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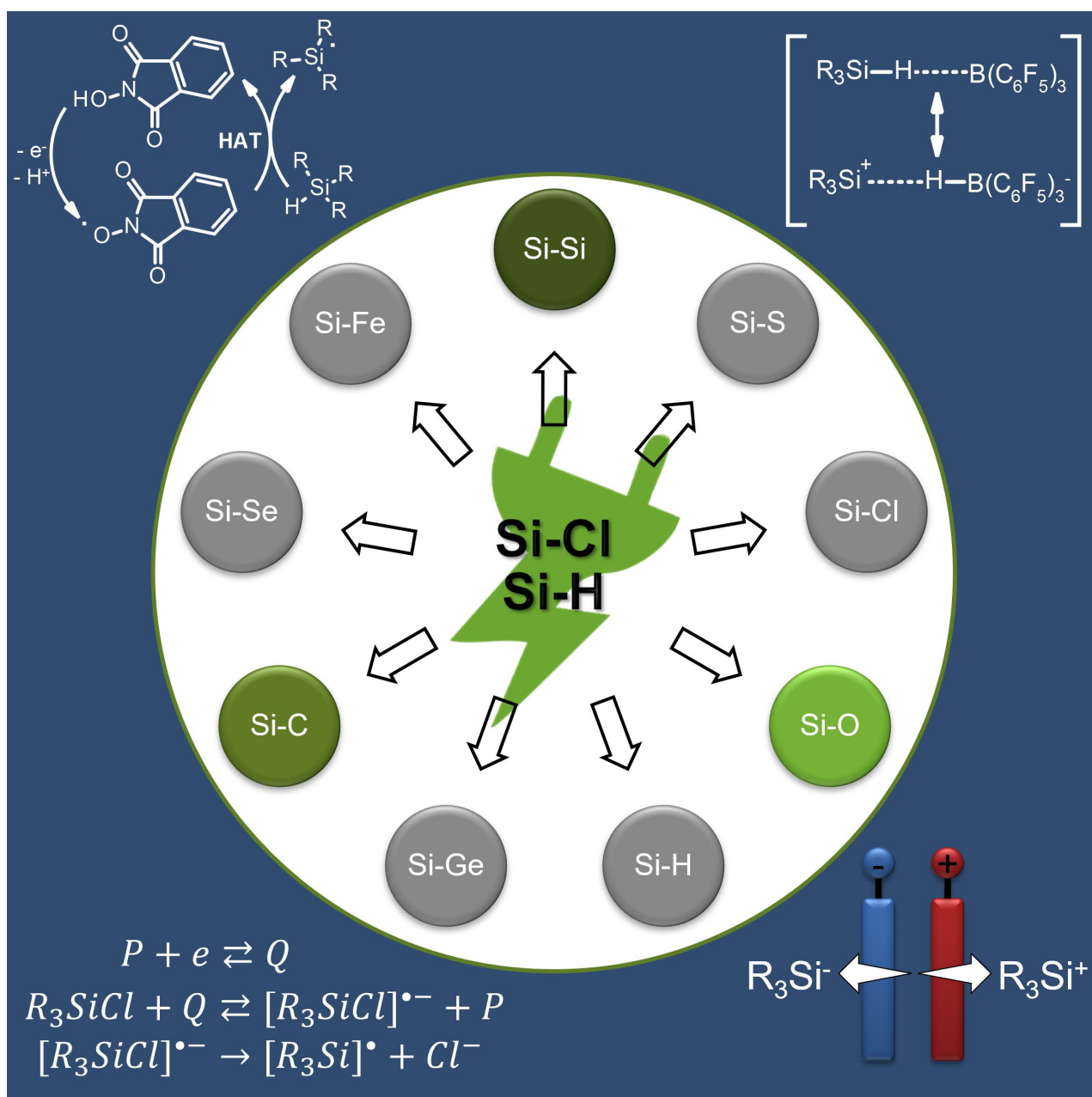European Chemical
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General Concepts and Recent Advances in the Electrochemical Transformation of Chloro- and Hydrosilanes

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Organosilanes play an important role in organic synthesis as well as in a variety of further areas, ranging from life science to transportation. Especially, the electrochemical access has become increasingly important in the past years and developed into an essential topic due to new conceptual approaches and mediated reaction control. With the commercial availability of high-quality electrochemical equipment, the technical requirements for electro-conversion are at hand to a wide audience. This results in the need for a concise survey of electrochemical silane transformation, appropriate for novices as well as experts alike. This review provides an overview of the most relevant work in this field, identifies common obstacles in working with chlorosilanes and hydrosilanes and bridges the gap between known techniques and novel methods with respect to their electrochemical conversion. The historical development is outlined with reference to the various cathodic as well as anodic conversions and should encourage to expand the research field of electrochemical silane transformation.

1. Introduction

Organosilicon compounds and silanes play a relevant role not only in organic chemistry,[1,2] but also in the fields of materials science,[3] pharmaceuticals,[4] transportation,[5,6] electronics and photonics,[5,6,7] life sciences and medical solutions,[5,6,8] as well as energy applications.[5] Due to their exceptional chemical and physical properties and unique Si bond construction features, a wide range of applications is established, leading to high demand. However, conventional synthetic routes for the preparation of organosilicon compounds are often based on Grignard-type conversions,[9] alkali metal-directed transformations such as Wurtz-type reactions,[10] or noble metal-catalyzed systems such as palladium based setups,[11] which represents not only a safety concern, but also environmental and cost considerations for industrial applications. This is very much in favor of the field of electrosynthesis which is experiencing a renaissance, providing an environmentally benign alternative to traditional synthesis protocols,[12] and emerging as a key discipline for future synthesis applications.[13] This methodology can easily pay off for compounds with highly added value.[14] The significant advantages of electrosynthesis are the avoidance of stoichiometric or even larger amounts of oxidizers or reducing agents and elevated temperatures.[15] Therefore, there is little or no reagent waste generated, and when renewable electricity is used, such processes become highly sustainable.[16] In addition, because the electricity can be simply switched off, thermal runaway reactions are not possible, making this method inherently safe.[17] However, several parameters and counter reactions seem to play a crucial role for success.[18,19] With modern screening and optimization techniques, determining the appropriate parameters can be accomplished in reasonable time.[20]

While the field of electrochemical synthesis of organosilanes and silane compounds is constantly expanding and new, exciting concepts are being published, to our knowledge, no review has appeared since 2000 on the holistic view of synthesis routes starting from hydro- and halosilanes.[21–26] Whereas there are reviews regarding the electrochemical synthesis of organosilicon species,[2,21–28] formation of polysilanes,[29,30] the electro-deposition of silicon starting from halosilanes,[31–34] and silyl radical driven conversions,[35] this review is focused on the electrochemical Si bond formation starting from chloro- and hydrosilanes. Ionic as well as the radical related type of conversion are the scope of the present analysis, further providing a general view on common obstacles regarding the work with chloro- and hydrosilanes. In addition, a compact overview of existing concepts of Si bond formation will be given, with emphasis on new methods as well as on the use of sacrificial anodes, continuing to play a major role in electrochemical conversion today. Reviews regarding the cleavage of Si bonds with the release of a "silyl super proton",[24,25] and functionalization of carbon in β-position to a Si-atom are already known and beyond the scope of this work.[25]

2. Useful information for electrochemical silane synthesis

For easier understanding of the work described here regarding the synthetic decisions and choice of parameters, some details on the work with halo- and hydrosilanes are first pointed out.

