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Synthesis of Silolide Dianions via Reduction of Dichlorosiloles: Important Role of the Solvent

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Dedicated to Prof. Rainer Streubel

The reduction of 1,1-dichloro-2,5-bis(trimethylsilyl)-3,4-diphenylsilole to silolide dianion by alkali metals was investigated. As previously demonstrated, the outcome of the reaction depends strongly on the applied alkali metal, solvent, reaction conditions, and substituent pattern. We showed that lithium is a powerful reducing agent in THF or DME solvents, the reaction is

even faster than the same reaction with sodium. The X-ray structures of the corresponding dilithio and disodium silolide dianion were investigated, interestingly recrystallization of the dilithio salt results in a coordination polymer. In order to support the synthetic work DFT calculations were performed.

Introduction

The chemistry of the cyclopentadiene analog siloles is well developed as is reviewed recently.^[1] The interest in this class of compounds is due to their possible optoelectronic applications.^[2] In particular, the fabrication of OLED's is facilitated by the aggregation-induced emission exhibited by several phenyl-substituted derivatives.^[3] Siloles have low-lying LUMO, due to the hyperconjugative interaction between the exocyclic σ^* orbitals of the central silyl group and the butadienic π^* orbitals. This facilitates electron uptake, and the reaction of

1,1-diamino-2,5-bis(trimethylsilyl)silole (**1a**) with alkali metals (Li, Na, K) has even furnished a stable 2,5-carbodianion (**1b**) (Scheme 1).^[4] With a good anionic leaving group such as chlorine at silicon (**2**) the Si–Cl bond can easily be cleaved under the above circumstances, resulting in a radical intermediate, which can be even detected (with a sufficiently stabilizing bulky Si(SiMe₃)₃ substituent at Si) using only one equivalent from the reducing agent.^[5] The radical, likewise the parent silole, is a good electron acceptor, which is reduced by a second equivalent of alkali metal (M) to an anion (**3**), forming an ion pair with M⁺.^[6] In the presence of a second chlorine at Si (**4**) the procedure can be repeated, and with altogether four equivalent (at least) of reducing agents a silolide dianion (**5** with two M⁺ counteranions) can be obtained (Scheme 1).^[7] When the above-mentioned radical is unprotected, it may dimerize yielding bis-siloles, which are again good electron acceptors. Thus, starting originally from dichlorosiloles (**4**), the above-discussed reduction procedure can be repeated on the remaining Si–Cl bond bis-siloles, and in the presence of three equivalent of reducing agents (M) bis-silolide dianion (**6**) can be obtained. Indeed such dianions were already detected.^[7]

The use of substoichiometric amount of the reducing agent, e.g. the reaction between 1,1-dichloro-tetraphenylsilole and three equivalents of lithium leads to a mixture of dianion (**5c**) and bis-silolide dianion (**6c**). Selective isolation of **6c** was unsuccessful even at different reactant to alkali metal ratios.^[7c] Similar observations were made for the dibenzannulated siloles.^[7i] Although it was suspected that **5c** is formed by reduction of **6c**, no conclusive evidence for this surmise was presented.

While in the classical silole chemistry, the 2,3,4,5-tetraphenyl^[7a-c,e] and the 2,3,4,5-tetramethyl^[7d,f,g] substituent pattern was dominating and also benzannulated siloles were studied,^[7h-j] recently several reports appeared on 2,5-bis(trimethylsilyl)-3,4-diphenyl-substituted silolide anions and dianions. Having noted the planarizing effect of this π -withdrawing

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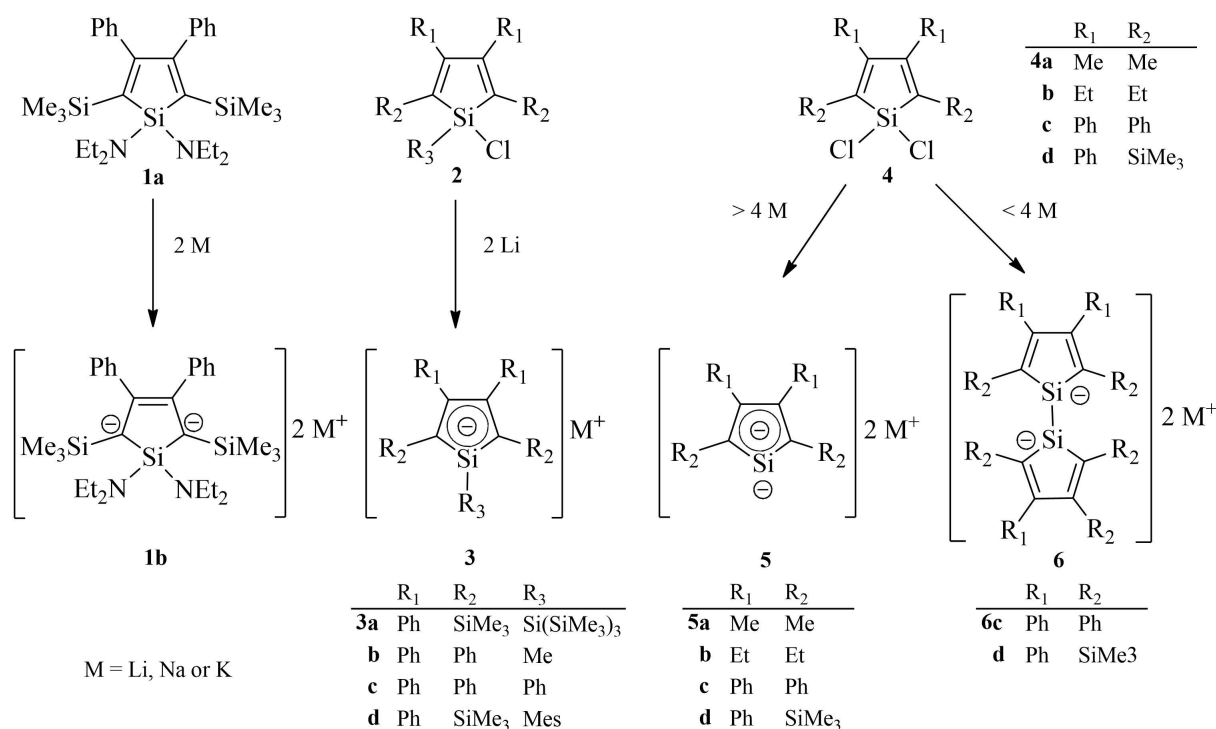
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Part of the celebratory collection for Rainer Streubel.

