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ARTICLE

Making and Breaking Si–Si Bonds under Mechanochemical Conditions

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Mechanochemistry offers a sustainable alternative to solution-based synthesis, yet its potential in main-group chemistry remains largely untapped. Here we demonstrate that both the formation and cleavage of Si–Si bonds can be efficiently achieved under mechanochemical conditions. Solvent-free Wurtz-type couplings enable rapid access to disilanes, higher silanes, and cyclic silicon frameworks, while controlled ball-milling with alkali metal bases allows the quantitative generation of silanide and disilanide species. These reactive intermediates undergo clean and selective derivatization with a range of electrophiles, frequently affording higher yields than reported solution-phase protocols. The methodology is operationally simple, scalable, and enables multistep transformations without intermediate workup. This work establishes mechanochemistry as a powerful platform for silicon–silicon bond manipulation and highlights its potential for advancing sustainable main-group synthesis.

Introduction

As the world faces the urgent challenge of climate change, the focus on sustainability has never been more relevant. Every industry, from manufacturing to agriculture, is being examined for its environmental impact. In this context, the chemical industry, which supplies key raw materials for countless products, faces a unique challenge: it must produce the chemicals it needs while minimizing its carbon footprint.

At the heart of this challenge is the concept of the circular economy - a system that aims to reduce waste, keep products and materials in use and regenerate natural systems. Within this framework, reducing or perhaps even completely eliminating the necessity for carbon-based solvents is an effective tool for reducing global greenhouse gas emissions and improving the sustainability of industrial processes.

For this global challenge, mechanochemistry can be a game changer. Usually, mechanochemistry refers to a chemical reaction that is induced by the direct absorption of mechanical energy. It is becoming more intensely studied partly because it can promote reactions between solids quickly and quantitatively. Moreover, its main advantage lies in the ability to operate with either no added solvent or only nominal solvent amounts.¹

More generally, the activation of zero-valent metals for reductive coupling reactions has a long history in synthetic chemistry employing sodium² or lithium metal.³ In these

systems, the efficiency of reductive coupling strongly depends on the activation state of the metal surface. Consequently, a variety of approaches including ultrasound irradiation and, more recently, mechanochemical ball milling have been explored to enhance the reactivity of elemental metals and facilitate electron-transfer processes.⁴

Based on these advantages, mechanochemical approaches in organic synthesis have received increased interest because of their wide applications in green methodologies. Ball milling has been fruitfully utilized in the synthesis of various (elemental) organic scaffolds, including common drugs or drug candidates. However, this type of chemistry has so far received limited attention in the context of main-group elements. For example, to the best of our knowledge, only five reports on group 14 compounds and six reports on group 15 compounds exist.⁵ Furthermore, for Si–C formation only carbon-nucleophiles like R–MgX,⁶ R–Li⁷ or R–Na⁸ with hydro- or chlorosilanes as electrophiles have been reported, and no Si–Si formation has been described. Nevertheless, studies from the 1980s demonstrated that ultrasonication can positively influence Wurtz-type reductive coupling reactions of chlorosilanes, highlighting the beneficial role of alternative mechanical energy input for Si–Si bond formation.⁹

Thus, the aim of this work is to apply mechanochemistry to the synthesis of polysilanes that have previously been prepared using conventional solution-based approaches. Our research institution can be regarded as a leading research facility in this particular field. Consequently, we want to test this new methodology for a variety of standard built-up reactions to silicon frameworks. A representative example is shown in Scheme 1, which also highlights why these molecules—despite being ideal candidates for a wide range of applications (e.g., pharmaceutical drugs, consumer materials, structural materials, and electronic devices)¹⁰—have not yet been