2.1. Solvent and additives

As in most systems of electro organic synthesis, a solvent is required for the electrolyte system. The solubility and dissociation of supporting electrolyte is mandatory, featuring sufficient conductivity. Further prerequisites are a suitable electrochemical window and inert behavior towards the substrates and intermediates. In addition, some special features must be considered in the conversion of halo- and hydrosilanes. Depending on the steric demand and electrophilic properties, these compounds are very prone to hydrolysis,[36–38] which requires working in aprotic solvents. In most cases, the solvent used must not contain any traces of moisture, which can otherwise easily result in misinterpretations, as we will outline

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in the further sections through conclusions from the literature (*vide infra*).[39–41] Especially, mechanistic studies based on cyclic voltammetry (CV) easily allow for misleading conclusions. Even traces of water can enable rapid hydrolysis of the halosilanes with formation of hydrogen halide, i.e. the formation of HCl by hydrolysis of chlorosilanes (Scheme 1, a). This results in the detection of relatively low cathodic reduction signals, which can be misinterpreted as the reduction potential of the halosilanes.[37] In particular, the hydrolysis of chlorosilanes occurs almost quantitatively, so that Corriu and co-workers have developed a polarographic method for water determination on this reaction, allowing accuracy comparable to the Karl-Fischer titration.[37]

The kinetics of the described hydrolysis can further be promoted by the use of nucleophilic solvents, such as *N,N*-dimethylformamide (DMF), tetramethyl urea (TMU), dimethyl sulfoxide (DMSO) or hexamethyl phosphoroustriamide (HMPT).[36,42] This effect can be explained by the coordination of halosilanes by nucleophilic solvents to form a pentacoordinated state (Scheme 1, b).[42–44] Favoring further nucleophilic attack on the silicon atom by water, for example, results in acceleration of hydrolysis or allows racemization of the product.[42] Pentacoordination can also be used specifically to support reactions with nucleophilic attack on the halosilane and thus increase the desired yield.[43,49] However, the determination of redox potentials can be impaired by this effect, making investigations using cyclic voltammetry difficult to compare and therefore ideally being conducted in non-nucleophilic solvents.[50]

In addition to coordinating properties, polarity plays a particularly important role in low-nucleophilic solvents. Increasing polarity increases the stabilization of reductively generated
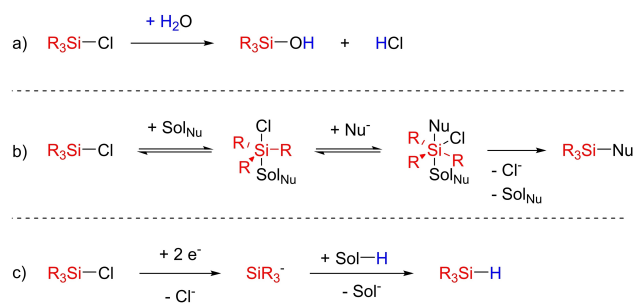
Scheme 1. Possible solvent interaction with halosilanes (Sol = solvent, Nu = nucleophile): a) hydrolysis of chlorosilanes by residual water in the electrolyte solvent,[36–38] b) coordination of chlorosilane by a nucleophilic solvent and acceleration of further nucleophilic access,[36,42–44] c) role of solvent as hydrogen donor with subsequent formation of Si–H bond.[41,45–48]

intermediates, which has been exploited selectively in the past, for example, for the synthesis of long-chain polysilanes.[51,52] By using 1,2-dimethoxyethane (DME) instead of tetrahydrofuran (THF), higher molecular masses of the polysilanes can thus be obtained.[52] Simultaneously, the stabilization of the intermediate is also related to acidity of the solvent. If the solvent represents a hydrogen donor, a proton can be abstracted from the solvent if the reactivity of the silyl species is sufficient, and thus an undesirable Si–H bond can be formed (Scheme 1, c). Acetonitrile (MeCN) in particular has been frequently discussed in this regard in the past.[41,45–47] However, proton abstraction can also occur with the use of DME as a solvent, as shown by Dessey and co-workers.[48] Further reactions caused by the choice of solvent is siloxane formation due to the high oxophilicity of silyl intermediates, generated from halo- and
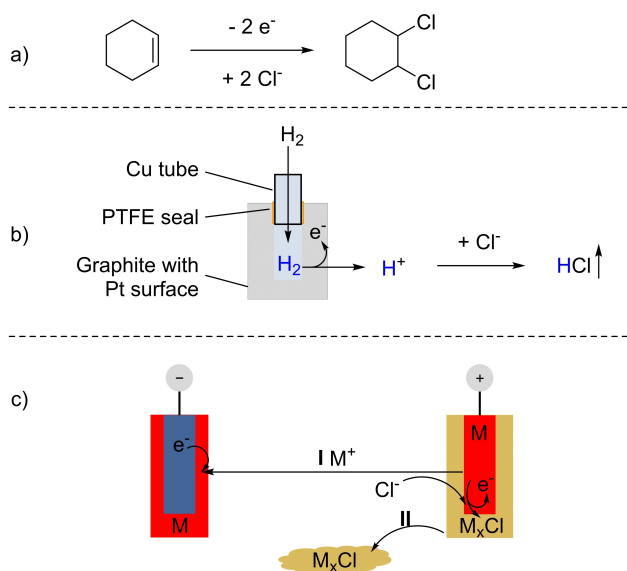
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hydrosilanes, especially in the presence of oxygen donors such as carbonates.[47] Another option is the use of solvent as a sacrificial system with respect to the electrochemical counter-reaction, for example by trapping chloride species in the anodic oxidation by means of chlorination of the solvent.[53–55]

2.2. Supporting electrolyte

The second component of the electrolyte, which has a decisive influence onto the course of reaction in the electrochemical conversion of halo- and hydrosilanes, is the supporting electrolyte. Anhydrous features represent also a prerequisite, which otherwise results in the undesired formation of Si−O bonds,[45] potentially coating the electrode surface.[39] Furthermore, the conductivity,[47] as well as the electron transfer, depending on the ions selected, contributes significantly to the desired conversion.[56] However, increase of conductivity is possible by using mixed salts, for example, the combination of LiCl and MgCl$_2$ in a 2:1 ratio results in the increase of conductivity by a factor of 100 compared to the individual components.[57] This impact is probably due to aggregation and dissociation effects, which gives rise to increased solubility of the supporting electrolyte. Halosilanes also take over a particular role concerning the subject of supporting electrolyte. Thus, halogen-containing components can result in halogen exchange at the silane. These effects have been described in particular for the conversion of chlorosilanes to fluorosilanes based on BF$_4^-$ and CF$_3$CO$_2^-$ (Scheme 2, a).[47,58–60] Fluorosilanes as electrochemically outstandingly stable species are usually no longer accessible for further conversions. Transformation to bromosilanes is also possible via this simple halogen exchange, for example by mixing the chlorosilanes with alkali and alkaline earth metal bromides in MeCN at room temperature (Scheme 2, a).[61,62] However, the effect can be suppressed by the addition of nucleophilic additives such as HMPT.[63]

