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Challenges in the Electrochemical Synthesis of Si_2Cl_6 Starting from Tetrachlorosilane and Trichlorosilane

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The strongly increasing demand for nano- and microelectronics calls for new and environmentally benign reaction pathways for the preparation of one of the most important substrates in the production of semiconductor materials: Si_2Cl_6. We present a comprehensive study of the opportunities and challenges for the selective electrochemical formation of higher halo-functionalized silanes to Si_2Cl_6 achieved by cyclic voltammetry measurements and electrochemical synthesis. Cathodic dehalo-dimerization reaction of $SiCl_4$ and the approach to halogen exchange for better substrate reduction are envisioned. An anodic halide-free dimerization pathway by dehydrogenation of $HSiCl_3$ is investigated, including Lewis acid activation of the Si–H bond. In addition, tertiary amine-driven, Benkeser-like in-situ formation of a $SiCl_3^-$ anion was tested as well. The target molecule Si_2Cl_6 is strongly promoted to direct electro-conversions making the anodic and cathodic electrosynthesis very challenging.

Introduction

The steady growth in the demand for nano- and microelectronics is leading to new challenges in processing semiconductor devices reaching sub-7-nm technology nodes.[1,2] The corresponding structure resolution requires selection of suitable precursor substrates in the production of insulating thin films by atomic layer deposition (ALD).[2] Si_2Cl_6 has shown to be a continuing promising silane-based precursor for the use in interlayer dielectrics.[3] Due to unique Si–Si construction features, Si_2Cl_6 met the strict requirements for desired SiN_x thin film deposition even in the industrial lower-temperature process with NH_3 plasma.[4] Since the first generation of Si_2Cl_6 150 years ago, various approaches to the synthesis of Si_2Cl_6 have been investigated,[5] including direct chlorination of silicon,[6] and oxidative cleavage of polychlorosilanes by chlorine.[7] While the synthesis of Si_2Cl_6 is hitherto challenging, chlorinated monosilanes like $SiCl_4$ are abundantly available. $SiCl_4$ is co-generated in large amounts as a by-product in the direct synthesis of $HSiCl_3$,[8] that itself is used as a primary feedstock in high volumes to produce silicon-based photovoltaics.[9]

The increasing demand for Si_2Cl_6 requires the investigation of new synthetic strategies, particularly in terms of low temperature, energy-efficient approaches starting from easily available chlorosilanes. This suggests the field of electrosynthesis that has experienced a renaissance, represents a green alternative to traditional synthesis protocols,[10] and evolves to a key discipline for future synthesis applications.[11] This methodology can easily pay off,[12] if highly value-added compounds are addressed.[13] The significant advantages of electrosynthesis are the avoidance of stoichiometric amounts of oxidizers or reducing agents.[14,15] Therefore, only little or no reagent waste is generated and due to the simple switch off, no thermal runaway reactions are possible making this method inherently safe.[16]

The first electrochemical synthesis of disilanes from halosilanes was reported by Hengge and Litscher (Scheme 1).[17] Instead of the hitherto known Wurtz-type pathway using alkali metals for the reductive coupling, mild reaction conditions applying electrons as reagents lead to the desired disilane formation in high current efficiency. With mono-functionalized substrates, a variety of disilanes have been obtained in the past decades by the reductive electrochemical route, mainly with metal anodes such as copper,[18] magnesium,[19] mercury,[17,20] and silver.[21] These metals form the corresponding chlorides as by-products. Alternative anode concepts have been tested,[22] refraining on sacrificial electrodes. While selective pathways for the dimerization of mono-functionalized substrates have been reported, difunctionalized halosilanes were reductively coupled to linear oligo- and polysilanes with varying chain length dependent on reaction conditions and substrate composition.[23] For higher halo substituted silanes there are only few reports in the literature with silicon deposition for appropriate reaction conditions and network polysilanes as sole products,[24–27] allowing the reduction of $SiCl_4$ to silicon nanoparticles.[28]

Besides the reductive pathway, an oxidative route to Si–Si bond formation of alkyl and allyl H-silanes is known in literature,[29] and a successful dimerization of Me_2PhSiH via cleavage of Si–H bond and cathodic proton reduction to H_2 has