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Scheme 1. Some examples for silole derivatives.

substituent pattern on silolide monoanions,^[8] we have reported the first fully planar specimen **3d** (with mesityl substituent at silicon).^[6c] It is noteworthy that the electronic structure of this aromatic molecule is dominated by resonance structures with Si–C double bond character (Figure 1b and c). It has been demonstrated that the presence of the η^5 -bonded counter-cation contributes to the planarity and the aromaticity of the system,^[6c] and by changing the coordination of the K counter-cation at the analogous germolide even the degree of pyramidalization could be modified.^[9]

Also, we were the first to report the formation of the bis-silyl-substituted silolide dianion (**5d**) from 1,1-dichloro-2,5-bistrimethylsilyl-3,4-diphenylsilole (**4d**) in dioxane with an excess (5 mol) of Na and K.^[10] Unfortunately, we were not able to obtain suitable single-crystals for an X-ray diffraction study, but the formation of dianion **5d** was proven by the near stoichiometric (90% isolated yield) formation of the corresponding 1,1-diethylsilole upon quenching with EtBr.^[10] However, in

the ²⁹Si spectrum we misassigned the low-intensity signals at 44.9 ppm and 49.3 ppm to the ring silicon of Na₂**5d** and K₂**5d**, respectively. It should be noted similar values, 68.5 ppm^[7c] and 29.8 ppm^[7d] were reported for **5c** and **5a**, respectively. The situation was cleared by Müller, reporting the formation of the potassium salt of **5d** upon treatment of **4d** with a tenfold excess of potassium in THF.^[11] They found unusually low field chemical shifts (δ ²⁹Si 148–169 ppm depending on the α -silyl substituent) for the ring silicon. This unexpected value was attributed to the presence of the π -withdrawing silyl groups at the α -positions. To explain the difference from our previously reported value of 44.9 ppm,^[10] they surmised that we had obtained **6d** instead of the claimed dianion **5d** since our reported data was much closer to the value of 36.7 ppm Na₂**6d** reported for this species by Han and coworkers.^[12] The X-ray structure of the K salt of **4d** – reported by the group of Müller^[11] – has clearly shown the formation of the dianion **5d**, and exhibited a K₂**5d**·2THF polymeric bonding motif (Figure 2C), with each K being

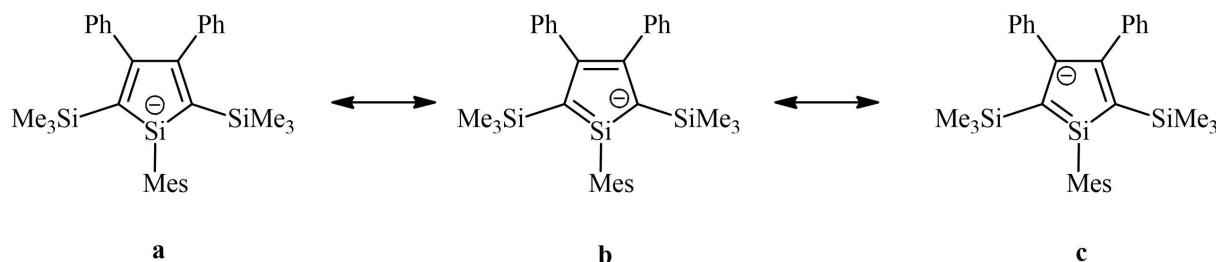


Figure 1. Mesomeric structures.

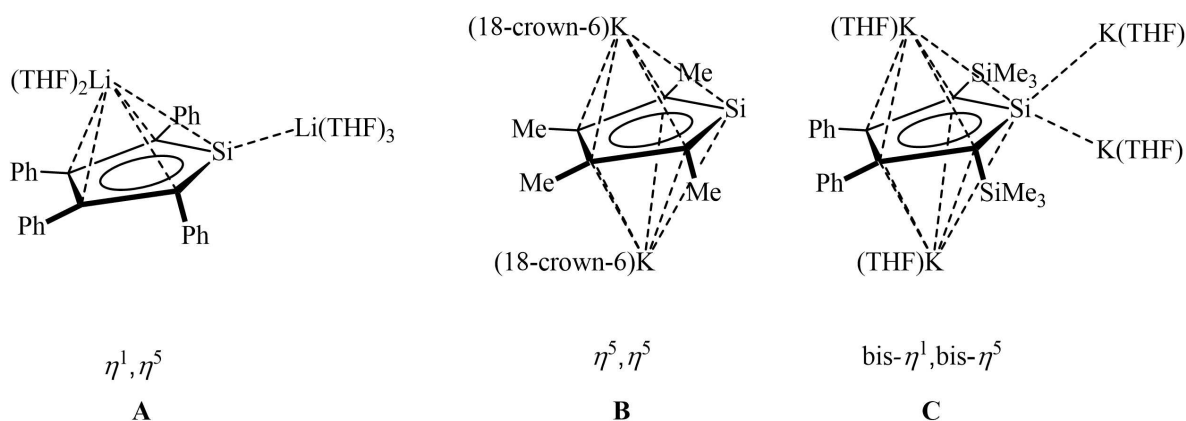


Figure 2. Reported structures of silolide dianions A,^[7e] B^[7g] and coordination polymer C.^[11]

bonded to two silolides, in η^1 and in η^5 fashion, respectively. Most interestingly, silolide (and the related germolide) dianions exhibit a silylene-type reactivity, as was shown in recent works by Müller.^[13]

Interestingly, with Li we did not observe reaction, although for the tetraphenyl-silole (4c) this light alkali metal was shown to be a sufficiently good reducing agent, yielding the corresponding dianion 5c. While for the tetraphenyl derivative the bis-silolide dianion (6c) formation was always accompanied by silolide dianion (5c), recently Han et al. reported the *exclusive* formation of the Na salt of the bis-silolide dianion 6d, from 1,1-dibromo-2,5-bis-trimethylsilyl-3,4-diphenylsilole by using 4 equivalent Na in DME.⁷ They have attributed this unexpected result to the fact that they used bromo- and not the usual chloro-silole as starting material, and have assumed that the reduction of the heavier halide is more facile than that of the chloride. It is worth to mention among the previously reported silolide crystal structures only monomeric arrangements were found (Figure 2 A and B).

Clearly, the outcome of the reduction reaction of the 1,1-dihalogeno-siloles by alkali metals seems to depend on subtle variations of the reducing agent, solvent, reaction conditions and substituent pattern, α -silyl substitution exhibiting a particularly interesting effect. In the present work we aim a comprehensive study to have a deeper understanding of the role of the reducing agents (Li, Na, K), and solvents (THF, DME, dioxane, diethyl ether) on the reaction of the chlorosiloles.

Results and Discussion

First, we decided to further investigate the formation of the silyl-substituted silolide dianion using lithium as a reducing agent for 4d. Having noted that the insoluble (presumably polymeric) product, what we obtained previously when working with Na and K in dioxane,^[10] could be dissolved in THF and DME, we have chosen these solvents for the reaction with Li. Our assumption was that with Li the reaction had started, yielding the insoluble product, which had covered the surface of the solid Li, while in the case of Na and K (which are molten

at refluxing dioxane temperature), the surface of the metal renewed continuously, allowing the reaction. Since THF or DME solubilizes the product, the above-mentioned problem should be circumvented by these solvents.

Gratifyingly, dichlorosilole (4d) reacted at room temperature with Li in THF. After one day the reaction mixture of 4d with 5 equivalent (25% excess) of Li in THF a deep red solution of lithium silolide dianion was formed at room temperature. The resulting lithium dianion ($\text{Li}_2\mathbf{5d}$) was isolated by crystallization from the THF solution at -30°C . ^{29}Si NMR measurement of the crystals was carried out in THF (in the presence of a sealed capillary containing C_6D_6) and showed a strong downfield chemical shift ($\delta^{29}\text{Si} = 108.6$ ppm, Figure S3), which, however, differs significantly from the value ($\delta^{29}\text{Si} = 148.5$ ppm) reported by Müller^[11] for the $\text{K}_2\mathbf{5d}$ salt, but even more so from our previously reported 44.9 ppm^[10] for the $\text{Na}_2\mathbf{5d}$ salt.