Another unique feature of halo- and hydrosilanes is the equilibration of functional groups, especially the hydrogen and halo substituents. Thus, in the presence of AlCl$_3$,[68] or especially by typical supporting electrolyte components such as quaternary ammonium ions,[64–66] catalytic exchange of the two functional groups can occur. As Weyenberg and co-workers have found,[64] this reaction is also possible on non-alkylated halosilanes, such as HSiCl$_3$. Thus, equilibration to SiCl$_4$ and H$_2$SiCl$_2$ is already possible at room temperature. For monohalogenated silanes, this can also result in conversion to perchlorinated silanes by the electrolyte (Scheme 2, b),[67] which can lead to undesirable electrochemical polymerizations. Although the mechanism is not fully understood, a nucleophilic attack via a halide ion is presumed.[64] By changing the supporting electrolyte components to alkali and alkaline-earth metal ions, this equilibration can be suppressed.[67]

Another important function of the supporting electrolyte is the stabilization of the silyl intermediate in the reaction. Anodically generated silyl species, i.e. via the oxidation of hydrosilanes, can be well stabilized by weakly coordinating anions, such as ClO$_4^-$,[60,69,70] BF$_4^-$,[71] and PF$_6^-$.[72] Mg^{2+} has been shown to be particularly suitable for the stabilization of cathodically generated intermediates, which has a positive effect on the yield obtained by electrochemical conversion.[56,67,73,74] One reason for this could be the catalytic influence due to the mild Lewis acidity of the most commonly used MgCl$_2$, which is also known in organic synthesis and is already addressed in a more detailed review.[75] In this context, the concentration of the supporting electrolyte can also have an impact on product formation, e.g. increased chain length in reductive polysilane synthesis.[56]

2.3. Sacrificial anode materials

Next, the most underestimated properties of sacrificial anodes will be surveyed, which will accompany the field of reductive conversion of halosilanes. Conversion of halosilanes releases the corresponding halides, e.g. chloride in the case of chlorosilanes. To prevent interfering side reactions these must be removed from the reaction mixture. Hengge and co-workers have already investigated various possibilities, such as the use of stable SiC anodes to oxidize chloride to chlorine.[76] However, due to the requirement of aprotic solvents, this results in solvent chlorination, an effect that is specifically exploited in some cases as a sacrificial electrolyte, such as DMF.[53–55]

The anodic conversion of cyclohexene as sacrificial agent and selective chlorination of the C=C double bond has also been investigated (Scheme 3, a).[63] This use of the halogenation of alkenes has proven to be a versatile halide shuttle by generation of vicinal dihalogenides and has sparked renewed interest in current organic synthesis.[77] Another possibility is the use of a hydrogen anode, to electrochemically generate protons in-situ at the anode surface to capture free chloride ions and release them as gaseous hydrogen chloride (Scheme 3, b).[63,78] In literature of electrochemical silane conversion this concept is hardly exploited, probably due to the technical complexity.

The most popular and simple alternative to these methods is the use of sacrificial anodes, metallic electrodes which trap the free halides as metal halides due to their low potential oxidation in the course of the reaction (Scheme 3, c).[19] Depending on the solubility of the metal ion in the electrolyte,

Scheme 2. Possible interactions of supporting electrolyte with halosilanes: a) halogen exchange at chlorosilane,[47,58–62] b) equilibration reaction of hydro-chlorosilanes via tetraalkylammonium cations.[64–67]

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Scheme 3. Possibilities to remove chlorides from the electrolyte: a) anodic chlorination of cyclohexene as sacrificial agent,[63] b) anodic generation of protons via the porous hydrogen anode to form gaseous hydrogen chloride,[63,78] c) formation of metal chloride via the oxidation of a sacrificial metal anode with possible coating of the cathode material at respective reduction potentials (M = metal).[79–82]

coating of the anode surface by the metal halide can occur, as for example on silver by AgCl.[79] However, no passivation layers have yet been observed in the context of halosilane reduction that represent a complete isolation of the anode,[79] and thus result in the premature termination of the electrochemical conversion. Presumably, dissolution, or precipitation of the metal chloride from the solution occurs, preventing complete anode isolation. When using sacrificial anodes, the reduction potentials of the soluble components should be considered. Usually, dissolved metal halides are present in the reaction mixture in addition to the reactant, product, and intermediate species. The appropriate choice of anode material can serve as reductive protection of the product. Preventing over-reduction of the target molecule, and achieving high product selectivity can be obtained via deposition of the dissolved metal ion instead of product reduction at the cathode, as reported by Pons and co-workers.[82] However, if the reduction potential is inappropriate, metallic coating of the cathode occurs as main reaction (Scheme 3, c **I**), lowering the Faradaic yield.[79–81]

Otherwise, the metal chloride precipitates off the mixture depending on their solubility (Scheme 3, c **II**). According to suitable oxidation potentials (Table 1), Mg,[56–58,67,73,83–89] Al,[80,82,85,90,91] Zn,[82,92] Ni,[85] Cu,,[59,85,93–95] Ag,[79] and Hg[81,96,97] could be used as sacrificial anode materials.

In addition, sacrificial anodes can interfere further in the reaction than just trapping undesired halides. In presence of an active metallic surface with low oxidation potential, this may result in Grignard-type conversions. Faradaic yields far exceeding 100 % can occur,[57,83,84,99] questioning the simple switch-off of the synthesis route and rendering the change to alternative anode materials futile. In particular, easily reducible substrates, such as organic bromides can be affected. As Ishifune and co-workers demonstrated,[73] pre-electrolysis with Mg electrodes to form Mg(0) and subsequent reduction at Pt electrodes allows the formation of a Si—Si bond, in contrast to electrolysis in the absence of Mg. The active Mg species is mandatory for the desired Grignard-type conversion, although it can be cathodically restored. Current-free experiments are used in recent studies to test the Grignard-type influence of sacrificial anodes.[88]

Oxidation of the sacrificial anode leads to the formation of corresponding cations, which can interfere in the reaction process analogue to supporting electrolyte components. Especially, the stabilization of the generated intermediate influences reaction properties and differs in yield and selectivity compared to sacrificial anode-free systems.[56,74,85,88] This effect could be used by Biran, Bordeau and co-workers to generate selectively Si—Al intermediates at low temperatures in the reduction of chlorosilanes on Al sacrificial anodes that are stable and storable for several weeks.[90] Only by the addition of further chlorosilanes the desired Si—Si bond linkage is obtained, demonstrating the high stabilization by released ions in the use of sacrificial anodes.

2.4. Tripwires with cyclic voltammetry

As highlighted in the previous chapters, hydro- and in particular halosilanes involve some peculiarities, such as hydrolysis, equilibration, halogen exchange or nucleophilic addition by the solvent. Besides influences on the reactivity, the redox potential of the investigated silane can be shifted, thus easily resulting in misunderstandings in cyclic voltammetry. In addition to the mandatory need for anhydrous electrolytes due to

Table 1. Standard oxidation potential of sacrificial anode materials commonly used for electrosynthesis with chlorosilanes.

Entry	Metal oxidation	Potential[a] E^0 [V]	Ref.
1	$Mg \rightarrow Mg^{2+} + 2e^-$	−2.37	[98]
2	$Al \rightarrow Al^{3+} + 3e^-$	−1.66	[98]
3	$Zn \rightarrow Zn^{2+} + 2e^-$	−0.76	[98]
4	$Ni \rightarrow Ni^{2+} + 2e^-$	−0.26	[98]
5	$Cu \rightarrow Cu^{2+} + 2e^-$	0.52	[98]
6	$Ag \rightarrow Ag^+ + e^-$	0.80	[98]
7	$Hg \rightarrow Hg^{2+} + 2e^-$	0.85	[98]

[a] Potential vs. SHE at 25 °C and 1 atm.