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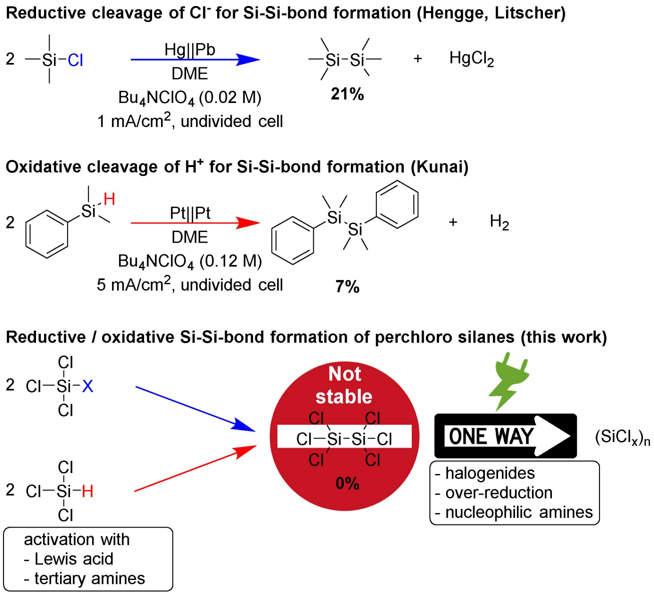
Supporting information for this article is available on the WWW under https://doi.org/10.1002/celc.202101374

An invited contribution to the Wolfgang Schuhmann Festschrift



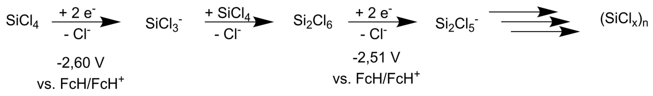
Scheme 1. Reported strategies for electrochemical Si–Si bond formation and attempts of this work.[17,30]

been described by Kunai and co-workers (Scheme 1).[30] This methodology provides a halide free pathway in the absence of otherwise often used sacrificial anodes. The route is discussed via a cationic intermediate stabilized by the perchlorate anion of the supporting electrolyte leading to reductive dimerization by successive cathodic conversion. To the best of our knowledge, neither the reductive nor the oxidative pathway was reported for selective dimerization of perchloro silanes. Here, a comprehensive study of the possibilities and challenges for a selective formation of higher halo functionalized silanes to Si_2Cl_6 is outlined.

Results and Discussion

The straightforward attempt to the formation of Si_2Cl_6 is the dehalo-dimerization of $SiCl_4$ under reductive displacement of chloride, as used for the Si–Si coupling of mono-functionalized halosilanes. This approach will indeed elongate the silicon backbone with Si_2Cl_6 as potential intermediate as Homma and co-workers reported.[26] However, Si_2Cl_6 could not be isolated. Depending on constant current or constant potential conditions, an orange polysilane $(SiCl_{0.7})_n$,[25] or deposits of elemental silicon at the surface of various cathodic materials are obtained.[26,27] This phenomenon is rationalized by a shift of the reduction potential towards less cathodic values, visible in cyclic voltammetry (CV) measurements at platinum electrodes with the elongation of the silicon backbone (Scheme 2).

The reduction of $SiCl_4$ shows two irreversible events, a wave at about −1.38 V vs. FcH/FcH^+ (Ferrocene/Ferrocenium) for the reduction of H^+ that is formed due to traces of water in the electrolyte and consequential formation of HCl with $SiCl_4$ and a second peak at −2.60 V vs. FcH/FcH^+ for the reduction of $SiCl_4$. This agrees with previously reported data by Bard and co-workers.[27] In comparison to $SiCl_4$, for Si_2Cl_6 a less cathodic reduction peak at −2.51 V vs. FcH/FcH^+ and a second one at −3.03 V vs. FcH/FcH^+ arises (Figure 1), that could be related to another silicon-chloride bond cleavage. The missing reduction wave of H^+ might be due to higher stability of Si_2Cl_6 towards protic media. For $SiCl_4$ and Si_2Cl_6 consecutive measurement cycles by CV show similar characteristics: the current density declines, the reduction wave vanishes and at the same time the onset reduction potential is shifted towards less cathodic values below −2.00 V vs. FcH/FcH^+. This trend is attributed to the possible generation of a surface layer of perchloro oligosilane species which is further reduced to deposit on the platinum cathode. The change in charge transfer properties of the electrode material due to this coating inhibits the hitherto occurring H^+ reduction and blocks the cathode, resulting in the decrease of current density also visible in electrochemical synthesis. The reduction potential declines for elongated perchlorinated silicon species, which further promotes the polymerization reaction starting from the oligosilanes instead of $SiCl_4$, favoring the polymerization and deposition over possible dimerization.