Since crystallization from the THF solution of $\text{Li}_2\mathbf{5d}$ yielded single crystals suitable for X-ray structure investigation (Figure 3), we could clearly identify the formation of the silolide dianion, coordinated to a $\text{Li}(\text{THF})^+$ fragment in a η^5 -fashion and

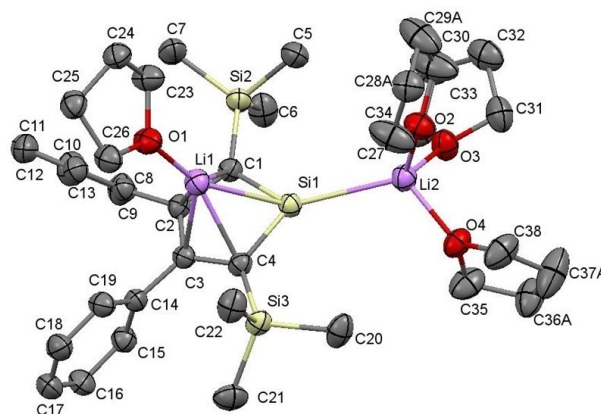


Figure 3. Molecular structure of 1,1-dilithiosilolide ($\text{Li}_2\mathbf{5d}$) with thermal ellipsoids at 50% probability. Hydrogens are omitted for clarity. Bond lengths [Å] and angles [deg]: Si(1)–C(1) 1.859(2), Si(1)–C(4) 1.854(2), C(1)–C(2) 1.439(3), C(2)–C(3) 1.409(3), C(3)–C(4) 1.448(3), Si(1)–Li(1) 2.480(4), Si(1)–Li(2) 2.712(4), C(1)–Si(1)–C(4) 89.89(9), C(1)–Si(1)–Li(2) 133.19(11), C(4)–Si(1)–Li(2) 136.91(11), Li(1)–Si(1)–Li(2) 135.99(12).

to a $\text{Li}(\text{THF})_3^+$ via η^1 -coordination. (It is worth to mention, only one broad ^7Li signal could be observed in THF solution.) A similar structure was reported for 1,1-dilithio-tetraphenylsilolide by West et al.,^[7e] however, in that case, the η^5 -Li was coordinated by two THF molecules. It is noteworthy in this respect that having compared the computed Gibbs free energies of a η^5 -Li coordinated silolide monoanion with different numbers of THF donors in a previous report,^[8] the mono- and dicoordinated assemblies exhibited similar stability. According to previous calculations of Schleyer on the parent silolide, the $\eta^5\eta^5\text{Li}$ complex was by 21.0 kcal/mol more stable than the $\eta^1\eta^5\text{Li}$ complex.^[14] We have found a similar (16.6 kcal/mol) Gibbs free energy difference between the $\eta^5\eta^5\text{Li}$ and the $\eta^1\eta^5\text{Li}$ complex of **5d** without any coordinating THF, showing that the ring substituents have a small influence on the stability of the different complexation modes. However, using explicit solvent molecules (different numbers of coordinating THF), it turns out the stability of the different complexation modes depends on the number of coordinating solvents and even the stability order can be changed (Table S1).

The C–C bond lengths in the ring of $\text{Li}_2\mathbf{5d}$ are quite equalized, as an indicative of aromaticity, and the $\text{C}\beta$ – $\text{C}\beta$ distance is somewhat shorter than $\text{C}\alpha$ – $\text{C}\beta$ (Difference of the $\text{C}\alpha$ – $\text{C}\beta$ and $\text{C}\beta$ – $\text{C}\beta$ distances: $\Delta\text{CC} = -0.035(4)$ Å) evidencing the importance of the non-classical resonance structure (Figure 1), and also showing the similarities of the π -systems of the planar monoanion and the dianion (NICS(1) **3d**: -8.2 ppm,^[8] $\text{Li}_2\mathbf{5d}$: -8.4 ppm). It is noteworthy that ΔCC in $\text{Li}_2\mathbf{5d}$ is nearly identical with the previously reported aromatic 1-lithio-1-mesitylsilolide value (**3d**; $\Delta\text{CC} = -0.038(8)$ Å),^[6c] while in 1,1-dilithio-tetraphenylsilolide ($\text{Li}_2\mathbf{5c}$) a nearly complete bond length equalization ΔCC ($-0.007(6)$ Å) was reported by West et al.^[7e] Interestingly, while the C–C distances are similar in **3d** to those in $\text{Li}_2\mathbf{5d}$ (Table S2) the Si–C bonds in $\text{Li}_2\mathbf{5d}$ (1.859(2) and 1.854(2) Å) are significantly longer than in **3d** (1.784(4) and

1.796(5) Å) and even slightly longer than those reported for $\text{Li}_2\mathbf{5c}$ (1.850(3) and 1.840(3) Å). Thus, the ring Si–C bonds of the dianions are significantly weaker than that of the monoanion, while the C–C distances (and the bond strengths) remain virtually unchanged. We should consider that the negative charge of the monoanion is placed on the p_z silicon orbital, and is then delocalized in the π -system, resulting in a significantly contributing “b” type resonance structure (Figure 1) with an excess charge at the α -carbons. The “second” negative charge of the dianion is located at an in-plane Si orbital forming the lone pair. The repulsion of the like charges at the neighboring atoms weakens the Si–C bonds, destabilizing this part of the ring. The effect is even more significant for the α -silyl-substituted system ($\text{Li}_2\mathbf{5d}$), where the silyl substitution (+I effect) further increases the negative charge at the α -carbon.

Recrystallization of $\text{Li}_2\mathbf{5d}$ from diethyl ether resulted in new measurable crystals. In this structure, the number of THF molecules has been reduced, and a coordination polymer ($\text{Li}_2\mathbf{5d_pol}$) was obtained (Figure 4). The polymeric coordination mode is similar to the earlier reported ones for germolide and stannolide dianions,^[15] however, in $\text{Li}_2\mathbf{5d_pol}$ the η^1 -coordinated Li^+ is in the plane (bond angle sum about Si is 359.5° , similarly to the 360.0° in $\text{Li}_2\mathbf{5d}$), while in the case of 1,1-lithiogermole^[15a] or 1,1-lithiostannole^[15b] the η^1 -Li is out of plane (bond angle sum 335.3° and 303.9° , respectively). The C–C bond length difference for $\text{Li}_2\mathbf{5d_pol}$ ($\Delta\text{CC} = -0.036(10)$ Å) remains almost the same as for $\text{Li}_2\mathbf{5d}$.

The formation of the second solid state structure ($\text{Li}_2\mathbf{5d_pol}$) from $\text{Li}_2\mathbf{5d}$ can be explained considering that upon dissolving $\text{Li}_2\mathbf{5d}$ in diethyl ether (Et_2O) the THF molecules at the η^1 -bonded lithium are gradually replaced by Et_2O , while the complexing THF at the η^5 -bonded lithium remains strongly bonded. (Note that THF exhibits better coordination ability than Et_2O , but the outnumbering molecules of the new solvent shift the equilibrium toward the Et_2O complexed η^1 -bonded lithium.)