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hydrolysis,[39–41] supporting electrolyte components, such as Mg^{2+},[100] and nucleophilic solvents can result in significant potential shifts.[50] Halogenated substrates are also dependent on the choice of electrode material, so the reduction process differs depending on the material. On non-catalytically active electrodes, such as glassy carbon, a concerted mechanism presumably occurs; on catalytically active surfaces, such as Ag, Cu, Pd, or mixtures thereof, the intermediate is stabilized via electrode surface interaction and thus more easily reducible,[101] also discussed in previous reviews.[102]

Since no standard electrolytes and electrode materials have yet been established for CV studies of hydro- and halosilanes, it is futile to compare reduction potentials of halosilanes in different environments, as shown by Jouikov.[24] In the past,[39,50,67,103,104–106] as well as in more recent studies,[43,61,107] reduction potentials of halosilanes are therefore found in a wide potential window, especially the frequently investigated Me_3SiCl (Table 2, entries 1–6). However, within an identical electrolyte and electrode system, clear trends can be identified for the reduction potential of halosilanes:

- Increase in steric demand of organic substituents shifts the reduction potential to more negative regime (Table 2, entries 7–11),
- resonance stabilizing substituents shift the potential to less negative potentials (Table 2, entries 11–13),
- a less electronegative halide substituent lead to less negative reduction potential (Table 2, entries 14–16),
- higher homologues of the 4th main group are more easily reducible (Table 2, entries 17–20).

However, CV data are to be interpreted with care, as they are often a basis for mechanistic interpretations. Besides the lack of direct comparability, the interpretation depends on the choice of electrolyte. Thus, there is still disagreement about the reduction of chlorosilanes, since in principle both a 1-electron

and a 2-electron process can occur, which induces the reduction to the radical or anion. Parallel reduction to the radical anion and diradical with further decomposition to the neutral radical and anion is discussed as well.[109] While for analogue Ge,[39,40,110] Sn[42,48] and Pb[48] compounds clearly distinguishable reduction signals can be detected and assigned to the respective reduction step, the interpretation of chlorosilanes is more complex. The mostly irreversible reduction takes place at highly cathodic potentials. In addition, a reversible signal often occurs in the low cathodic range, which can be caused by traces of moisture and accompanying HCl formation,[36,39–41] or by the presence of oxygen,[24,63] if not carefully dried and prepared, at best in a glovebox. Mechanistic conclusions based on CV studies without synthetic evidence should therefore be treated with caution, since standing alone they leave much room for interpretation.[107] One trend by which the verisimilitude to the discussion of chlorosilane reduction can be estimated is the decreasing reduction potential of oligo- and polychlorosilanes with increasing Si–Si chain length.[41,61] Reduction of chlorosilanes in the low cathodic range should accordingly allow readily accessible reduction to silicon deposition, which is not the case in practice.[105,111,112,113] Corriu and co-workers, who have worked extensively on the subject of hydrolysis of chlorosilanes in the electrolyte, were able to show that reversible reduction potentials in the less negative regime often correspond to the reduction of HCl and do not provide evidence for a 2-electron process.[37] Holm and co-workers referred the reduction of Ph_3Si radical by photo modulated CV studies to −1.39 V vs. SCE,[114] thus, the reduction of the radical to the anion seems to be much easier than from the chlorosilane to the radical. The two-step reduction presumably occurs via a consecutive highly cathodic process if the reactive species is not trapped by a suitable substrate, such as an alkene.[88]

Table 2. Overview of reduction potential of halosilanes.

Entry	Substrate	Potential [V] vs. SCE	Conditions	Ref.
1	Me_3SiCl[a]	−0.1[c]	DME, Bu_4NClO_4, Pt	[63]
2	Me_3SiCl[a]	−0.5[c]	DMF, Et_4NClO_4, Pt	[50]
3	Me_3SiCl[a]	−1.1[c]	PhOMe, Bu_4NClO_4, Pt	[50]
4	Me_3SiCl[b]	−2.2[d]	DME, Bu_4NClO_4, Pt	[81]
5	Me_3SiCl[a]	< −3.0[c]	DMF, Et_4NOTs, Pb	[108]
6	Me_3SiCl[a]	−3.1[c]	THF, Bu_4NClO_4 | GC	[88]
7	Me_2SiCl_2[a]	−2.3[d]	MeCN, Et_4NClO_4 | Pt	[109]
8	$EtMeSiCl_2$[a]	−2.4[d]	MeCN, Et_4NClO_4, Pt	[109]
9	$nPrMeSiCl_2$[a]	−2.6[d]	MeCN, Et_4NClO_4, Pt	[109]
10	$nHexMeSiCl_2$[a]	−2.9[d]	MeCN, Et_4NClO_4, Pt	[109]
11	$cHexMeSiCl_2$[a]	−3.2[d]	MeCN, Et_4NClO_4, Pt	[109]
12	$PhMeSiCl_2$[a]	−3.1[d]	MeCN, Et_4NClO_4, Pt	[109]
13	Ph_2SiCl_2[a]	−3.0[d]	MeCN, Et_4NClO_4, Pt	[109]
14	Ph_3SiF[b]	−2.2[e]	THF, Bu_4NI, dme	[110]
15	Ph_3SiCl[b]	−2.0[e]	THF, Bu_4NI, dme	[110]
16	Ph_3SiBr[b]	−1.9[e]	THF, Bu_4NI, dme	[110]
17	Ph_3SiCl[a]	−3.1[d]	DME, Bu_4NClO_4, dme	[48]
18	Ph_3GeCl[a]	−2.8[d]	DME, Bu_4NClO_4, dme	[48]
19	Ph_3SnCl[a]	−1.6[d]	DME, Bu_4NClO_4, dme	[48]
20	Ph_3PbCl[a]	−1.4[d]	DME, Bu_4NClO_4, dme	[48]

DME = 1,2-dimethoxyethane, DMF = N,N-dimethylformamide, OTs = $H_3CC_6H_4SO_2^-$, THF = tetrahydrofuran, GC = glassy carbon, MeCN = acetonitrile, dme = dropping mercury electrode, [a] Value of E_p [b] Value of $E_{1/2}$ [c] measured vs. SCE [d] vs. 0.001 M $Ag/AgClO_4$, converted to SCE by the respective author [e] referenced to sat. Ag/AgI, converted to SCE (−0.44 V vs. SCE) by the respective author.

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However, for future CV studies, it would be a good practice to check whether hydrolysis resulted in HCl formation. In addition to prior Karl-Fischer titration of the electrolyte,[61,70] it is very easy to show in-situ by cyclic voltammetry whether HCl formation has occurred.[38,115] For this purpose, the start of the CV is selected in the oxidative regime. If no oxidation potential of chloride can be detected in the first run, the subsequently measured reduction signals are independent of HCl. In the second cycle an oxidation signal of chloride should be visible, caused by reductive cleavage of the Si–Cl bond.[38,115] The same applies to synthesis. Here a pre-electrolysis at low potentials, if conducted by potentiostatic means or with low applied charge until cathodic hydrogen gas evolution ceased, if conducted via galvanostatic conditions is generally used to remove traces of HCl.[43,58,82–84,99,106,116,117] The disiloxane species formed via hydrolysis are generally non-reactive towards further electrochemical conversions.