Scheme 2. Proposed pathway for the reductive coupling of $SiCl_4$ with Si_2Cl_6 as potential intermediate in consecutive elongation to polysilane with parameter x dependent on electrode material and reaction conditions (FcH/FcH^+: Ferrocene/Ferrocenium).

While the straightforward attempt is hindered by the preferential reduction of polysilanes, respective bromosilanes are easier reduced as shown by the difference of 170 mV for the reduction of $SiBr_4$ vs. $SiCl_4$ facilitating silicon-bromine bond cleavage (see Supporting Information). A pathway favoring dimerization over polymerization for a monobromo halosilanes is conceivable. The halogen exchange of chloro to bromo silanes has been reported by Schmidt and Russ for in-situ bromination of Me_3SiCl to Me_3SiBr in MeCN with group 1 and 2

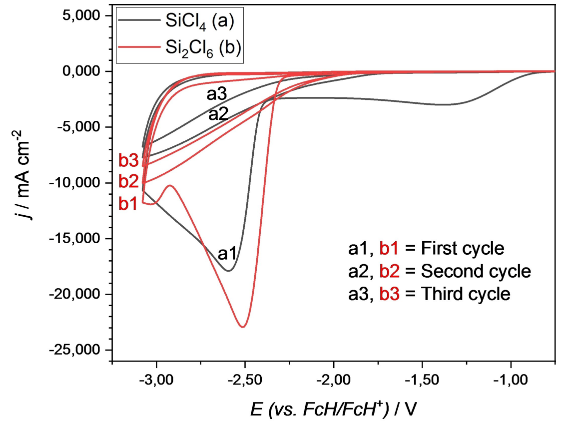


Figure 1. Cyclic voltammogram of (a) 15 mM $SiCl_4$ in 0.1 M Bu_4NCl / MeCN, (b) 15 mM Si_2Cl_6 in 0.1 M Bu_4NCl and 0.1 M Bu_4NClO_4 / MeCN showing identical results, respectively. W.E. Pt (A = 8.0 mm²), sweep rate $\nu = 0.2$ V/s.

bromide salts.[31] This exchange reaction could be reproduced with yields of 3–20% depending on bromide source at room temperature. The reaction is in equilibrium with identical yields for one hour to 7 days reaction time, solely shifted by increasing solubility of the individual metal bromide ($NaBr < MgBr_2 < LiBr$). When the mild and easy halogen exchange method is applied to $SiCl_4$ using LiBr or $MgBr_2$ as bromide source, a monobromination to $SiCl_3Br$ with 9% and 5% yield occurs, respectively. No further bromide displacement to $SiCl_2Br_2$, $SiClBr_3$ or $SiBr_4$ was observed. This can be a useful concept for the selective reductive dimerization of further silane species. However, Si_2Cl_6 is not stable towards chloride as reported by Holthausen and co-workers.[32] Chloride catalytically participates in the formation of elongated oligosilane species with consecutive cleavage of $SiCl_4$. This effect is not limited to chloride ions, as comparable results with cleavage of $SiCl_4$ and precipitation of insoluble oligosilanes in the presence of bromide indicates, that cannot be suppressed by variation of temperature or concentration of the respective halide ion. For the desired product stability, a halide free reaction pathway to Si_2Cl_6 is required.

Besides the already mentioned reductive pathway, the oxidative route to Si–Si bond formation inspired by Kunai and co-workers is examined.[30] Corresponding yields are relatively low given with 7% disilane and 15% disiloxane which is probably formed by a decomposition reaction with the supporting electrolyte. Own experiments show that disilane is no longer detectable, but the yield of disiloxane increases to 20% when access to the cathode for the intermediate is prevented by using a divided cell. This indicates a necessary subsequent reduction step for disilane formation. Another reason for low disilane yield is the distinct less anodic potential for the Si–Si bond cleavage of the desired product in comparison to the Si–H bond cleavage of the educt with a difference of 0.91 V (see Supporting Information). Despite the addressed hurdles this pathway provides the possibility of halide-free dimerization and has hitherto not been described for halo functionalized silanes like $HSiCl_3$.