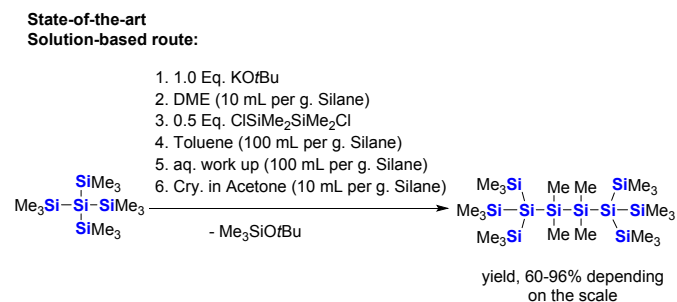
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implemented. As pointed out below, the tedious, multi-step, low yield and solvent-intensive synthesis of these derivatives is the major bottleneck of the compound class. Moreover, the conventional routes towards polysilanes typically require large amounts of dry, oxygen-free, and often expensive solvents such as dimethoxyethane (DME) or toluene, in combination with highly reactive alkali metals or strong bases. These conditions not only impose practical and economic limitations, but also generate significant solvent waste and complicate scalability. Finally, as shown in Scheme 1, the yield can vary significantly depending on the scale of the reaction.^{11,12}



Scheme 1: State-of-the-art synthesis of 1,1,4,4-tetrakis(trimethylsilyl)-cyclohexasilane as a representative building block for silicon frameworks.

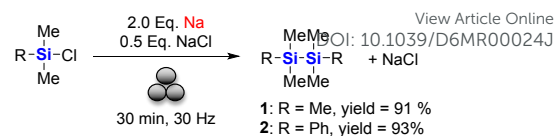
Here mechanochemistry offers an attractive alternative by enabling direct solid-state activation of silicon reagents through the application of mechanical force, thereby minimizing or completely eliminating the need for bulk solvents.

Results and Discussion

Mechanochemical Si-Si bond formation by Wurtz-type coupling

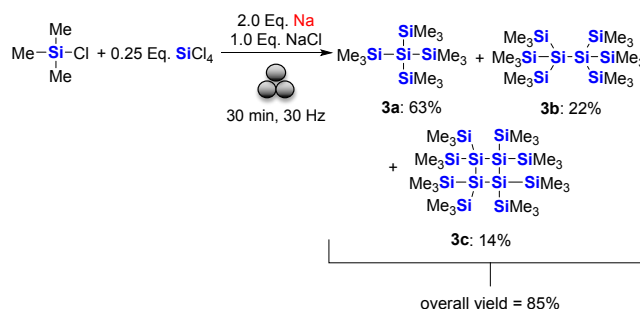
First, we evaluated the formation of Si-Si bonds via Wurtz-type couplings. Mechanochemical activation proved to be a highly effective strategy for the formation of Si-Si bonds. Under solvent-free ball-milling conditions using sodium in the presence of sodium chloride as a grinding additive, couplings of chlorosilanes were performed. As shown in Scheme 2 and detailed in the Experimental Section (see *Supporting Information*), simple disilanes such as hexamethyldisilane (**1**) and diphenyltetramethyldisilane (**2**) were obtained in excellent yields (up to 93%) after only 30 minutes of milling at 30 Hz. In contrast to the literature, where aqueous workups are commonly employed for the synthesis of polysilanes, our mechanochemical protocol requires no aqueous workup and instead relies solely on extraction with *n*-pentane.

Their clean formation under these conditions was confirmed by ¹H NMR spectroscopy. Moreover, the characteristic ²⁹Si NMR resonances were observed in the expected chemical shift range (ca. -20 ppm), indicating efficient reductive coupling without detectable over-reduction or decomposition.



Scheme 2: Synthesis of disilane **1** and **2**.

Importantly, the mechanochemical protocol could be extended beyond simple disilanes. Co-milling of trimethylchlorosilane with tetrachlorosilane and sodium in the presence of sodium chloride enabled access to mixtures of higher silanes (**3a-c**), demonstrating that mechanical activation can promote Si-Si bond formation even in more complex coupling scenarios (see Scheme 3). Product formation and composition were confirmed by ¹H and ²⁹Si NMR spectroscopy. The crude reaction mixture was obtained in 85% yield. NMR and GC/MS analysis revealed a product distribution of 63% **3a**, 22% **3b**, and 14% **3c**. The product distribution remained consistent across multiple attempts. Analogous milling experiments employing lithium metal, as well as combinations of lithium and lithium chloride, were conducted under otherwise identical conditions; however, these attempts did not result in the formation of the desired products. It was noted that the lithium metal became mechanically smeared onto the surface of the milling balls, effectively coating them and preventing efficient grinding and mixing of the reaction components, which is presumed to be responsible for the lack of reactivity. On the basis of these findings, no optimizations were investigated.