3. Electrochemical silane synthesis

The electrochemical synthesis of silane species started in the 70's with the reductive coupling to form Si–Si bonds by Hengge and Litscher.[96] This easy and controllable alternative to the hitherto known Wurtz-type pathway was especially useful for the conversion of chlorosilanes. Instead of using alkali metals for the desired conversion towards the Si bond formation, electrons could be applied as reagents leading to mild reaction conditions. Since their pioneering discovery, much has developed in the field of reductive as well as oxidative synthesis. In the following, we will give a brief overview of various possibilities, as well as recent advances achieved via new and exciting synthetic aspects, especially regarding the field of mediated electrochemistry.

3.1. Cathodic conversion

For the reductive coupling of halide species towards Si bonds, two possibilities arise. Reduction of the halosilane itself (Scheme 4, a) or of an organic halide with trapping of the nucleophilic intermediate by the electrophilic halosilane (Scheme 4, b). The course of reaction depends on the presence of organic moieties with sufficient reduction potential, as well as appropriate stability of the carbanion for selective nucleophilic attack at the halosilane.

While the reduction of organic substrates generally results in the formation of a carbanion, the state of reduction of halosilanes is a frequently discussed topic and depends on stabilization of the intermediate and presence of trapping agents, as unsaturated hydrocarbons,[118] as we will see later. As mentioned, it is difficult to discuss mechanistic aspects based on cyclic voltammograms alone, which is why attempts were made to convert two chlorosilane species with different reduction potentials in the same cell (Scheme 4, c). Formation of the radical anion (pathway **I**) should lead to only the dimer of the more easily reducible substrate under cleavage of
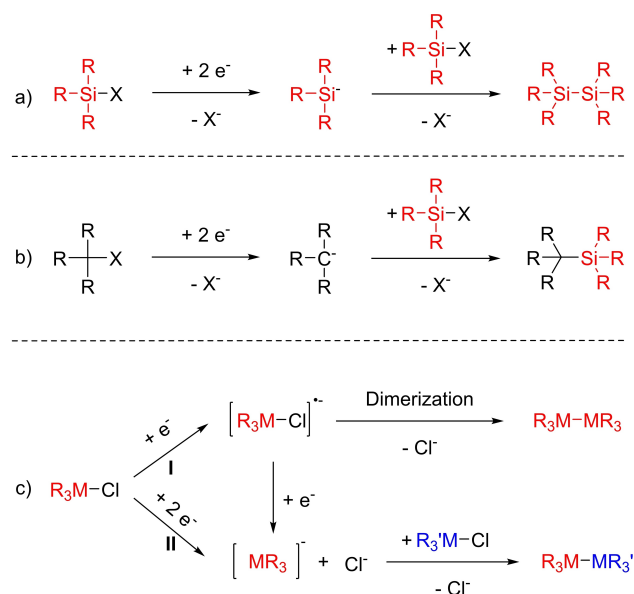
Scheme 4. Pathways for the cathodic conversion of halosilanes: a) reduction of the halosilane species, b) trapping of an electrogenerated carbanion by a halosilane, c) discussed electrochemical pathway of radical anion vs. anion (M = Si, Ge).[56,58,81,97]

chloride. The anionic 2-electron process (pathway **II**) would form a mixture of dimers arising from both chlorosilanes due to trapping of the formed silyl anion nucleophile. However consecutive reduction of the radical to the anion at the electrode surface is possible. In independent studies, Hengge and co-workers,[81,97] as well as Kashimura and co-workers,[56,58] could show with different sacrificial anodes and electrolytes that the mixed dimer is the only product arising, clearly indicating the anionic pathway or very fast consecutive reduction in the absence of trapping agents. In analogy synthetic approaches by electrolyzing a mixture of chlorosilanes and -germanes at increasingly cathodic potentials were conducted.[110] With germanium species being able to form radicals (pathway **I**), the selective dimerization to Ge–Ge bonds can be achieved. Choosing more negative cathodic potentials, Ge is further reduced to the anionic form (pathway **II**), generating Ge–Ge and Ge–Si bonds by nucleophilic attack of the respective electrophilic species.

3.1.1. Si–Si bond formation

The general idea of reductive access to Si–Si bonds via conversion of halosilanes is straightforward, given the effects mentioned above. The simplest product to achieve is via a dimerization reaction of monochlorosilanes (Scheme 4, a). Although the reduction potential of Me$_3$SiCl is still unresolved, dimerization to Me$_3$Si–SiMe$_3$ has been shown using electrolyte compositions with high cathodic stability such as THF, HMPT and DME in combination with low coordinating supporting electrolytes such as Bu$_4$NClO$_4$, Et$_4$NBF$_4$ or LiClO$_4$ at sacrificial,[58,96,119,120] as well as inert anode materials.[63,76,121] In

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Review
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addition to the symmetric dimerization of Ph$_3$SiCl,[40,58,76,81,96,110] Me$_2$PhSiCl,[56,73,79] MePh$_2$SiCl,[47,58,79] HMe$_2$SiCl,[67] HPhMeSiCl,[67] HPh$_2$SiCl,[67] H$_2$PhSiCl,[67] and alkoxychloro-silanes,[59] various asymmetric disilanes were prepared in high yields in undivided cells using the sacrificial anode technique.[79,97] Usage of hydro-chlorosilanes enables easily further product functionalization. The dimerization of organofunctional chlorosilanes possessing amine groups were so far unsuccessful due to very high reduction potentials, exceeding the electrolytic stability.[67] However, different approaches via reductive mediation of chlorosilanes have been attempted to lower the reduction potential for the desired conversion. Phosphonium salts,[38] nitrobenzene derivatives,[38] and aromatic compounds,[38,43,115] constitute possible substrates as redox mediators. They exhibit the typical CV characteristics of active mediators. A reversible cathodic potential is detectable, due to the generation of a radical anion that is significantly less negative than the chlorosilane to be converted (Scheme 5). Further, by the addition of chlorosilane, the reversibility of the mediator signal disappears, and the current density rises, indicating electron transfer from the mediator radical anion to the chlorosilane.

The general idea of redox mediators is the convenient generation of a redox active species, here the radical anion Q by reduction of the mediator starting material P (Equation 1). This generated radical anion transfers the electron to the actual substrate, here a chlorosilane, in a chemical reaction step and is itself oxidized back to P in the process (Equation 2). In a stepwise reaction, cleavage of chloride occurs with generation of the desired substrate radical species (Equation 3), to allow for further dimerization.

$$P + e^- \leftrightarrow Q \tag{1}$$

$$R_3SiCl + Q \leftrightarrow [R_3SiCl]^{\bullet-} + P \tag{2}$$

$$[R_3SiCl]^{\bullet-} \rightarrow [R_3Si]^{\bullet} + Cl^- \tag{3}$$

One challenge in the study of mediators is the hydrolysis of chlorosilanes. In some cases after only a few minutes,[38] the
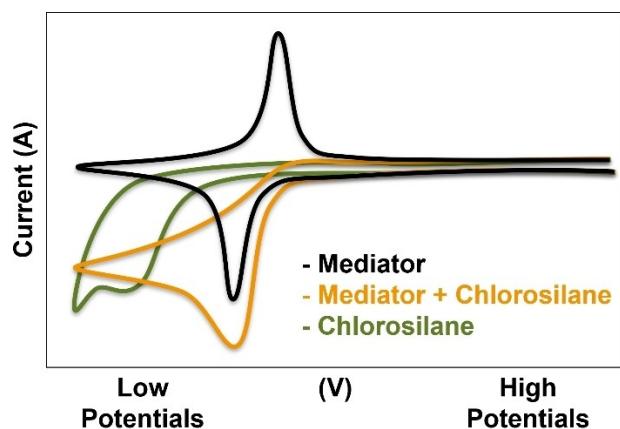
mediator shows reductive reversibility again, since electron transfer to the hydrolyzed silane is no longer possible. Instead of equation 2, re-oxidation of the radical anion Q back to P takes place (Equation 1). In particular, sterically non-hindered alkylchlorosilanes are very sensitive to hydrolysis, so that they have not yet proved suitable for this mediated bulk electrolysis. Another obstacle is the high electrophilicity of chlorosilane species. As shown by Jouikov and co-workers,[43] in competition with the pure electron transfer, substrate-mediator addition may occur (Equation 4).

