NMR (50 MHz, [D₈]THF): δ = -8.1 (*SiMe₃*), -9.4 (*Si*Ph₃), -121.0 (*Si*_{central}). C₆₁H₆₄OSi₅: found (calcd.): C 74.9 (74.8), H 6.28% (6.39)%.

Synthesis of KSi(SiPh₃)₃ [KHyp^{Ph9}] (5): Following the general procedure, Si(SiMe₃)(SiPh₃)₃ (4, 5 g, 5.7 mmol) and KOtBu (0.7 g, 6.5 mmol) were used leading to 5 (yield 3.6 g, 4.3 mmol, 75%) Single crystals could be obtained over two weeks directly from a THF solu-

tion by layering with pentane. ¹H NMR (250 MHz, $[D_8]THF$): $\delta = 1.79$ (m, 6 H, 3THF), 3.63 (m, 6 H, 3THF), 6.75 (m, 18 H, SiPh₃), 6.92 (m, 9 H, SiPh₃), 7.17 (m, 18 H, SiPh₃); ¹³C{¹H} NMR (62.5 MHz, $[D_8]THF$): $\delta = 26.2$ (s, THF), 68.1 (s, THF), 126.2 (s), 126.5 (s), 137.5 (s), 140.0 (S, all SiPh₃). ²⁹Si{¹H} NMR (50 MHz, $[D_8]THF$): $\delta = -0.5$ (s, SiPh₃). $C_{73}H_{77}KO_3Si_4$: found (calcd.): C 75.3 (75.9), H 6.26% (6.73)%.

Synthesis of HSi(SiMe₃)(SiPh₃)₂ [HHyp^{Ph6}] (6_H): KHyp^{Ph6} (**3**, 10 g, 15,1 mmol) was dissolved in THF. The orange mixture was quenched with 100 mL of diluted aqueous HCl. The liquid phases were separated and the aqueous phase was extracted three times with 100 mL Et₂O. All organic phases were combined and dried with Na₂SO₄. Afterwards, all solvents were evaporated. The remaining residue was recrystallized from hot ethanol leading to single crystalline HSi(SiMe₃)(SiPh₃)₂ **6**_H in 77% yield (7.2 g, 11.6 mmol). ¹H NMR (250 MHz, C₆D₆): δ = 0.00 (s, 9 H, SiMe₃), 7.07 (m, 18 H, SiPh₃), 7.54 (m, 12 H, SiPh₃); ¹³C{¹H} NMR (62.5 MHz, C₆D₆): δ = 2.0 (s, SiMe₃), 128.1 (s), 129.4 (s), 136.2 (s), 136.7 (s, all SiPh₃); ²⁹Si NMR (50 MHz, C₆D₆): δ = -10.3 (decet, *Si*Me₃), -12.4 (s, *Si*Ph₃), -116.1 (d, *Si*H). EA: found (calcd.): C 74.8 (75.4), H 6.49% (6.43%).

Synthesis of ClSi(SiMe₃)(SiPh₃)₂ [ClHyp^{Ph6}] (6_{Cl}): Dissolving HHyp^{Ph6} 6_H (7 g, 11.2 mmol) in CCl₄ and stirring at room temperature for one week resulted in NMR pure ClHyp^{Ph3} (6_{Cl}) (yield 7 g, 10.8 mmol, 96%) after evaporating all volatile components, which could be recrystallized from Et₂O to get X-ray suitable single crystals. ¹H NMR (250 MHz, C₆D₆): $\delta = 0.05$ (s, 9H SiMe₃), 7.07 (m, 18 H, SiPh₃), 7.59 (m, 12 H, SiPh₃); ¹³C{¹H} NMR (62.5 MHz, C₆D₆): $\delta = 0.0$ (s, SiMe₃), 128.3 (s), 129.7 (s), 134.6 (s), 137.0 (s, all SiPh₃); ²⁹Si{1H} NMR (50 MHz, C₆D₆): $\delta = -8.5$ (s, SiMe₃), -13.5 (s, Si_{central}), -18.5 (s, SiPh₃). C₄₆H₄₇ClSi₄: found (calculated): C 71.9 (71.4), H 5.89% (6.00%).

Synthesis of CISi(SiPh₃)₃ [CIHyp^{Ph9}] (7_{Cl}): A solution of KHyp^{Ph9} (5, 1.7 g, 2 mmol) in THF was added to a solution of 190 mg (1 mmol) SnCl₂ in THF at -78 °C. The color of the solution immediately turned red. The mixture was allowed to reach room temperature over a period of 12 h. After that, a grey precipitate appeared and the color of the solution changed to light yellow. The solution was filtered and stored without further purification at -28 °C to get colorless single crystals of ClHyp^{Ph9} (7_{Cl}) (yield 600 mg, 0.7 mmol, 35%). ¹H NMR (250 MHz, [D₈]THF): δ = 7.02 (m, 18 H, SiPh₃), 7.12 (m, 18 H, SiPh₃), 7.26 (m, 18 H, SiPh₃). ¹³C{¹H} NMR (62.5 MHz, [D₈]THF): δ = 128.3 (s), 129.9 (s), 134.4 (s), 137.7 (s); ²⁹Si{¹H} NMR (50 MHz, [D₈]THF): δ = -17.2 (s, *Si*Ph₃). C₅₄H₄₅ClSi₄: found (calcd.): C 77.4 (77.0), H 5.54% (5.39%).