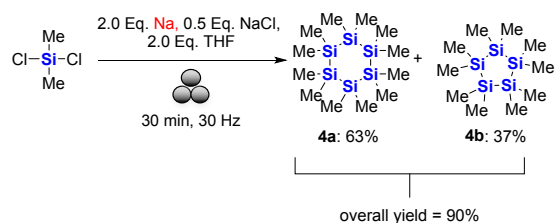
Scheme 3: Co-milling of trimethylchlorosilane with tetrachlorosilane.

The first successful synthesis of tetrakis(trimethylsilyl)silane **3a** was reported by Gilman and Smith in 1964.¹³ This work represents a seminal contribution to the chemistry of highly substituted silanes and early polysilane research. In their approach, the target compound was prepared using lithium in a solution-phase synthesis. Trimethylchlorosilane and lithium metal were dissolved in dry tetrahydrofuran. Subsequent slow addition of silicon tetrachloride led to the formation of tetrakis(trimethylsilyl)silane. The reaction required prolonged stirring at room temperature and produced polymeric byproducts, which were removed during workup. Nevertheless, the desired compound was isolated in high yield (approximately 70%) and purified by sublimation. Notably, the authors did not report the formation of compounds **3b** and **3c**. However, as we have previously synthesized tetrakis(trimethylsilyl)silane following the standard literature procedure, we likewise observed the formation of **3b** and **3c** after workup of these solution-phase reactions. This indicates that both species are also present under classical solution conditions, despite not being described in the



original report. Moreover, both the overall yield and the product distribution among compounds **3a-c** were also found to be strongly dependent on the form of the lithium employed. The use of lithium ribbon led to an almost exclusive formation of **3a**, whereas lithium granules resulted in a product distribution comprising compounds **3a-c**. In this context, the use of sodium represents a distinct practical advantage. Owing to recent advances and the rapidly increasing demand for lithium in lithium-ion battery technologies, lithium resources are subject to growing supply constraints and cost fluctuations. Sodium, by contrast, is significantly more abundant, readily available, and economically favorable. Consequently, sodium-based methodologies offer a more cost-effective and potentially more sustainable alternative to lithium-mediated processes, particularly for large-scale or routine synthetic applications.

Next, we investigated the mechanochemical formation of cyclic silanes. Dimethyldichlorosilane was reacted under mechanochemical Wurtz-type coupling conditions using sodium metal and sodium chloride under an inert atmosphere (see Scheme 4).



Scheme 4: Milling of dimethyldichlorosilane.

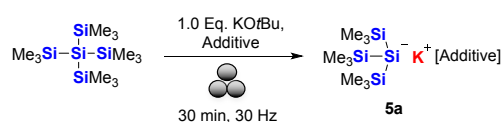
The reaction mixture was subjected to ball milling (30 Hz, 30 min), with tetrahydrofuran added as a liquid-assisted grinding additive. After completion of the milling process and subsequent workup, a mixture of two products (**4a,b**) in an overall yield of 90% was obtained. ^1H and ^{29}Si NMR spectroscopic analysis revealed the presence of two major derivatives, consistent with the formation of cyclic oligomeric silanes. In order to further assess the product distribution, mass spectrometry was employed. GC-MS analysis indicated that six-membered cyclic silanes constitute approximately 63% of the product mixture, with the remaining fraction assigned to five-membered ring systems.