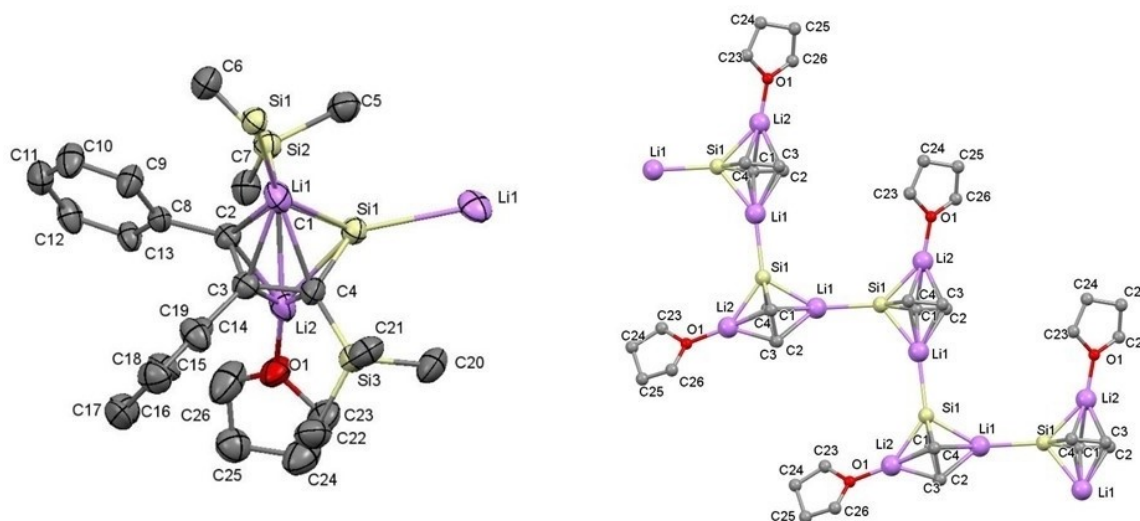


Figure 4. On the left molecular structure of 1,1-dilithiosilolide ($\text{Li}_2\mathbf{5d_pol}$) with thermal ellipsoid plots at 50% probability. Hydrogens are omitted for clarity. Bond lengths [Å] and angles [deg]: Si(1)–C(1) 1.864(7), Si(1)–C(4) 1.872(7), C(1)–C(2) 1.460(9), C(2)–C(3) 1.427(10), C(3)–C(4) 1.466(10), C(1)–Si(1)–C(4) 89.7(3), C(1)–Si(1)–Li(2) 142.8(4), C(4)–Si(1)–Li(2) 127.0(4), in-plane Si(1)–Li(1) 2.672(14). On the right stereo view of polymeric structure of $\text{Li}_2\mathbf{5d_pol}$ in solid state. All hydrogens, phenyl, and trimethylsilyl groups are omitted for clarity.

$\text{Li}_2\mathbf{5d}$ was also investigated by ^1H and ^{13}C NMR spectroscopy. ^{13}C NMR signals were interpreted using HMBC and HSQC measurements for clear identification of the ring carbon atoms (Figure 5 and Figure S1–S6). The *ipso*-C signal of the phenyl group appears at the lowest field at 149.1 ppm followed by the signal of the β and α ring carbon signals at 141.8 and 141.4 ppm.

Repeating the reaction in DME the reaction proceeded similarly (e.g. color changes) and the reaction is completed after 24 hours based on NMR measurements (Figure S7–S10).

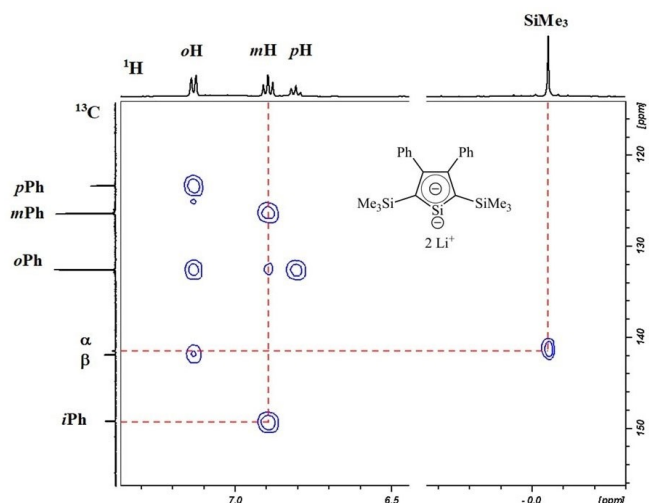
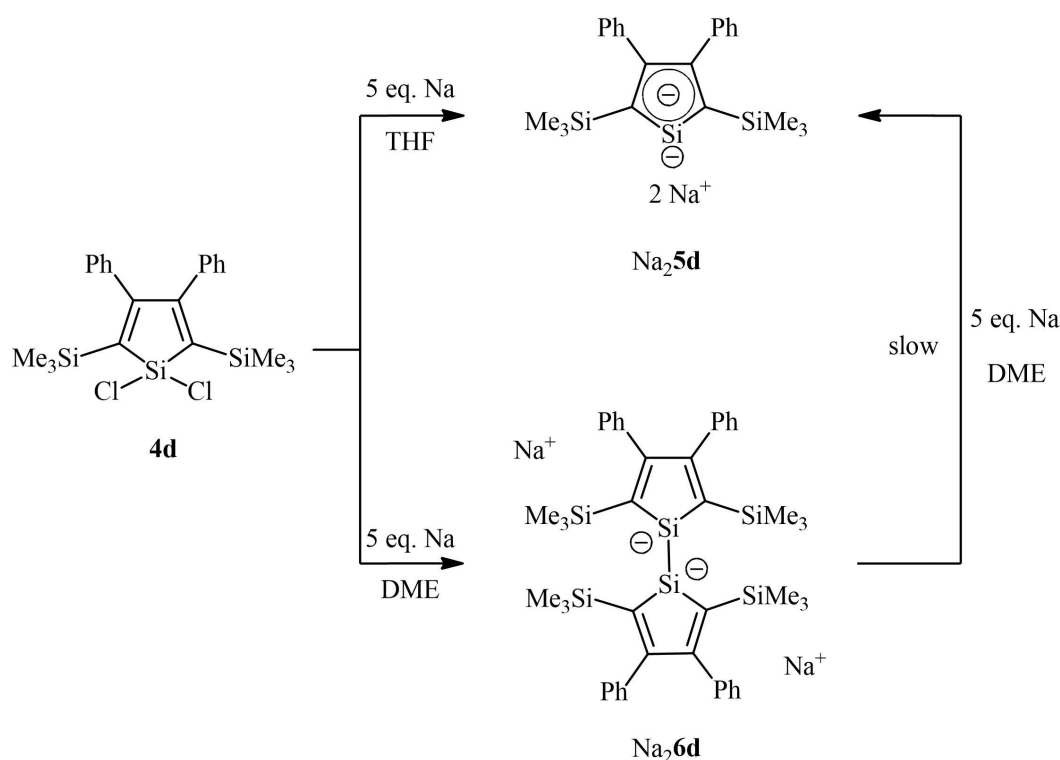


Figure 5. ^1H – ^{13}C NMR spectrum of $\text{Li}_2\mathbf{5d}$ in THF-d_8 .