In a first step the stability of Si_2Cl_6 towards oxidative cleavage of the Si–Si bond is studied. By substitution of silicon-carbon bonds through electron withdrawing chlorine, the oxidation potential shifts to higher anodic region linearly with the amount of chlorine functionalization (Figure 2). The oxidation potential of Si_2Me_6 is at 1.51 V vs. FcH/FcH^+, raising the chlorine content to Si_2Me_5Cl and $Si_2Me_4Cl_2$ shifts the potential to 1.84 V vs. FcH/FcH^+ and 2.15 V vs. FcH/FcH^+, respectively. Following this trend of anodic stabilization of about 320 mV per substitution with chlorine, it is not surprising that the oxidation potential for the Si–Si bond cleavage of Si_2Cl_6 is not measurable before electrolyte decomposition.

A reduction potential for oxidizable silane compounds at about −0.16 V vs. FcH/FcH^+ occurs on platinum electrodes, that is identical for different disilanes and H-silanes (see Supporting Information). This is very likely linked to a desorption process of the respective silyl cationic species. Neither the oxidation of Si_2Cl_6 nor the reductive desorption can be observed confirming the oxidative stability.

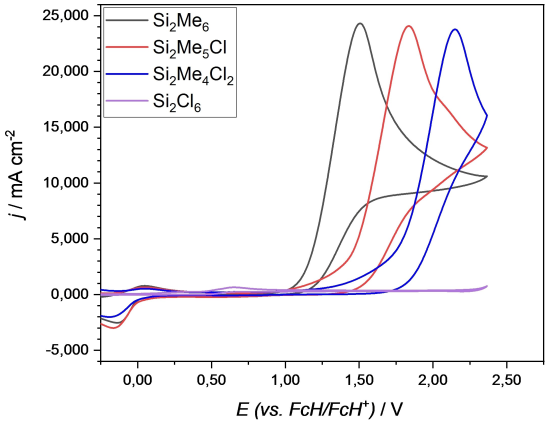


Figure 2. Cyclic voltammogram of 20 mM Si_2Me_6, Si_2Me_5Cl, $Si_2Me_5Cl_2$, Si_2Cl_6 in 0.1 M Bu_4NClO_4 and MeCN. W.E. Pt (A = 8.0 mm^2), sweep rate $\nu = 0.2$ V/s, first cycle each.

Our experiments reveal that the electrolyte system based on 1,2-dimethoxyethane used for oxidative Si–Si bond formation[30] slowly dismutates $HSiCl_3$ to $SiCl_4$ and H_2SiCl_2 and does not provide the needed anodic stability. Anodic stable acetonitrile does not show this dismutation reaction and is used for further investigations. A pale yellow polysilane $(SiCl_{0.1})_n$, analogue to $SiCl_4$, is formed at the platinum cathode by the reductive polymerization of $HSiCl_3$ in an undivided cell. A divided H-type cell with diaphragm is used to prevent cathodic access of $HSiCl_3$. Electrode material and reaction parameters are screened (see Supporting Information for experimental details). The high anodic reaction conditions limit the choice for anode materials to (electro)chemical robust boron-doped diamond (BDD) and glassy carbon (GC).[15,33]

Diffusion of $HSiCl_3$ to the cathode is delayed but not inhibited by the diaphragm. The synthesis duration elongates with higher applied charge, increasing the amount of polysilane formed on the cathodic surface due to diffusive mass transport in the cathodic compartment. At the anode the desired oxidative cleavage of Si–H bonds seems to occur promoted by BDD, forming $SiCl_4$ and Si_2OCl_6 in the anodic cell compartment, increasing with rising applied charge (Table 1). In the cathodic compartment the products obtained are polymeric $(SiCl_{0.1})_n$, H_2SiCl_2 and traces of $SiCl_4$ due to diffusion. The low yield for the

Table 1. Oxidation of $HSiCl_3$ in a divided H-type cell at BDD anode.[a]