The Wurtz-type coupling of dimethyldichlorosilane has been investigated in great detail in the literature.¹⁴⁻¹⁶ Using a sodium-potassium alloy, this coupling reaction led to the formation of a series of permethylated silanes, affording a product mixture dominated by cyclic species, with five- and six-membered silane rings constituting the major products. In contrast to these solution-phase studies employing sodium-potassium alloys, our mechanochemical approach to the Wurtz-type coupling of dimethyldichlorosilane reveals notable differences in both reaction conditions and product distribution. Under solvent-free ball-milling conditions using sodium in the presence of sodium chloride and tetrahydrofuran as a liquid-assisted grinding additive, the coupling reaction predominantly afforded two cyclic permethylated silanes. In the literature, a broad distribution of ring sizes has been reported for this transformation, with cyclic silanes containing up to 35 silicon atoms.¹⁵ These results demonstrate that mechanochemical activation enables efficient Si-Si bond formation without the need for sodium-potassium alloys,

while simultaneously influencing ring-size selectivity compared to classical solution-phase protocols. West and co-workers further demonstrated that the addition of naphthalene to the Wurtz-type coupling of dimethyldichlorosilane leads to a pronounced, though not fully exclusive, preference for the formation of six-membered cyclic silanes.¹⁶ Consequently, we investigated the influence of naphthalene under mechanochemical Wurtz-type coupling conditions. In contrast to the reported solution-phase behavior, the presence of naphthalene during ball milling did not affect either the overall product distribution or the ring-size selectivity, and no enhancement of six-membered ring formation was observed. These results indicate that the directing effect of naphthalene reported in solution does not translate to mechanochemical conditions.

Mechanochemical Si-Si bond cleavage to silanides/disilanides

Subsequently, we tested the controlled Si-Si bond cleavage via the generation of silanide species. To investigate the influence of various additives, we examined the ball milling of tetrakis(trimethylsilyl)silane with potassium *tert*-butoxide (Scheme 5). In the absence of any additive, no reaction was observed. In contrast, coordinating ether-based additives such as tetrahydrofuran (3 equiv) and 1,2-dimethoxyethane (2 equiv) enabled quantitative conversion. Similarly, the addition of 18-crown-6 (1 equiv) resulted in quantitative product formation. Non-coordinating additives, including toluene (2 equiv) and *n*-pentane (3 equiv), did not promote the reaction, and no conversion was detected (see *Supporting Information Table S1*). In agreement with analogous solution-based chemistry, which likewise only proceeds in the presence of polar solvents, we propose that coordinating additives such as THF, DME, or crown ethers enhance the reactivity of the alkali metal species through coordination to the metal center. This coordination likely promotes metal surface activation and facilitates electron-transfer processes during the reductive coupling reaction.



Scheme 5: Role of additives in the mechanochemical activation of tetrakis(trimethylsilyl)silane with potassium *tert*-butoxide.

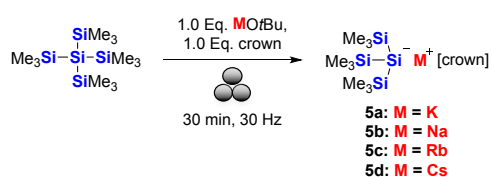
Although all ether-based additives investigated were found to promote efficient conversion under mechanochemical conditions, the use of 18-crown-6 resulted in the formation of a solid product (see Figure 1).



Figure 1: Solid 18-crown-6 adduct of **5a**. (for better representation the silanide was made in a 25 mL milling jar with 2 balls instead of a 10 mL milling jar with 1 ball)



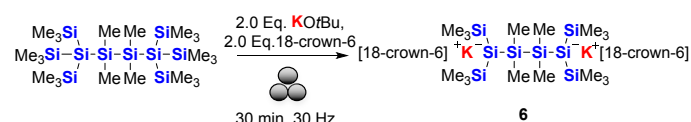
This proved advantageous for subsequent transformations, facilitating handling and follow-up chemistry. Consequently, 18-crown-6 (for M = K, Rb and Cs) and 15-crown-5 (for M = Na) were selected as the additive of choice, and employed for all subsequent reactions involving different counterions (see Scheme 6).



Scheme 6: Mechanochemical generation of silanides from tetrakis(trimethylsilyl)silane.