In order to get deeper insight into the influence of the reducing agent the reaction was carried out in the presence of sodium as well. Reacting $\mathbf{4d}$ with 5 equivalent (25% excess) sodium in THF at room temperature resulted the 1,1-disodiodianion ($\text{Na}_2\mathbf{5d}$) (Scheme 2). The ^{29}Si NMR signal of the ring silicon appears at 123.4 ppm (Figure S13) which is between the chemical shift of the lithium derivative ($\text{Li}_2\mathbf{5d}$) and the potassium derivative ($\text{K}_2\mathbf{5d}$),^[11] however far more downfield than we previously reported (in $\text{C}_6\text{D}_6/\text{THF}$: 44.9 ppm)^[10] where the reaction was carried out in dioxane. The ^{13}C NMR chemical shifts of $\text{Na}_2\mathbf{5d}$ are nearly identical to the previously reported ones^[10] with the exception, that the previous tentative assignment of the C_α and PhC_i signals should be swapped. Based on the recent HMBC and HSQC measurements, the correct values for C_α and PhC_i are 143.5 and 149.5 ppm, respectively (Figure S14 and S15). This result is also in accordance with the above-discussed assignment for $\text{Li}_2\mathbf{5d}$ (in $\text{Li}_2\mathbf{5d}$ C_α : 141.4 and PhC_i : 149.1 ppm; and also with the assignment of Müller for the potassium derivative $\text{K}_2\mathbf{5d}$ ^[11] C_α : 145.8 and PhC_i : 149.9 ppm).

Single crystals of $\text{Na}_2\mathbf{5d}$ suitable for X-ray diffraction analysis were obtained from its THF solution. In this structure 1,1-disodiosilolide forms a dimer, where one silolide dianion is connected to three Na^+ , two of them have a η^5 -, while one has a η^1 -coordination. From the aspect of the Na^+ , there are two bonding environments: one Na^+ is coordinated by two THF molecules and one silolide ring in a η^5 -fashion, and the other one is coordinated by one THF and two different silolide rings with η^5 - and η^1 -fashion (Figure 6). Interestingly, while $\text{Li}_2\mathbf{5d}_{\text{pol}}$ has a polymeric structure, where the arrangement around the



Scheme 2. Preparation of silolide dianion ($\text{Na}_2\mathbf{5d}$) and bis-silolide dianion ($\text{Na}_2\mathbf{6d}$).

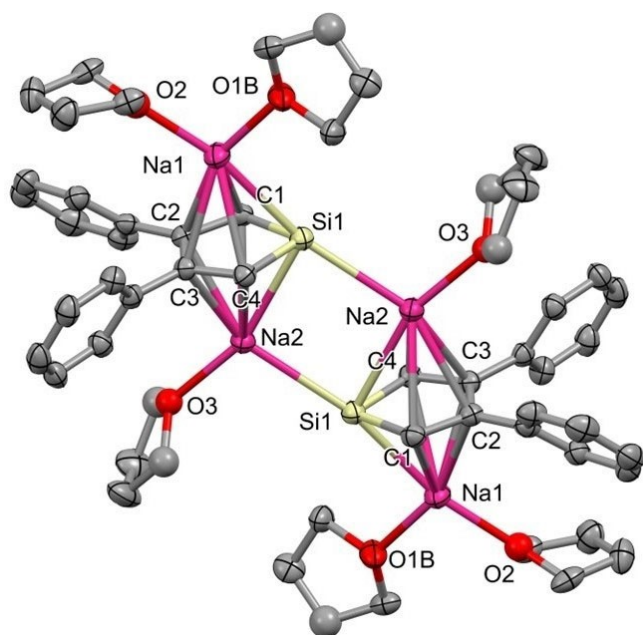


Figure 6. Molecular structure of 1,1-disodiosilolide ($\text{Na}_2.5\text{d}$) with thermal ellipsoid plots at 50% probability. Hydrogens and Me_3Si groups are omitted for clarity. Bond length [Å] and angles [deg]: Si(1)–C(1) 1.849(4), Si(1)–C(4) 1.849(4), C(1)–C(2) 1.440(5), C(2)–C(3) 1.419(5), C(3)–C(4) 1.442(5), C(1)–Si(1)–C(4) 89.85(16), C(1)–Si(1)–Na(2)^{#1} 127.87(13), C(4)–Si(1)–Na(2)^{#1} 116.65(12) (#1: Symmetry codes to generate equivalent atoms: [5_655] $-x + 1, -y, -z$).

ring silicon is nearly planar, in this dimeric structure the η^1 -coordinating Na^+ is out of the heterocycle ring plane.

The Si–C bond distances in $\text{Na}_2.5\text{d}$ are close to those found in 1,1-dilithiosilolides ($\text{Li}_2.5\text{d}$ and $\text{Li}_2.5\text{d}_{\text{pol}}$), and also to those reported by Müller and coworkers for $\text{K}_2.5\text{d}$.^[11] Also, the difference in the ring C–C bond length (ΔCC) is $-0.022(6)$ Å, which indicates aromatic character, however, the bond lengths are slightly more equalized in this case than for the Li compounds.

As we have realized that the bonding of the counteraction depends also strongly on the applied donor solvent, we have carried out the reduction of **4d** with sodium in DME (Scheme 2) using similar conditions as mentioned above. The reaction of **4d** with 5 equivalent sodium in DME for one day at room temperature resulted exclusively in the formation of 1,1'-disodio-bis-silolide ($\text{Na}_2.6\text{d}$) as previously reported by Han et al,^[12] according to ^{29}Si NMR chemical shifts for ring silicon (36.7 ppm was reported by Han et al, while we have observed the same signal at 39.4 ppm Figure S18). Since in our present experiment, we used the dichlorosilole **4d**, for the exclusive formation of the 1,1'-disodio-bis-silolide ($\text{Na}_2.6\text{d}$) the presence of the Si–Br bond is not a necessity.

Leaving the reaction mixture at room temperature for an additional 24 hours, the formation of the 1,1-disodiosilolide ($\text{Na}_2.5\text{d}$) can be observed while the 39.4 ppm signal from ($\text{Na}_2.6\text{d}$) is also present in the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum (Figure 7).

After 5 days, but otherwise under the same circumstances, all the signals belong to $\text{Na}_2.6\text{d}$ disappear, and the mixture contains only the 1,1-disodiosilolide ($\text{Na}_2.5\text{d}$) according to ^{29}Si and ^{13}C NMR measurements. Based on these results our assumption is that in DME the rate of the reduction's second step is slower than in THF, which makes the isolation of the 1,1'-disodio-bis-silolide ($\text{Na}_2.6\text{d}$) possible. In the case of the 1,1-dilithiosilolide ($\text{Li}_2.5\text{d}$), we were unable to detect the corresponding 1,1-dilithio-bis-silolide (Figure 7).