Applied Charge	$SiCl_4$ Yield[b] [%]	Si_2OCl_6 Yield[b] [%]	$(SiCl_{0.1})_n$ Yield[b] [%]	H_2SiCl_2 Yield[b] [%]
0.5 *F*	4%[c]	1%[c]	–	–
0.5 *F*	1%[d]	–	6%[d]	7%[d]
1.0 *F*	10%[c]	2%[c]	–	–
1.0 *F*	2%[d]	–	10%[d]	17%[d]
1.5 *F*	11%[c]	2%[c]	–	–
1.5 *F*	5%[d]	–	23%[d]	18%[d]

[a] Electrolysis with platinum cathode in 0.2 M TBAP in MeCN at 10 °C with 3.3 mA/cm^2. [b] Yield determined by NMR referenced to TMS. [c] Obtained from anodic compartment. [d] Obtained from cathodic compartment.

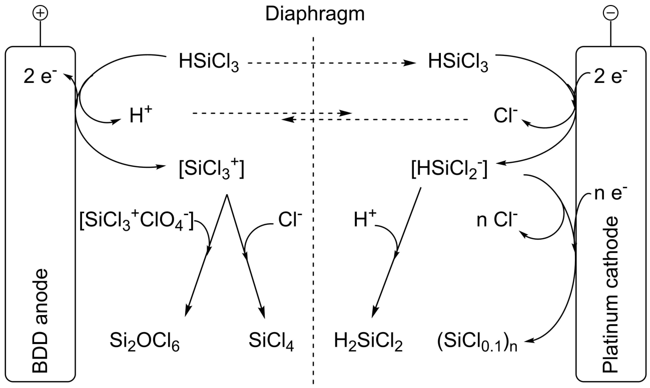
applied charge of 0.5 *F* indicates that the dehydrogenation of $HSiCl_3$ is in concurrence with electrolyte decomposition.

Electrolyte decomposition can be diminished with lower current density, at the same time the diffusion of $HSiCl_3$ to the cathodic compartment rises with the elongating synthesis duration. The same applies for increasing the applied charge. Rising from 0.5 *F* to 1.0 *F*, the amount of anodic dehydrogenated $HSiCl_3$ as well as cathodic formed polysilane and H_2SiCl_2 increase due to elongated diffusion time. At 1.5 *F* the polysilane formation is the main reaction occurring with 23% yield and current density declines accordingly.

These results reveal that anodic and cathodic reactions, due to diffusion of $HSiCl_3$ are occurring. Anodic dehydrogenation of $HSiCl_3$, in which the intermediate formed is probably oxidized to the corresponding $SiCl_3^+$ shows two possible ways: recombination with reductively released chloride forming $SiCl_4$ or decomposing with the stabilizing perchlorate anion, analogue to the Me_2PhSiH system, leading to Si_2OCl_6 (Scheme 3). Simultaneously, after diffusion into the cathodic compartment, $HSiCl_3$ is reduced presumably to an anionic intermediate. Recombining with the anodic generated H^+ to H_2SiCl_2 or polymerizing to $(SiCl_{0.1})_n$ is possible under release of chloride that itself restricts stability of Si_2Cl_6 as discussed previously.

This consecutive reaction expresses the main difficulty towards the desired disilane Si_2Cl_6. A cationic intermediate needs cathodic access for the dimerization to Si–Si bond formation. At the same time the cathodic access reduces and polymerizes $HSiCl_3$ as cathodic coating further inhibiting H^+ reduction leading to a self-suppressing system and the subsequent release of chloride destabilizes the desired product. To overcome this hurdle two promising possibilities are discussed: activation of Si–H bond for easier oxidation and proton abstraction by additives to form the silyl anion in the anodic compartment, so the direct dimerization with the cationic species is available.

Facilitating the oxidation of $HSiCl_3$ by activation of Si–H bond could prevent its competing reduction. $B(C_6F_5)_3$ is known in literature as a strong enough Lewis acid for the Si–H bond activation by partial abstraction of hydride from electron-rich alkyl and allyl H-silanes.[34] The use in organic chemistry and its electrochemical properties have been investigated previously, surprisingly it has not been used in electrochemical synthesis for substrate activation so far.[34,35]



Scheme 3. Proposed mechanism for the dehydrogenative Si–H bond cleavage and reductive Si–Cl bond cleavage due to diffusion.

