# Catechol-Mediated Activation and Functionalization of SiO₂

Motivation

Silicon, the second most abundant element on earth, is of paramount relevance, e.g., for industrial materials, such as glasses, ceramics, and semiconductors.[1] Despite its high demand in daily life, organosilanes need to be produced under extreme conditions in at least two steps from SiO₂ (carbothermal reduction of SiO₂ at 1200 °C to elemental silicon,[2] followed by Müller-Rochow process at 200 - 350 °C in the presence of copper and tin to yield substituted silane, which reacts with organometallic reagent to tetrasubstituted silanes (Fig. 1(a)).[1] Both steps consume tons of energy and produce waste, whereas chlorine is regarded as an environmental issue from a green chemistry perspective. Alternative mass production of organosilanes is urgently desired.
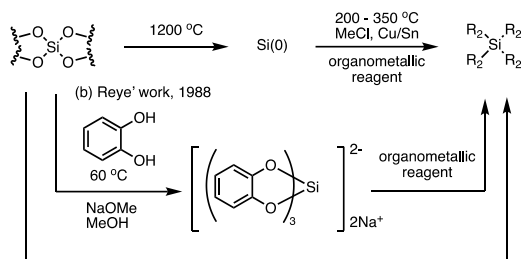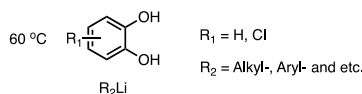

Figure 1. (a) Conventional mass production of organosilanes starting from carbothermal reduction of SiO₂, followed by Müller-Rochow process.[1] (b) Work from Corriu in 1988: synthesis of Na₂[Si(cat^H)₃] from SiO₂ using catechol in basic condition, followed by nucleophilic substitution with organometallic reagents to organosilanes.[3] (c) In this project: one-pot reaction from SiO₂ with organolithium reagent mediated by (substituted-)catechol.

The present project was inspired by the work from Corriu in 1988.[3a] In this work, catechol was used under basic condition to generate sodium tris(catecholato)silicate Na₂[Si(cat^H)₃] (Fig. 1(b)). These complexes can undergo nucleophilic substitution with organometallic reagents to give tetrasubstituted silanes. At the same time, catechols are known to depolymerize silica or even SiO₂. Although these two processes were investigated separately, they might be combined in one pot, ultimately achieving a direct route from SiO₂ to organosilanes. In this one-pot reaction, proposed in the present project, the organometallic reagents would function as a base and nucleophilic agent in a suitable solvent, where catechol acts as a mediator (Fig. 1(c)).

Results and Discussion In the first part of the project, the literature results from Corriu were reproduced, and the validity of the procedure was examined (Fig. 2). Indeed, the tris(catecholato)silicate dianions [Si(cat^H)₃]²⁻ can be obtained purely with different counterions in yields from 55% - 93%.
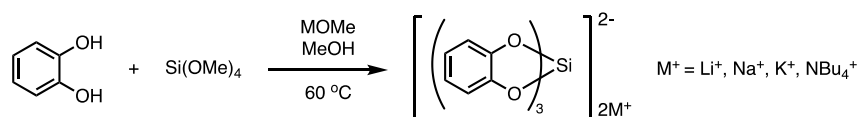

Figure 2. Synthesis of tris(catecholato)silicate dianions [Si(cat^H)₃]²⁻ with M⁺ = Li⁺, Na⁺, K⁺, NBu₄⁺.[3a]

Furthermore, the sodium tris(perchlorocatecholato)silicate Na₂[Si(cat^Cl)₃]) was also successfully synthesized following the same reaction scheme.