^{13}C chemical shifts of $\text{Na}_2.6\text{d}$ were assigned with the aid of HMBC and HSQC measurements (Figure S19 and S20), and the previously reported assignment of the ring carbons has been corrected. In $\text{Na}_2.6\text{d}$ the C_α signal is in fact at 129.2 ppm – instead of 147.7 ppm^[12] reported by Han et. al. – based on the HMBC measurements, using the coupling of the SiMe_3 protons for identification. While for dianions with α -trimethylsilyl groups the ^{13}C NMR signals of α carbons appear in the range of 142–146 ppm, for monoanions these signals are surprisingly up-fielded (to 103.1 ppm in **3d**^[6c]). The bis-silolide dianion $\text{Na}_2.6\text{d}$ (which is a Si–Si coupled pair of monoanions) exhibits a signal

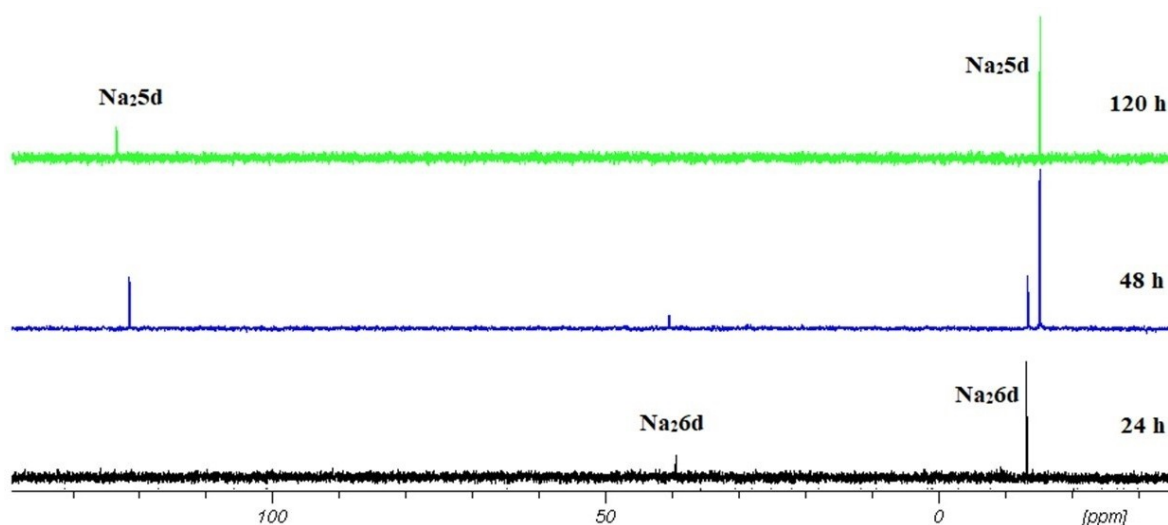


Figure 7. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of reaction mixture of **4d** with 5 eq. sodium in DME depending on the reaction time.

at 129.2 ppm. According to these results the most noticeable difference between the carbon chemical shifts of the dianions and the monoanions is the value of the $C\alpha$ signals (Scheme 3). Calculated NMR chemical shifts (bis-silolide dianion $Na_2\mathbf{6d}$: $C\alpha$: 129.6 ppm; dianion $Na_2\mathbf{5d}$ $C\alpha$: 148.5 ppm at B3LYP/6-311 + G* pcm (solvent = THF), reference $SiMe_4$) also confirm this statement (Table S3).

These signals, which are characteristic for dianion $Na_2\mathbf{6d}$ were reported in our previous publication,^[10] confirming that the main product we had obtained was indeed $Na_2\mathbf{5d}$ as we stated, and not $Na_2\mathbf{6d}$, as Müller^[11] has recently surmised.

Repeating the reaction at elevated temperature in dioxane $Na_2\mathbf{5d}$ was obtained already after 24 hours. It should be mentioned that the limited solubility of the product in dioxane forced us to use THF as solvent during the ^{29}Si and ^{13}C NMR measurements, thus in the dioxane/THF mixture the position of the signals differs somewhat from those observed in pure THF. Altogether we obtained ^{29}Si NMR signals at both 39.4 and 123.4 ppm, assignable to $Na_2\mathbf{6d}$ and $Na_2\mathbf{5d}$, respectively.

After the removal of NaCl by filtration we attempted to recrystallize the residue from THF, however single crystals for X-ray diffraction cannot be obtained. It is assumed that the dioxane-coordinated $Na_2\mathbf{5d}$ has lower solubility than the THF-coordinated $Na_2\mathbf{5d}$, due to the possible polymeric chain formation, which is specific for the dioxane-coordinated organometallic compounds.^[16] It seems in this case always the dioxane coordinated precipitate forms independently from the solvent used for recrystallization, and consequently only poor-quality crystals form.

Conclusions

In conclusion, we have demonstrated that besides the heavier alkali metals such as sodium or potassium, $\mathbf{4d}$ dichlorosilole can react with lithium in THF even at room temperature giving the corresponding dilithosilolide and 1,1-disilolide. It is worth to highlight the importance of the solvent, the products do not

solve in 1,4-dioxane, blocking the surface of the alkali metal, while in THF no solubility problem occurs, after one day the corresponding silolide salt ($Li_2\mathbf{5d}$, $Na_2\mathbf{5d}$) formed. Repeating the reaction in DME, the outcome is similar in the case of lithium, but the reaction with sodium is slower, after one day only the $Na_2\mathbf{6d}$ can be detected in the reaction mixture and the reaction is complete only after 5 days. Crystals growing from THF were measured by single crystal X-ray diffraction, $Li_2\mathbf{5d}$ crystallized in monomeric form, while $Na_2\mathbf{5d}$ is forming dimers in the crystal lattice. Recrystallization of $Li_2\mathbf{5d}$ in diethyl ether results in a coordination polymer.

Experimental Section

General procedure: All reactions were performed in oven-dried glassware under dried nitrogen or argon using standard Schlenk techniques. Solvents were dried according to well-known procedures (THF, THF- d_6 , diethyl ether, dioxane, DME, and C_6D_6 over sodium/benzophenone, hexane over $LiAlH_4$) and distilled freshly before use. Solids were dried in vacuum. 1.6 M *n*-butyl lithium solution in hexane from Merck Ltd. was used directly. All NMR spectra were recorded at 298 K on a Bruker Avance 300 and a Bruker DRX-500 spectrometers using benzene- d_6 solvent as external lock and TMS (for 1H , ^{13}C , ^{29}Si) and 1 M LiCl (for 7Li) as external standards. NMR measurements were carried out in THF- d_6 or in THF or DME in the presence of a sealed capillary containing C_6D_6 . 1H - ^{13}C HMBC, HSQC 2D experiments, and DEPT measurements were carried out to interpret the signals of the phenyl- and silole-rings. 1,1-Dichloro-3,4-diphenyl-2,5-bis(trimethylsilyl)-1-silacyclopentadiene ($\mathbf{4d}$) was prepared according to Tamao's produce.^[17] The results of elemental analysis for all dianions were not satisfactory, due to the high air sensitivity of the samples and to the variable amounts of THF.