By CV measurements the evidence for an activation of Si–H bond in presence of perchlorate anion is not clear. Adduct formation without hydride abstraction by $B(C_6F_5)_3$ elongates the Si–H bond,[36] and should shift the oxidation potential to less anodic values due to decreasing activation barrier for Si–H cleavage. For the borohydride stabilized silyl cation an oxidation peak for $[HB(C_6F_5)_3]^-$ at about 0.88 V vs. FcH/FcH^+ was reported by Wildgoose and co-workers.[37] 5.0 mol% $B(C_6F_5)_3$ increases the oxidation current of Me_2PhSiH by 5-fold at GC with a shift of the oxidation potential of about 0.09 V to higher anodic values (Figure 3). This indicates that adduct formation with bond elongation is not the measured intermediate. This current gain is equal for further electron-rich H-silanes like Ph_3SiH (see Supporting Information). A very weak and ill-defined oxidation wave appears at about 0.88 V vs. FcH/FcH^+ prior to oxidation of Me_2PhSiH. This appearance is not conclusive enough to be related to $[HB(C_6F_5)_3]^-$, although it was reported to form only small amount at equilibrium in the absence of a substrate.[37]

Activation of Si–H bond with $B(C_6F_5)_3$ in electrochemical synthesis lowers the needed applied charge. In presence of 2.5 mol% $B(C_6F_5)_3$ 7% disilane and 15% disiloxane are already obtained at 2.0 *F* instead of 4.4 *F*. While the yield of disilane is not increased, the needed applied charge is less than half, indicating a mediator like functionality: formation of silyl cation stabilized borohydride enables direct reduction to the silyl anion with anodic regeneration of borohydride to the Lewis acid for consecutive activation of Si–H bond.

Applying this concept to the activation of $HSiCl_3$, CV measurements indicate that the activation of electron-poor H-silanes is hindered by the Lewis acidity of $HSiCl_3$ itself as has been mentioned in literature.[38] $B(C_6F_5)_3$ is oxidized with a peak potential at 2.26 V vs. FcH/FcH^+ at GC, an identical trend is obtained by $HSiCl_3$ with 5 mol% of $B(C_6F_5)_3$ (Figure 4). Neither the previously mentioned oxidation wave at 0.88 V vs. FcH/FcH^+ nor the increase of oxidation current at GC electrode is observed. This interpretation is further supported by data of synthesis in an undivided cell, due to the needed cationic

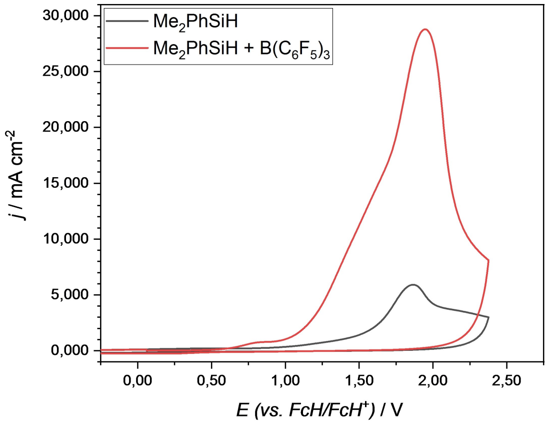


Figure 3. Cyclic voltammogram of 40 mM Me_2PhSiH in absence and presence of 2 mM $B(C_6F_5)_3$ in 0.1 M Bu_4NClO_4 and MeCN. W.E. GC ($A = 8.0\ mm^2$), sweep rate $\nu = 0.2$ V/s, first cycle each.

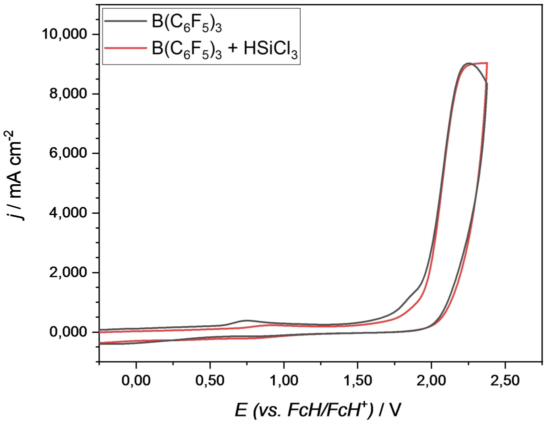


Figure 4. Cyclic voltammogram of 2 mM $B(C_6F_5)_3$ in absence and presence of 40 mM $HSiCl_3$ in 0.1 M Bu_4NClO_4 and MeCN. W.E. GC (A = 8.0 mm^2), sweep rate $\nu = 0.2$ V/s, first cycle each.