We found that ball milling of tetrakis(trimethylsilyl)silane with alkali metal *tert*-butoxides in the presence of crown ether additives led to the formation of isolable silanides (**5a–d**), as evidenced by strongly upfield-shifted quaternary silicon signals in the ²⁹Si NMR spectra (around –190 ppm).¹⁷

Encouraged by these findings, we next investigated the synthesis of disilanides under mechanochemical conditions. Ball milling of hexakis(trimethylsilyl)disilane with potassium *tert*-butoxide in the presence of 18-crown-6 led to the efficient formation of the corresponding disilanide, compound **6** (see Scheme 7).



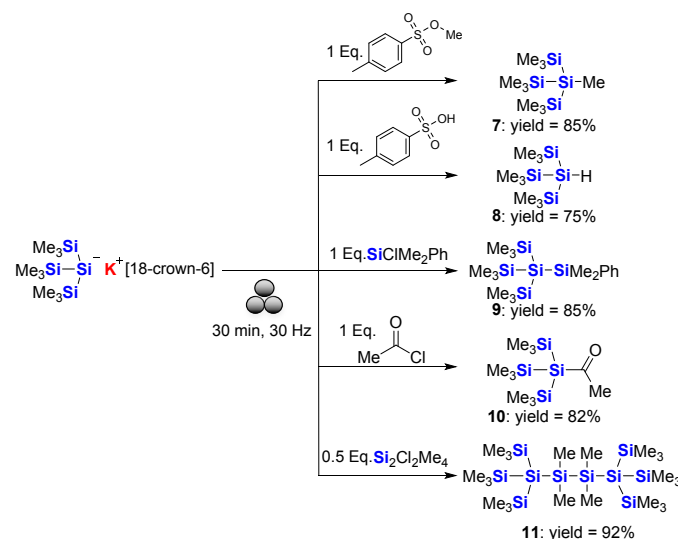
Scheme 7: Mechanochemical generation of disilanides from 1,1,1,4,4,4-hexakis(trimethylsilyl)tetramethyltetrasilane.

The reaction proceeded smoothly under the applied milling conditions and afforded the disilanide quantitatively, as confirmed by ¹H and ²⁹Si NMR spectroscopy. This represents a stark contrast to reported solution-phase procedures for the generation of disilanide dianions, which typically require prolonged reaction times of up to 16 hours at room temperature or heating under reflux conditions for 2 hours.¹⁸ The markedly reduced reaction time highlights the efficiency of mechanochemical activation for accessing highly reduced silicon species.

Mechanochemical Derivatization of Silanides with Electrophiles

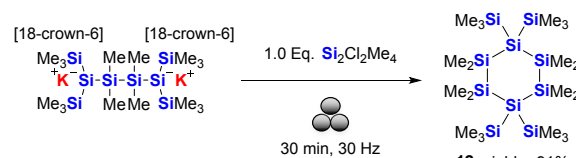
Compound **5a**, generated mechanochemically as a silanide species, was employed as the nucleophile for subsequent derivatization with a series of electrophiles, affording compounds **7–11** (see Scheme 8). In contrast to the above-mentioned Wurtz-type coupling products, toluene was used for extraction to ensure sufficient solubility. In all cases, the freshly prepared silanide intermediates reacted cleanly upon additional ball milling with the respective electrophiles, typically requiring only 30 minutes of milling time for complete conversion. The derivatization reactions proceeded with high efficiency, delivering the desired products in good to excellent isolated yields (75–92%). Notably, the transformations showed high selectivity, with no significant formation of side products observed by NMR spectroscopy. The electrophilic trapping encompassed

alkylation, protonation, acylation, and Si–Si bond-forming reactions, demonstrating the broad reactivity profile of the silanides generated under mechanochemical conditions.



Scheme 8: Mechanochemical derivatization of silanides with electrophiles.