Suitable crystals of $Li_2\mathbf{5d}$, $Li_2\mathbf{5d}_{pol}$, and $Na_2\mathbf{5d}$ were mounted on a loop. Intensity data were collected on a R-RAXIS-RAPID diffractometer using monochromator, Mo-K α radiation, $\lambda = 0.71075 \text{ \AA}$ at 103(2) K for $Li_2\mathbf{5d}$ and $Li_2\mathbf{5d}_{pol}$, respectively, and using monochromator, Cu-K α , $\lambda = 1.54187 \text{ \AA}$ at 103(2) K for $Na_2\mathbf{5d}$. Crystal Clear^[18] (developed by Rigaku Company) software was used for data collection and refinement. Numerical absorption corrections^[19]

Silolide dianions					Silolide anions		
M	$\delta C\alpha$	$\delta C\beta$	$\delta^{29}Si(\text{ring})$		$Na_2\mathbf{6d}$	$\mathbf{3d}^{[6c]}$	
$Li_2\mathbf{5d}$	Li	141.4	141.8	108.6	$\delta C\alpha$	128.8	
$Na_2\mathbf{5d}$	Na	143.5	140.5	123.4	$\delta C\beta$	140.9	
$K_2\mathbf{5d}^{[11]}$	K	145.8	140.5	148.5	$\delta^{29}Si(\text{ring})$	40.5	
						103.1	
						135.0	
						65.7	

Scheme 3. Ring carbon ^{13}C and ring silicon ^{29}Si NMR signals (ppm) of 2,5-trimethylsilyl silolide mono- and dianions.

were applied to the data. The structures were solved by direct methods. Anisotropic full-matrix least-squares refinements were performed on F^2 for all non-hydrogen atoms. Hydrogen atoms bonded to C atoms were placed in calculated positions and refined in a riding-model approximation. The computer programs used for the structure solution, refinement, and analysis of the structures were Shelx,^[20,21] Sir2014,^[22] Platon,^[23] Olex2^[24] and Wingx^[25]. The solid-state structure of Li₂5d and Na₂5d contain disordered THF molecules, which were also modeled. Program Mercury^[26] was used for the graphical representation. The crystal data, data collection, and refinement parameters are summarized in Table S4 in the Supporting Information.

Deposition Numbers 1561389 (for Li₂5d), 1561390 (for Li₂5d_pol), and 2261806 (for Na₂5d) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Computations: Quantum chemical calculations were carried out with the Gaussian09^[27] package at the M06-2X/def2-DZVP level of theory. Silolide dianions were always (unless otherwise stated) real minima on the potential energy surface. NMR chemical shifts and NICS(1) values have been calculated at B3LYP/6-311+G* level of theory. For the NICS(1) calculations of the η^5 -Li complexes the ghost atoms were placed at the opposite side of the ring. For the visualization of the structures the Molden program^[28] was used.

1,1-Dilithio-3,4-diphenyl-2,5-bis(trimethylsilyl)-1-silacyclopentadien (Li₂5d). 500 mg (1.12 mmol) 4d dissolved in 10 mL THF was added to 39 mg granulated lithium (5.60 mmol). The mixture was stirred for one day at room temperature while the color slowly turned to deep red-brown. The solution was filtrated and the filtrate was concentrated by evaporation. The pure product was obtained by recrystallization from THF at -30°C as pale-yellow crystals. Yield: 624 mg (82%). ¹H NMR (500.13 MHz, THF-d₈): $\delta = -0.05$ (s, 18H, SiMe₃), 6.78–6.83 (m, 2H, PhpH), 6.87–6.92 (m, 4H, PhmH), 7.11–7.16 (m, 4H, PhoH). ¹³C{¹H} NMR (125.77 MHz, THF-d₈): $\delta = 5.3$ (SiMe₃), 123.3 (pPh), 126.4 (mPh), 132.5 (oPh), 141.4 (C_α), 141.8 (C_β), 149.1 (PhC_γ). ²⁹Si{¹H} NMR (99.37 MHz, THF): $\delta = 108.6$ (Si-ring), -13.1 (SiMe₃). ⁷Li NMR (194.37 MHz, THF): $\delta = -1.32$.

Investigation of the reaction of 4d with lithium in DME. 1,1-Dilithio-3,4-diphenyl-2,5-bis(trimethylsilyl)-1-silacyclopentadien (Li₂5d). 174 mg (0.39 mmol) 4d dissolved in 5 mL DME was added to 14 mg granulated lithium (1.95 mmol). The mixture was stirred for one day at room temperature while the color slowly turned to deep red-brown. The solution was filtrated and the filtrate was concentrated by evaporation. This solution was investigated by NMR spectroscopy. ¹H NMR (500.13 MHz, THF-d₈): $\delta = 0.51$ (s, 18H, SiMe₃), 7.35–7.40 (m, 2H, PhpH), 7.43–7.48 (m, 4H, PhmH), 7.75–7.79 (m, 4H, PhoH). ¹³C{¹H} NMR (125.77 MHz, THF-d₈): $\delta = 4.9$ (SiMe₃), 123.3 (pPh), 126.1 (mPh), 132.3 (oPh), 141.1 (C_α), 142.8 (C_β), 147.8 (PhC_γ). ²⁹Si{¹H} NMR (99.37 MHz, THF): $\delta = 113.1$ (Si-ring), -12.7 (SiMe₃). ⁷Li NMR (194.37 MHz, THF): $\delta = -1.44$.

1,1-Disodio-3,4-diphenyl-2,5-bis(trimethylsilyl)-1-silacyclopentadien (Na₂5d). 500 mg (1.12 mmol) 4d dissolved in 10 mL THF was added to 129 mg sodium (5.60 mmol). The mixture was stirred for one day at room temperature while the color slowly turned to deep red-brown. The solution was filtrated, and the filtrate was concentrated under reduced vacuum. The pure product was obtained by recrystallization from THF at -30°C as yellow crystals. Yield: 537 mg (75%). ¹H NMR (500.13 MHz, THF): $\delta = 0.20$ (s, 18H, SiMe₃), 6.88–6.94 (m, 2H, PhpH), 7.01–7.07 (m, 4H, PhmH), 7.14–7.19 (m, 4H, PhoH). ¹³C{¹H} NMR (125.77 MHz, THF): $\delta = 5.5$ (SiMe₃), 121.5 (pPh), 125.7 (mPh), 131.4 (oPh), 140.5 (C_β), 143.5 (C_α), 149.5 (PhC_γ). ²⁹Si{¹H} NMR (99.36 MHz, THF): $\delta = 123.4$ (Si-ring), -15.2 (SiMe₃).

Investigation of the reaction of 4d with sodium in DME. 1,1'-Disodio-1,1'-bis(3,4-diphenyl-1-(2,4,6-trimethylphenyl)-2,5-bis(trimethylsilyl)-1-silacyclopentadien (Na₂6d). 500 mg (1.12 mmol) 4d was dissolved in 10 mL DME and 129 mg sodium (5.60 mmol) was added to the solution. The mixture was stirred for one day at room temperature while the color slowly turned to deep red. The solution was filtrated, and the residue was concentrated by evaporation. The product was an orange powder, which was studied by NMR spectroscopy without further purification.

¹H NMR (DME): $\delta = -0.22$ (s, 18H, SiMe₃), 6.51–6.57 (m, 2H, PhpH), 6.61–6.66 (m, 4H, PhmH), 6.83–6.86 (d, 4H, PhoH). ¹³C{¹H} NMR (DME): $\delta = 5.1$ (SiMe₃), 122.1 (pPh), 125.6 (mPh), 129.2 (C_α), 132.3 (oPh), 141.7 (C_β), 150.4 (PhC_γ). ²⁹Si{¹H} NMR (DME): $\delta = 39.4$ (Si-ring), -13.2 (SiMe₃).