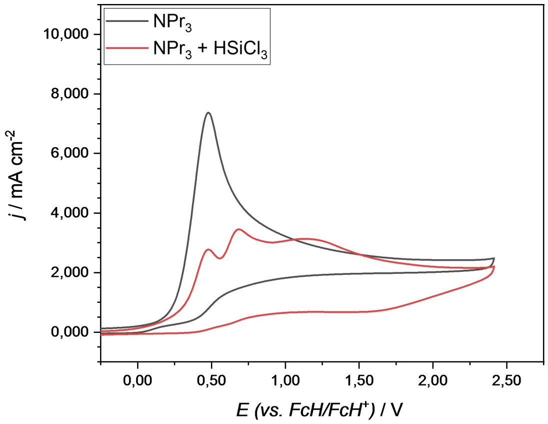


Figure 5. Cyclic voltammogram of 10 mM nPr$_3$N in absence and presence of 40 mM $HSiCl_3$ in 0.1 M Bu_4NClO_4 and MeCN. W.E. GC (A = 8.0 mm^2), sweep rate $\nu = 0.2$ V/s, first cycle each.

access for possible dimerization. With increasing amount of $B(C_6F_5)_3$ additive, the yield for the dehydrogenative oxidation as well as the reductive polymerization of $HSiCl_3$ decline over proportional (see Supporting Information). $B(C_6F_5)_3$ is reported to be reduced to the respective radical anion at −1.59 V vs. FcH/FcH$^+$ at GC at significant less cathodic potential than the respective reduction of $HSiCl_3$ with an onset potential of −2.23 V vs. FcH/FcH$^+$ at GC electrode.[37] This indicates the occurrence of a borane driven redox shuttle between radical anion and $B(C_6F_5)_3$ decreasing the current efficiency for oxidative and reductive $HSiCl_3$ conversion due to lacking formation of borohydride with $HSiCl_3$.

Another concept to prevent reductive polymerization is the proton abstraction by less sterically hindered tertiary amines like nPr$_3$N and nBu$_3$N as known in Benkeser systems in organic chemistry to provide the $SiCl_3^-$ anion.[39] In combination with a good leaving group this has already been reported for Si–Si coupling by trichlorosilylation of trimethylsilyltriflate,[40] but the Benkeser system has hitherto not been evaluated electrochemically. As ^{1}H NMR data reveals a 1:1 mixture of $HSiCl_3$ and nBu$_3$N deprotonates 50% of $HSiCl_3$ forming an equilibrium at room temperature with broadening of the nBu$_3$N-H$^+$ signal, indicating high proton mobility at the ammonium cation. The arising ^{29}Si NMR chemical shift of 29.6 ppm agrees with previously reported data for $SiCl_3^-$.[32,41] For the use as additive in electrochemical synthesis the anodic stability of the respective amine needs to exceed that of the $SiCl_3^-$ formed, to avoid amine overoxidation and shift of the equilibrium reaction off $SiCl_3^-$. CV measurements show oxidation of nPr$_3$N and nBu$_3$N with an irreversible oxidation peak at 0.48 V vs. FcH/FcH$^+$ in absence of $HSiCl_3$ at GC electrodes. By addition of $HSiCl_3$ the original oxidation current declines due to amine protonation and a second oxidation peak at 0.68 V vs. FcH/FcH$^+$ arises (Figure 5). This indicates the formation of oxidizable $SiCl_3^-$ accompanied by a broad oxidation wave at about 1.17 V vs. FcH/FcH$^+$ most likely correlating with further oxidation of the chlorosilane species. The amine oxidation is electrochemically favored compared to the oxidation of $SiCl_3^-$ anion. A shift of the oxidation potential of tertiary amines to higher anodic values does not occur for more sterically hindered species as nOc$_3$N, but for less basic ones like Ph$_3$N. CV measurement data agree with previously reported data,[42] yet the increasing oxidative stability does not suffice the oxidation potential of $SiCl_3^-$. Further, the low basicity prevents the proton abstraction as NMR and CV data reveal. Due to their high basicity, amines suitable for proton abstraction at $HSiCl_3$ disproportionate Si_2Cl_6 forming higher oligosilanes depending on reaction temperature under the release of $SiCl_4$, as already described in the literature,[43] even in the presence of a 10-fold excess of $HSiCl_3$.