$$R_3SiCl + Q \rightarrow R_3SiQ + Cl^- \tag{4}$$

Even with poorly nucleophilic delocalized anion radicals as anthracene, and further aromatic derivatives, this reaction is highly efficient. Si–C bond formation to the mediator occurs in high yield with subsequent (di-)silylation of the mediator as the main reaction (Scheme 6), allowing the desired dimerization of chlorosilanes only in traces. Depending on the selected mediator, Si–N bond formation as for benzonitrile due to negative charge localization on the N atom can occur. Si–O bond formation of the oxophilic chlorosilane with used methyl benzoate as mediator is another possibility. By choosing more sterically demanding chlorosilane species as t-BuMe$_2$SiCl, the desired electron transfer is dominating compared to S$_N$-like nucleophilic addition. Simultaneously, the high bulkiness of the chlorosilane results in H-abstraction by the reduced silyl species with formation of Si–H bonds instead of the dimerization to Si–Si bonds.[43]

Apart from mediated techniques, sacrificial anodes, especially Mg are taking a special role in the chlorosilane conversion. In the dimerization of Me$_2$PhSiCl shown by Ishifune and co-workers,[73] the presence of an active Mg species is essential for the conversion. In absence of Mg no product is formed, while pre-electrolysis to provide Mg for further reduction at Pt electrodes enables the dimerization. However, pre-electrolysis to generate Mg and addition of the chlorosilane under current-less conditions also forms the dimer in low yields, indicating the Grignard-type conversion in some cases with Mg electrodes. Using the sacrificial anode technique, formation of metal chlorides at the anode surface may increase the electrical resistance, therefore the use of ultrasonication in a symmetrical electrode setup with switching polarity to remove the metal

Scheme 5. Schematic mediator functionality, visible in a typical CV measurement.[43]
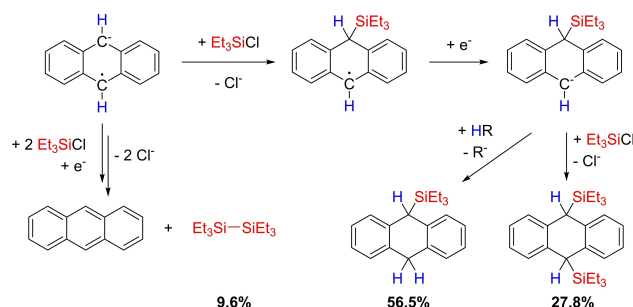
Scheme 6. Undesired silylation of the anthracene redox mediator as main reaction with the use of chlorosilane substrates.[43]

ChemElectroChem

Review

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chloride surface layer of the electrode,[120] as well as additional supporting electrolytes,[119] are some used tricks to provide high conductivity and generate high product yields.

Entering the field of dichlorosilanes, so far only the use of sterically highly demanding mesityl groups results in dimerization,[122] allowing the special case of a Si=Si double bond. Aside this rarity, the additional degree of freedom by the use of dichlorosilanes results in Si–Si chain formation. By selective mixing of di- and monochlorosilanes, with the monochlorosilanes present in significant excess as chain terminators, synthesis of oligosilanes in various chain lengths can be achieved. The first representatives to be obtained are the corresponding trisilanes via end capping of a dichlorosilane by monochlorosilanes.[56,79,81,87,94,123] Accordingly, tetrasilanes are achieved via the dimerization of monochlorodisilanes,[94] or by end capping of dichlorodisilanes.[56,58] Pentasilanes are accessible via reductive conversion of dichloromonosilanes and monochlorodisilanes.[94] Using hydrochlorosilanes as end capping agents, the resulting H-terminated oligosilanes can be functionalized for further Si–Si elongation. As shown by Ishifune and co-workers,[87] and Kashimura and co-workers,[56] chlorination with benzoyl peroxide (BPO) and carbon tetrachloride yields dichlorotrisilanes, which can be further elongated to pentasilanes according to the same procedure of reductive elongation (Scheme 7).[56]

However, oligosilanes consisting of only the sterically demanding Ph_2Si units tend to cyclization and the formation of $[Ph_2Si]_4$,[76,97] instead of linear products as for methylated or mixed sterically demanding silanes. By analogy, cyclic methylsilanes such as $[Me_2Si]_5$ or $[Me_2Si]_6$ can also be obtained by significant lowering of the concentration of the starting material.[76]

In non-diluted systems in the absence of monochlorosilanes as chain terminators, reduction of dichlorosilanes results in polysilane formation.[67] Mechanistically, the process is comparable to the previous reductive Si–Si bond formation, with reduction of the substrate to the anion and nucleophilic attack on another chlorosilane.[124] As shown by Okano and co-workers,[51] the polysilane synthesis proceeds from the reduction of the monomeric species with the formation of dimers and short-chain oligomers (Scheme 8, a). The extension of the Si–Si backbone results in easier reducibility, so that further chain elongation to polysilanes starts from oligomeric structures. At the same time, the Si–Si backbone can be reductively cleaved again to generate anionic intermediates as an undesired side reaction (Scheme 8, b),[51,125] a process becoming more domi-
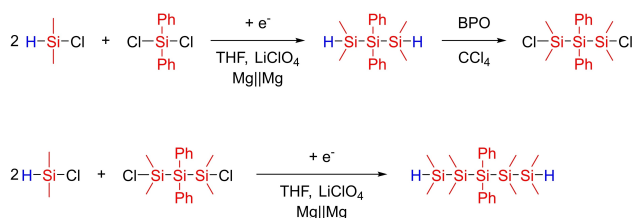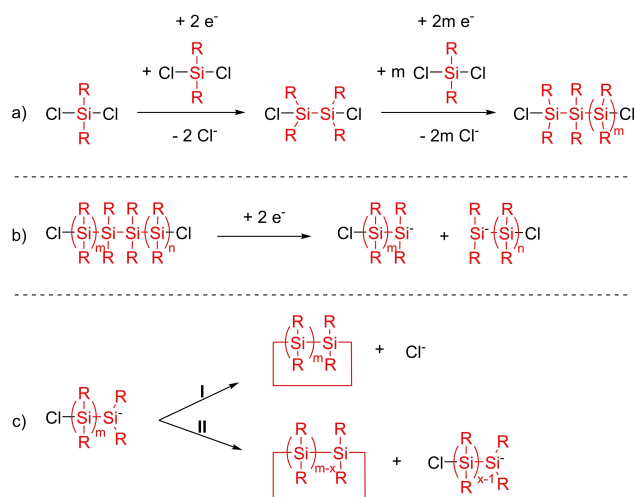
Scheme 8. Mechanistic details on the formation of polysilanes starting of dichlorosilanes:[51,56,125,126] a) formation of di- and oligosilanes via reductive transformation, b) reductive cleavage of polysilanes to anionic intermediates, c) "back-biting" reactions with the cleavage of chloride (**I**) or anionic oligosilanes (**II**).

nant with increasing chain length. In addition, "back-biting" reactions can occur above a certain chain length, with termination of the chain growth by ring closure (Scheme 8, c), with cleavage of chloride via path **I** or cleavage of an anionic oligosilane via path **II**.