The pH-dependent stability of the tris(catecholato)silicate dianion $[Si(cat^H)_3]^{2-}$ is a vital aspect for a one-pot protocol and was investigated next. Thus, an aqueous $Na_2[Si(cat^H)_3]$ solution was adjusted with NaOH and HCl to specific pH values and measured by ^{1}H-, ^{13}C-NMR and ^{29}Si-INVGATE spectroscopy, respectively. In Fig. 3, the ^{29}Si-INVGATE spectra are shown for comparison. The spectra showed mainly two ^{29}Si signals, at -144 ppm ($Na_2[Si(cat^H)_3]$) and -71 ppm (silicic acid).
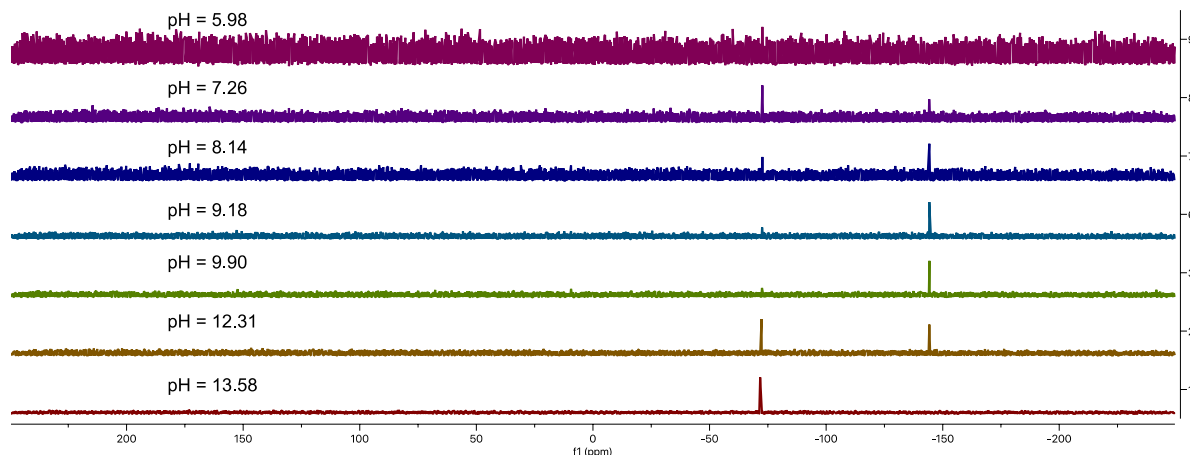

Figure 3. ^{29}Si-INVGATE spectra of $Na_2[Si(cat^H)_3]$ (D$_2$O, 120 MHz) in aqueous solution between pH 6 - 13.

Below pH 7, the silicic acid polymerized, which can be observed visually by precipitation in the NMR tube. The free catechol is fully protonated below pH 8, and fully deprotonated above pH 12; in between catechol should exit in its single deprotonated form. The complex $Na_2[Si(cat^H)_3]$ does not exist below pH 7 or above 13.

Next, the reaction of $Na_2[Si(cat^H)_3]$ with organometallic reagents was tested, as shown in Fig. 4. The chosen reactions showed consistent results with the literature. [3a]

Entry	RM	Product	δ ^{29}Si [ppm]
7	PhMgBr	SiPh$_4$	-14.4
8	PhLi	SiPh$_4$	-14.4
9	⬈⬈MgBr	Si(⬈⬈)$_4$	-2.3

Figure 4. Nucleophilic substitution of $Na_2[Si(cat^H)_3]$ using different organometallic reagents.

Furthermore, $[Si(cat^H)_3]^{2-}$ with different counterions were tested in the reaction with PhMgBr, to compare how other cations may impact the nucleophilic substitution reaction. All nucleophilic substitutions were completed within 2 hours, regardless of the cations. Notably, the reaction of $Na_2[Si(cat^{Cl})_3]$ with PhMgBr reagent only happens when heated to 60 °C, which was ascribed to the steric hindrance of perchloro-substituents.

Knowing that nucleophilic substitution reactions were feasible in THF, the more challenging SiO$_2$ depolymerization was studied in this solvent ("SiO$_2$" was used in the form of silica gel, 70-230 mesh). Notably, from our stability investigation shown above, it was known that the crucial formation of the silicate dianions is unfavorable under extreme basic conditions. Therefore, it was considered that the organometallic reagent should be added stepwise, namely first with two equivalents to deprotonate the catechol for depolymerization, and then further aliquots for functionalization. Two equivalents of PhMgBr reagent were added at first (Fig. 5, top). Unfortunately, no ^{29}Si signal indicative of $[Si(cat^H)_3]^{2-}$ was detected after heating to 60 °C overnight. Thus, phenyl-Grignards are no suitable bases to induce SiO$_2$-