The mechanochemical synthesis of silanes **7–11** shown in Scheme 8 demonstrates a clear improvement in efficiency compared to previously reported literature methods. In the literature, compound **7** was obtained in only 54% yield,¹⁹ whereas the mechanochemical approach affords this compound in significantly higher yield. Similarly, compounds **8**,¹⁷ **9**,¹⁷ and **10**,²⁰ which were previously reported with yields of 93%, 81%, and 76%, respectively, are obtained in comparable or improved yields under mechanochemical conditions. Most notably, compound **11**, which already showed a high literature yield of 95%,¹¹ is also produced in near-quantitative yield via mechanochemistry, highlighting the robustness and efficiency of this solvent-free approach. Furthermore, scale and purification can be compared to the solvent-based approach. Next, the derivatization of the mechanochemically generated disilanide **6** with a silicon electrophile was targeted to access the six-membered ring **12**. Accordingly, the bisilanide was first formed from 1,1,1,4,4,4-hexakis(trimethylsilyl)tetramethyl-tetrasilane under the established milling conditions (KOtBu/18-crown-6), and the freshly prepared dianion was then directly reacted with tetramethyldichlorosilane as the Si-electrophile. A second milling step (30 Hz, 30 min) enabled efficient Si–Si bond formation and clean ring closure to furnish **12** (see Scheme 9).



Scheme 9: Mechanochemical derivatization of silanides with electrophiles.

The transformation proceeded rapidly and with high selectivity, as confirmed by ¹H and ²⁹Si NMR spectroscopy. In the original literature, the corresponding six-membered cyclic silane was reported to be obtained in a yield of 96%.²¹ Under mechanochemical conditions,



compound **12** was formed in a slightly lower but still high isolated yield of 91%, demonstrating that comparable efficiency can be achieved without recourse to classical solution-phase protocols.

Gram-Scale Reaction

Compound **11** was further subjected to a gram-scale reaction in order to demonstrate the scalability of the mechanochemical protocol. Accordingly, 5.0 g of tetrakis(trimethylsilyl)silane were employed in a 50 mL milling jar and 5 balls (10 mm, diameter). The material was converted into the corresponding silanide **5a** by reaction with potassium *tert*-butoxide and subsequent reaction with the silicon electrophile, affording compound **11** in an isolated yield of 89%. As already pointed out by Su and co-worker, and also in our own observations, the yield in the solution-based synthesis drops significantly to around 60% by upscaling the reaction.¹²

Direct Mechanochemical Access to Compound **12** as a showcase example

As outlined in the introduction, access to polysilanes is often time-consuming and typically requires several discrete reaction steps, including aqueous workup, purification, and recrystallization. In order to address these limitations, we targeted the direct mechanochemical access to compound **12** as a showcase example. Starting from tetrakis(trimethylsilyl)silane, ball milling with potassium *tert*-butoxide afforded the corresponding silanide **5a**, which was subsequently reacted with tetramethyldichlorodisilane to give compound **11**. Notably, no intermediate workup was performed. The crude material was directly subjected to a second desilylation using two equivalents of potassium *tert*-butoxide, followed by reaction with the same silicon electrophile, which led to the formation of compound **12** in a moderate isolated yield of 50%.

Conclusions

In conclusion, this work demonstrates that mechanochemistry provides a highly effective and sustainable platform for both the construction and selective cleavage of Si–Si bonds. Solvent-free or solvent-minimized ball-milling protocols enable efficient Wurtz-type couplings of chlorosilanes, granting access to disilanes, higher silanes, and cyclic silanes under mild and operationally simple conditions. In addition, mechanochemical activation allows the rapid and quantitative generation of silanide and disilanide species, markedly reducing reaction times compared to established solution-phase procedures. Subsequent derivatization with a broad range of electrophiles proceeds cleanly and with high selectivity, frequently delivering products in yields that are comparable to or exceed reported literature values. The scalability of the approach and the possibility to conduct multistep sequences without intermediate workup further highlight the practical advantages of this methodology. Taken together, these results underscore the significant potential of mechanochemistry as a green and versatile tool for advancing silicon chemistry and expanding access to functional polysilane architectures.

Author contributions

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T. L. was responsible for experimental investigations, formal analysis, visualization, data presentation and writing original draft (lead). M. H. was in charge of methodology and conceptualization, review and editing of the manuscript (lead), project administration and funding acquisition.

Conflicts of interest

There are no conflicts to declare.

Data availability

All data supporting the findings of this study are available in the *Supporting Information*.

Acknowledgements

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All data supporting the findings of this study are available in the *Supporting Information*.