With dichlorodisilanes and -oligosilanes as starting material, "back-biting" reactions dominate the early stage of reaction and cooling of the reaction to 0 °C is needed to shift the kinetics towards chain elongation instead of ring closure.[56,126]

Especially in the synthesis of polysilanes, stabilization of the anionic polysilane intermediate plays a crucial part of the desired reaction. Polarity of the solvent,[47,51,52,127] as well as cationic species help to generate long chain polysilanes. Therefore, Mg as sacrificial anode material and subsequent as Mg^{2+} solvated species shows not only outstanding performance relating to yield and chain length,[56,58,85,128,129,130] but does allow the product formation in some cases in the first place.[58] Again, to prevent coating of the anode material, sonication,[56,129,131] as well as switching polarity,[56,80,129,131] are established methods. As Kunai and co-workers showed,[47] the combination of polar solvents, low coordinating supporting electrolytes, high substrate concentration and high applied charge can achieve polysilanes with molecular weights exceeding 100 kDa, outperforming the Wurtz-type polysilane formation. In special cases polysilanes can be generated in the absence of a solvent, using only the dichlorosilane monomer with a complexing agent, such as HMPT, to solubilize the anodic generated metal chloride.[91] The less toxic tris(N,N-tetramethylene) phosphoric triamide (TPPA) might be a suitable stabilizing agent as well, as shown in the synthesis of organosilicon compounds.[132] The synthesis of functionalized polysilanes with more challenging side chains, such as hydroxy-related,[56,123] or vinyl groups,[133] not accessible via the Wurtz route, can be achieved via the mild electrochemical reduction with molecular masses above 16 kDa.

Scheme 7. Synthesis of oligosilanes via reductive coupling, followed by chlorination of hydrosilanes, BPO = benzoyl peroxide.[56,87]

The same applies for the convenient synthesis of block copolysilanes with Mg sacrificial anodes.[130,131,134]

Changing the reactant to trichlorosilanes provides access to polysilane networks. Defined structures with high molecular masses of up to over 60 kDa and good optical properties in the visible region can be achieved for sterically demanding silanes with octyl,[135] butyl,[135,136] *t*-butyl,[136] phenyl,[136,137] and *c*-hexyl groups,[136] inaccessible via Wurtz reaction. Polymeric networks were also generated with sterically low demanding silanes such as MeSiCl$_3$,[136] HSiCl$_3$[97] and SiCl$_4$[97] in DME. Further information on the synthesis of polysilane structures can be found in additional literature.[29]

Choosing high cathodic potentials in a potentiostatic setup with perchlorinated chlorosilanes, reductive transformation up to the deposition of elemental silicon can be achieved. So far, the amorphous film thickness is still in the range of some µm.[105,111,113,138] However, electrodeposition of silicon at different electrode surfaces at room temperature is in the focus of research, and already covered by comprehensive reviews.[31–34]

Scheme 9. Multiple silylation of perchlorinated alkanes (STST = stainless steel):[82] a) selective monosilylation of CCl$_4$ via Zn anode, b) enabling the disilylation of CCl$_4$ via Mg anode, c) successful tri- and tetrasilylation of CCl$_4$ via Al anode.

3.1.2. Si-C bond formation

As mentioned earlier, reductive coupling with halosilanes to form Si–C bonds yielding organosilanes typically originates from organic halides. In the course of the reaction, these organic halides are reduced to the respective carbanions, acting as strong nucleophiles to attack the electrophilic halosilanes. This nucleophilic trap functionality has long been considered to be the only role for halosilanes in cathodic Si–C bond formation,[25] exhibiting a wide repertoire of examples.[24] However, we will highlight additional possibilities for the reductive conversion towards organosilanes below.

This conceptual summary will start with the general principles of the classic nucleophilic trap function. Depending on the organic substrate, it is possible to achieve multiple silylation at an organic halide. As shown by Pons and co-workers,[82] choosing the organic halides CCl$_4$, CHCl$_3$ and CH$_2$Cl$_2$ mono-, di-, tri- and tetrasilylation in polar solvents as DMF and TMU are accessible. However, care must be taken regarding the choice of anode material using the sacrificial anode technique, due to the reduction potential shift of the silylated organic halide. Starting with CCl$_4$ the monosilylation with Me$_3$SiCl as nucleophile trap is possible at a Zn anode in excellent yields and selectivity (Scheme 9, a). The same applies for fluorohalo-carbons, as shown by Martynov.[92] However, to achieve a higher degree of silylation, the anode material must be changed, otherwise coating of the cathode with Zn metal occurs.[82] With Mg as anode material, disilylation is possible with 68% yield, by doubling the applied charge compared to the monosilylation (Scheme 9, b). For the tri- and tetrasilylation, Al is a suitable sacrificial anode material, leading to about 60% of (Me$_3$Si)$_4$C (Scheme 9, c). A comparable result is obtained for the use of CHCl$_3$ and the corresponding mono-, di- and trisilylation depending on the anode material. Silylation of the high cathodically reducible CH$_2$Cl$_2$ is more challenging and HMPT as
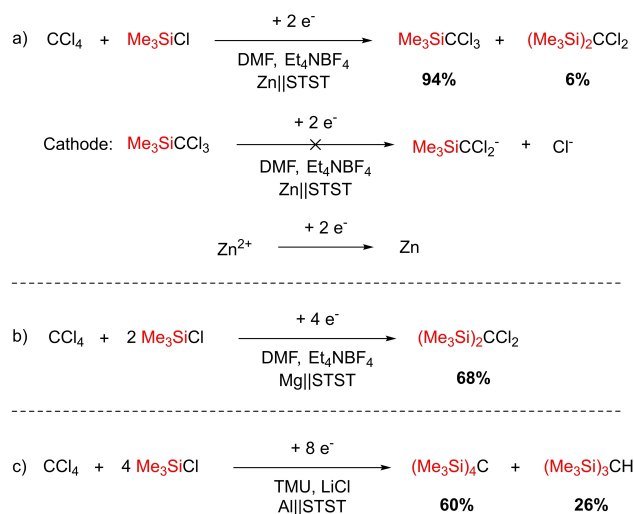
additional complexing agent needs to be used with an Al anode for the desired conversion.