depolymerization in the form of the MgBr-catecholates. Therefore, the reaction was conducted with PhLi (Fig. 5, bottom). After heating overnight, an intensive [29]Si signal at -141 ppm in THF was detected. Apparently, the respectively formed Li-catecholates can depolymerize SiO_2 in THF at a sufficient rate.
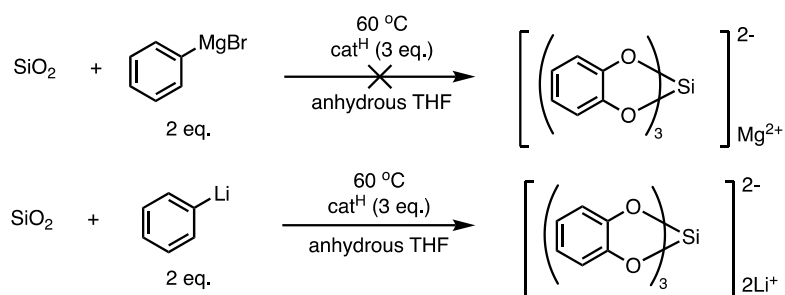

Figure 6. Synthesis of $[Si(cat^H)_3]^{2-}$ anion starting from SiO_2 using PhMgBr reagent (Entry 20) and PhLi reagent (Entry 21).

Next, about 7 equivalents of PhLi reagent were added. Indeed, after heating overnight, a solid [29]Si signal at -14.5 ppm was detected, which belongs to $SiPh_4$. ^{1}H-, and ^{13}C-NMR spectra provided additional evidence for the successful formation of $SiPh_4$.

Accordingly, we were able to activate and functionalize SiO_2 in a one-pot fashion by the mediating role of catechol!

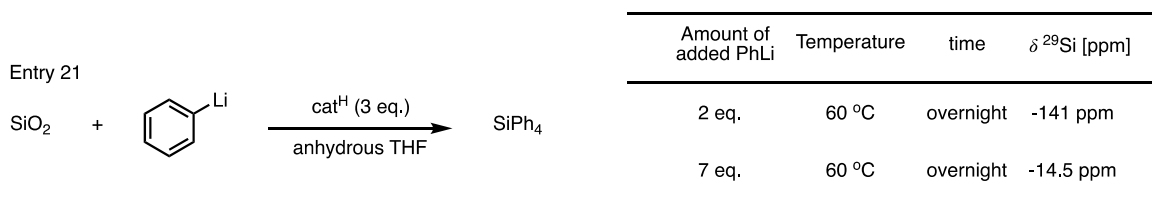|	Amount of added PhLi	Temperature	time	δ [29]Si [ppm]
	2 eq.	60 °C	overnight	-141 ppm
	7 eq.	60 °C	overnight	-14.5 ppm

Figure 8. One-pot reaction of SiO_2 with PhLi reagent catalyzed by catechol. The PhLi reagent was added in two shots. In the first shot, 2 eq. of PhLi were added and heated overnight. Afterwards, 7 eq. of PhLi were added and heated overnight. [29]Si signal at -141 and -14.5 ppm were detected for each step, respectively.

These findings are highly encouraging, as it now allows to optimize reaction conditions to establish a high-yielding process, e.g., by the continuous addition of RLi-reagents to SiO_2 in the presence of catechol and pH-buffering to prevent prohibitively basic conditions.

Reference

[1]   L. Rösch, P. John, R. Reitmeier, *Ullmann's Encyclopedia of Industrial Chemistry* **2000**.

[2]   J. G. Lee, P. D. Miller, I. B. Cutler, in *Reactivity of Solids* (Eds.: J. Wood, O. Lindqvist, C. Helgesson, N.-G. Vannerberg), Springer US, Boston, MA, **1977**, pp. 707-711.

[3]   a) A. Boudin, G. Cerveau, C. Chuit, R. J. P. Corriu, C. Reye, *Organometallics* **1988**, *7*, 1165-1171; b) A. Boudin, G. Cerveau, C. Chuit, R. J. P. Corriu, C. Reye, *Angew. Chem. Int. Ed.* **1986**, *25*, 474-476.