Besides reductive and oxidative dimerization, the possibility of a mediated radical pathway is examined. Through hydrogen-atom-transfer (HAT) mediators a coupled one-electron one-proton abstraction of a substrate is possible, generating a radical intermediate.[44] N-Hydroxyphthalimide (NHPI) is known as electrochemical HAT mediator by oxidation to the phthalimide-N-oxyl (PINO) radical.[45] Recently, Liang and co-workers selectively oxidized electron-rich H-silanes to the respective silanols in aqueous MeCN by NHPI / PINO HAT mediator.[46] Their investigation indicates consecutive oxidation of the arising silyl radical intermediate to cationic SiR_3^+ and subsequent reaction with water to form the desired silanol. Own results showing no increase of disilane by radical dimerization in a water-free NHPI mediated system, support the suggested cationic pathway. By exchanging the H-silane substrate to $HSiCl_3$, cathodic polymerization with similar product distribution to the unmediated anodic dehydrogenation occurs in synthesis. This indicates a favored reduction of $HSiCl_3$ compared to oxidation of NHPI. Further the high oxophilicity precludes the N-oxyl radical mediated pathway for chlorosilane compounds to Si_2Cl_6 as NMR measurements show. Pietschnig and co-workers reported the respective ^{29}Si NMR chemical shift arising by Si–O bond formation of TEMPO and $SiCl_4$ to the respective TEMPO-$SiCl_3$ to be −30.6 ppm.[47] Results obtained for Si_2Cl_6 agree and feature preferential TEMPO-$SiCl_3$ formation in presence of N-oxyl radical. Additional HAT mediators as bicyclic tertiary amines like quinuclidine and DABCO disproportionate

Si_2Cl_6 with cleavage of $SiCl_4$ analog to the reaction with tertiary amines of Benkeser systems. The high oxophilicity and reactivity with Lewis bases of Si_2Cl_6 and the very likely cationic pathway due to the easy oxidizability of a resulting radical represent the hurdles for the mediated pathway to the desired dimerization.

Conclusion

As outlined, the electrochemical route to Si_2Cl_6 shows significant challenges that need to be overcome. For the reductive pathway an elongated silicon backbone lowers the reduction potential. Thus, a Si–Si bond formation does not stop at Si_2Cl_6 but generates a polymeric coating at the cathode. Furthermore, Si_2Cl_6 is not stable against the released halogenide ions. The oxidative pathway requires harsh conditions, due to high anodic stability of $HSiCl_3$. While all experimental data suggest a cationic pathway with the need of cathodic access for $SiCl_3^+$ to Si–Si bond formation, the cathodic access leads to over-reduction of $HSiCl_3$ to a polymeric coating at the cathode with blockage of the targeted H^+ reduction. High Lewis acidity of $HSiCl_3$, low stability of Si_2Cl_6 towards Lewis basic amines and easier oxidation of amines than $SiCl_3^-$ prevent the described methods for Si–H bond activation.

In conclusion, the electrochemical synthesis of Si_2Cl_6 starting from chlorosilanes is very prone to over-reduction. Consecutive release of halogenides prevents the accumulation of Si_2Cl_6 due to oligomerization. In addition, the anodic oxidation of the Si–H bond in silanes by various strategies also does not lead to the desired disilane. While there is an urgent need for an environmentally benign access to Si_2Cl_6, several challenges need to be overcome. The most promising option might be a halide-free dimerization pathway with Si–H bond activation.

Experimental Section

Detailed information on general procedures, electrochemical conversions, cyclic voltammetry measurements and product characterization can be found in the Supporting Information.

Acknowledgements

Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Dehalogenation · Dimerization · Oxidation · Reductive coupling · Silicon

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Manuscript received: October 11, 2021
Revised manuscript received: November 10, 2021
Accepted manuscript online: November 23, 2021