X-ray Crystallography: Table 1 contains the crystal data and details of the X-ray structure determination for all crystallized compounds. The data were collected at 150 K with a Bruker APEXII microsource diffractometer employing monochromated Mo- K_{α} ($\lambda = 0.71073$ Å) radiation and equipped with an Oxford Cryosystems cryostat. A semiempirical absorption correction was applied using SADABS. The structures were solved by direct methods and refined by full-matrix least-square techniques (Programs used: Olex2 program package, SHELXS and SHELXL).^[23] The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were calculated using a riding model. The coordination of the Li cation in $\mathbf{1_{Li}}$ is best described as a disorder model of 60% Li(THF)₃(Et₂O) and 40% Li(THF)₄, whereby all carbon atoms in the minor part are refined isotropically. In compound **4** and **6**_{CI}, additional solvent molecules could be identified and refined: in case of **4** one diethyl ether molecule and in case of **6**_{CI} one

Table 1. Crystal data and details of structural determinations.

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| | 1_{Li} | 2 | 3 _{crown} | 4 | 5 | 6 _{Cl} | 7 _{Cl} |
|----------------------------------------|-------------------|-------------|--------------------|--------------------------------------------------|--------------|-----------------|-----------------|
| Formula | C70H78.2LiO4Si4 | C42H48Si5 | C45H51KO3Si4 | C ₆₁ H ₆₄ OSi ₅ | C73H77KO3Si4 | C46H47ClSi4 | C54H45ClSi4 |
| Formula wt. | 1102.83 | 693.25 | 791.31 | 953.57 | 1153.80 | 747.64 | 841.71 |
| <i>T</i> /K | 150 | 150 | 150 | 150 | 150 | 150 | 150 |
| Crystal system | monoclinic | monoclinic | triclinic | monoclinic | monoclinic | monoclinic | hexagonal |
| Space group | $P2_1/c$ | $P2_1/n$ | $P\bar{1}$ | $P2_1/c$ | $P2_1/c$ | $P2_1/n$ | P63 |
| a/Å | 18.9660(10) | 10.9419(5) | 13.3724(10) | 24.4476(8) | 18.9638(3) | 19.4084(4) | 18.6937(6) |
| b /Å | 18.5491(10) | 21.5934(11) | 13.5189(11) | 10.9900(4) | 17.9510(3) | 10.1884(2) | 18.6937(6) |
| c /Å | 18.7665(19) | 16.5871(8) | 13.8914(11) | 39.6879(13) | 18.8246(3) | 21.4625(4) | 10.0792(4) |
| a /° | 90 | 90 | 117.893(2) | 90 | 90 | 90 | 90 |
| β /° | 110.811(3) | 92.1460(10) | 95.463(2) | 91.193(2) | 93.0690(10) | 104.3740(10) | 90 |
| γ /° | 90 | 90 | 93.948(2) | 90 | 90 | 90 | 120 |
| V/Å ³ | 6171.4(6) | 3916.3(3) | 2191.0(3) | 10661.0(6) | 6399.06(18) | 4111.15(14) | 3050.3(2) |
| Z | 4 | 4 | 2 | 8 | 4 | 4 | 2 |
| μ /mm ⁻¹ | 0.144 | 0.211 | 0.268 | 0.174 | 0.205 | 0.241 | 0.168 |
| $\rho / \text{g} \cdot \text{cm}^{-3}$ | 1.187 | 1.176 | 1.199 | 1.188 | 1.198 | 1.208 | 0.916 |
| Reflns. meas. | 163867 | 79251 | 24770 | 182083 | 283191 | 61340 | 114494 |
| Independent | 12685 | 9654 | 8912 | 20950 | 24327 | 12584 | 6290 |
| Reflns. | | | | | | | |
| R(int.) | 0.0630 | 0.0461 | 0.0432 | 0.0570 | 0.0460 | 0.0449 | 0.0499 |
| Goof | 1.030 | 1.030 | 1.020 | 1.130 | 1.022 | 1.044 | 1.036 |
| $R_1 (I > 2\sigma)$ | 0.0469 | 0.0332 | 0.0418 | 0.0619 | 0.0475 | 0.0413 | 0.0279 |
| wR_2 (all data) | 0.1231 | 0.0853 | 0.0911 | 0.1477 | 0.1372 | 0.1045 | 0.0736 |

toluene molecule. However, in case of 7_{CI} solvent molecules are heavily disordered, which could not be reasonably modeled, therefore SQUEEZE^[24] was used to refine the structure (void: 1009 Å³, electrons: 277, solvent: 7 THF).

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1563723 (**1**_{Li}), CCDC-1563720 (**2**), CCDC-1563718 (**3**_{crown}), CCDC-1563721 (**4**), CCDC-1563726 (**5**), CCDC-1563725, (**6**_{Cl}) and CCDC-1563722 (**7**_{Cl}) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

Supporting Information (see footnote on the first page of this article): Synthesis and molecular structure of donor free KHyp^{Ph6} and HHyp^{Ph6} and proton NMR spectra of all compounds.

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Keywords: Chlorsilane; Silanes; Silanide ligand

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