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: alkali metals · coordination modes · silolides · solvent effects · structure elucidation

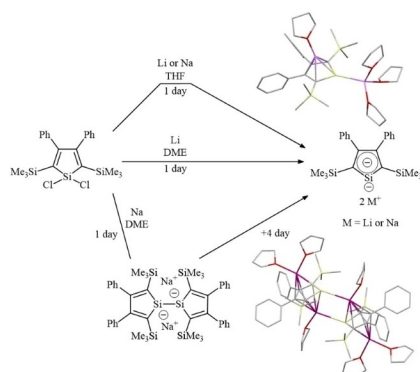
- [1] S. Santra, *ChemistrySelect* **2020**, *5*, 9034.
- [2] a) K. Tamao, M. Uchida, T. Izumizawa, K. Furukawa, S. Yamaguchi, *J. Am. Chem. Soc.* **1996**, *118*, 11974; b) S. Yamaguchi, K. Tamao, *J. Chem. Soc. Dalton Trans.* **1998**, 3693.
- [3] J. Liu, J. W. Y. Lam, B. Z. Tang, *J. Inorg. Organomet. Polym.* **2009**, *19*, 249.
- [4] Z. Han, J. Li, H. Hu, J. Zhang, J. C. Cui, *Inorg. Chem.* **2014**, *53*, 5890.
- [5] C. R. W. Reinhold, M. Schmidtman, B. Tumanskii, T. Müller, *Chem. Eur. J.* **2021**, *27*, 12063.
- [6] a) H. Sohn, D. R. Powell, R. West, J.-H. Hong, W.-C. Joo, *Organometallics* **1997**, *16*, 2770; b) H. Sohn, *J. Organomet. Chem.* **2004**, *689*, 134; c) Cs. Fekete, I. Kovács, L. Nyulászi, T. Holczbauer, *Chem. Commun.* **2017**, *53*, 11064.
- [7] a) W.-C. Joo, Y.-C. Park, S.-K. Kang, J.-H. Hong, *Bull. Korean Chem. Soc.* **1987**, *8*, 270; b) W.-C. Joo, J.-H. Hong, S.-B. Choi, H.-E. Son, *J. Organomet. Chem.* **1990**, *391*, 27; c) J.-H. Hong, P. Boudjouk, S. Castellino, *Organometallics* **1994**, *13*, 3387; d) U. Bankwitz, H. Sohn, D. R. Powell, R. West, *J. Organomet. Chem.* **1995**, *499*, C7; e) R. West, H. Sohn, U. Bankwitz, J. Calabrese, Y. Apeloig, T. Mueller, *J. Am. Chem. Soc.* **1995**, *117*, 11608; f) W. Freeman, T. D. Tilley, L. M. Liable-Sands, A. L. Rheingold, *J. Am. Chem. Soc.* **1996**, *118*, 10457; g) W. P. Freeman, T. D. Tilley, G. P. A. Yap, A. L. Rheingold, *Angew. Chem. Int. Ed.* **1996**, *35*, 882; h) S.-B. Choi, P. Boudjouk, P. Wei, *J. Am. Chem. Soc.* **1998**, *120*, 5814; i) S.-B. Choi, P. Boudjouk, *Tetrahedron Lett.* **2000**, *41*, 6685; j) Y. Liu, T. C. Stringfellow, D. Ballweg, I. A. Guzei, R. West, *J. Am. Chem. Soc.* **2002**, *124*, 49; k) J.-H. Hong, *Molecules* **2011**, *16*, 8033.

- [8] Cs. Fekete, I. Kovács, L. Könczöl, Z. Benkő, L. Nyulászi, *Struct. Chem.* **2014**, *25*, 377.
- [9] Z. Dong, M. Schmidtman, T. Müller, *Chem. Eur. J.* **2019**, *25*, 10858.
- [10] Cs. Fekete, I. Kovács, L. Nyulászi, *Phosphorus Sulfur Silicon Relat. Elem.* **2014**, *189*, 1076.
- [11] Z. Dong, C. R. W. Reinhold, M. Schmidtman, T. Müller, *Organometallics* **2018**, *37*, 4736.
- [12] Z. Han, K. Xie, X. Ma, X. Lu, *Phosphorus Sulfur Silicon Relat. Elem.* **2018**, *193*, 488.
- [13] a) Z. Dong, L. Albers, T. Müller, *Acc. Chem. Res.* **2020**, *53*, 532; b) L. Albers, P. Tholen, M. Schmidtman, T. Müller, *Chem. Sci.* **2020**, *11*, 2982; c) Z. Dong, J. M. Winkler, M. Schmidtman, T. Müller, *Chem. Sci.* **2021**, *12*, 6287.
- [14] a) B. Goldfuss, P. R. Schleyer, *Organometallics* **1995**, *14*, 1553. B. Goldfuss, P. R. Schleyer, F. Hampel, *Organometallics* **1996**, *15*, 1755.
- [15] a) R. West, H. Sohn, D. R. Powell, T. Müller, Y. Apeloig, *Angew. Chem. Int. Ed.* **1996**, *35*, 1002; b) M. Saito, K. Kuwabara, C. Kambayashi, M. Yoshioka, K. Ishimura, S. Nagase, *Chem. Lett.* **2010**, *39*, 700.
- [16] E. Kharhakhaneei, M. H. Zebrajadian, M. Shamshipur, *J. Inclusion Phenom. Macrocyclic Chem.* **2001**, *40*, 309.
- [17] S. Yamaguchi, R. Z. Jin, K. Tamao, *Organometallics* **1997**, *16*, 2230.
- [18] CrystalClear SM 1.4.0 Rigaku/MSI Inc., **2008**.
- [19] NUMABS: Higashi, T. (1998), rev. 2002 (Rigaku/MSI Inc.).
- [20] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112.
- [21] G. M. Sheldrick, *Acta Crystallogr.* **2015**, *C71*, 3.
- [22] M. C. Burla, R. Caliandro, B. Carrozzini, G. L. Cascarano, C. Cuocci, C. Giacovazzo, M. Mallamo, A. Mazzzone, G. Polidori, *J. Appl. Crystallogr.* **2015**, *48*, 306.
- [23] A. L. Spek, *Acta Crystallogr.* **2009**, *D65*, 148.
- [24] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339.
- [25] L. J. Farrugia, *J. Appl. Crystallogr.* **2012**, *45*, 849.
- [26] C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler, J. van de Streek, *J. Appl. Crystallogr.* **2006**, *39*, 453.
- [27] Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, **2013**.
- [28] G. Schaftenaar, J. H. Noordik, *J. Comput.-Aided Mol. Des.* (2000) *14*, 123.

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RESEARCH ARTICLE

The reduction of 1,1-dichloro-2,5-bistrimethylsilyl-3,4-diphenylsilole to the corresponding silolide dianion was investigated in the presence of lithium and sodium in different solvents. The products were characterized by various NMR techniques and single crystal X-ray diffraction. The applied solvents have crucial impact on the reaction.



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Synthesis of Silolide Dianions via Reduction of Dichlorosiloles: Important Role of the Solvent