Analogue, Bordeau and co-workers have shown,[116] that multiple silylation of the aromatic system of aryl halides is possible. After monosilylation of PhBr to PhSiMe$_3$, the use of Al as sacrificial anode with HMPT as additional complexing agent allows for the partial reduction of the aromatic ring, generating a strong carbanion to be trapped by Me$_3$SiCl, yielding the tri- and pentasilylated cyclic (di)enes (Scheme 10, a). The same applies for the multiple silylation of *o*-dichlorobenzene by Biran, Bordeau and co-workers.[139] Again, the combination of Al sacrificial anode material and additional HMPT complexing agent allows selective mono-, di- and tetrasilylation, first by
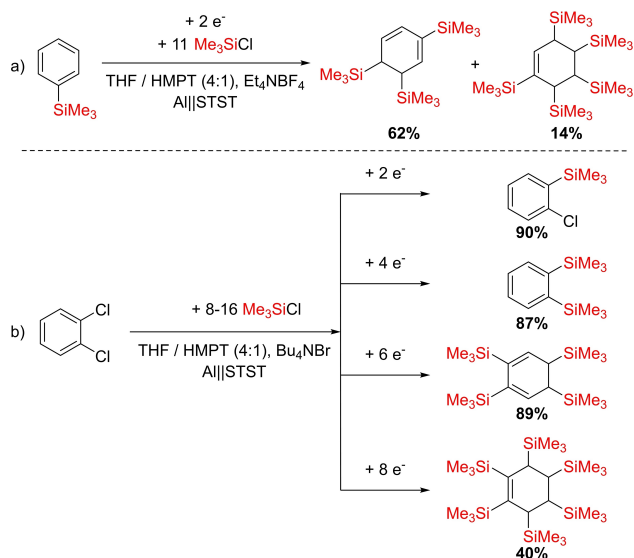
Scheme 10. Multiple silylation of aromatic systems (STST = stainless steel): a) di- and tetrasilylation of the aromatic system of trimethylphenylsilane,[116] b) mono-, di-, tetra-, and hexasilylation of *o*-dichlorobenzene.[139]

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reduction of the C–Cl bond and further by partial reduction of the aromatic ring (Scheme 10, b). Even hexasilylation can be achieved in yields of 40%, however with increasing reduction potential, side reactions for the overreduction of electrolyte components rise.

Conversely, multiple silylation can also be achieved by using a di- or perchlorosilane. As shown by Jouikov and co-workers,[117] the reduction of α,ω-dihalides with methylated and vinylated dichlorosilanes using an Al anode leads to the formation of cyclic silanes. Respective compounds can also be obtained without sacrificial anode, but with the sacrificial electrolyte DMF in a divided cell. While silacyclopropyl derivatives are inaccessible due to the high ring tension, corresponding silacyclobutyl, especially -pentyl, -hexyl and also -heptyl systems can be generated in particular with α,ω-dibromides (Scheme 11). However, reduction potential of the organic dihalide rises with increasing chain length. The use of α,ω-
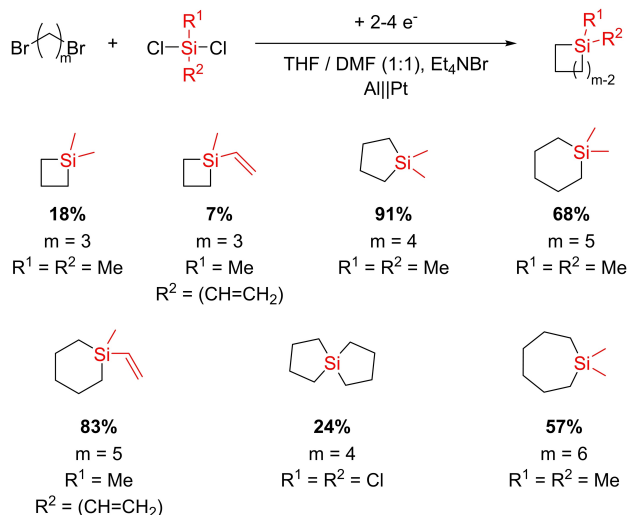
Scheme 11. Multiple silylation of α,ω-dibromides with di- and tetrachlorosilanes leading to cyclic silanes.[117]
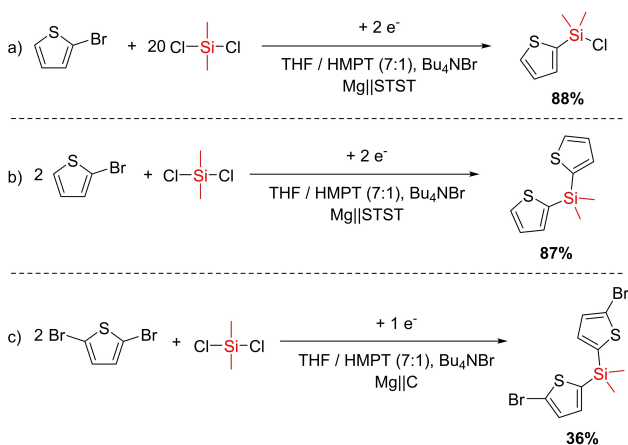
Scheme 12. Selective silylation of mono- and dihalothiophenes with dichlorosilanes (STST = stainless steel): a) with retention of Si–Cl bond,[84,99] b) complete conversion of dichlorosilane,[84] c) retention of C–Br bond after reductive silylation.[83]

dibromides, which have suitable reduction potentials, results in the highest yields and even allows dicyclic structures starting from $SiCl_4$ as nucleophile trap. Selectivity can be achieved by the slow generation of nucleophiles, here via low current densities in combination with an excess of chlorosilane. The subsequent ring formation is supported by a 5- or 6-coordinated transition state.

Comparably, the reduction of halothiophenes with dichlorosilanes as nucleophilic traps leads to the respective silylation, as shown by Biran, Bordeau and co-workers.[83,84,99] Again, the sacrificial anode technique, here with the use of Mg as most promising material in an electrolyte with additional HMPT as complexing agent was used. Applying the above-mentioned principles,[117] low current densities of 1 mA/cm² in combination with an twentyfold excess of dichlorosilane are favored to yield the single silylated product with retention of one Si–Cl bond (Scheme 12, a).[84] Changing the substrate ratio to 2:1 of halothiophene to dichlorosilane, results in dual Si–C bond formation to the thiophene species (Scheme 12, b). In the conversion of dihalothiophenes, low current densities and applied charge allowed the retention of C–Br bond after single silylation (Scheme 12, c). However, it should be noted, that Faradaic yields are fare above 100%, indicating a Grignard-type influence on the conversion.[83,84]

As Bordeau and co-workers showed,[140] even more difficult substrates are accessible with this technique. Via the use of a sacrificial anode based on Al and HMPT complexing agent, the silylation of ethyl trifluoroacetate to the respective ethyltrimethylsilyl ketal could be achieved (Scheme 13). Low temperatures of −25°C and a fifteenfold excess of chlorosilane were needed to favor the formation of the desired ketal over the silylation of the trifluoro substituent.

While halothiophenes, especially bromothiophenes, show a reduction potential in the low reductive range, p-substituted halobenzenes are much more difficult to reduce. For the single Si–C bond formation high excess of dichlorosilane is needed. However, due to similar reduction potentials of halobenzenes and dichlorosilanes, the excess of dichlorosilane leads to polysilane formation as main reaction. To specifically target the halobenzenes, Bordeau and co-workers,[99] applied a redox mediator system for the reductive Si–C bond formation. Instead of the organic moieties, seen in the reductive formation of Si–Si bonds,[38,43,115] a Ni(0) redox mediator was used here. An excess of 2,2'-bipyridine (bipy) was applied, as has been shown promising in the reductive coupling of allyl chlorides and α-chloro esters with carbonyl compounds.[141] The reduction potential of the $Ni(bipy)Br_2$ is at an easily achievable −1.2 V vs. SCE compared to the reduction of the desired p-bromoanisole with −2.45 V vs. SCE.[99] Via the mediated technique, the
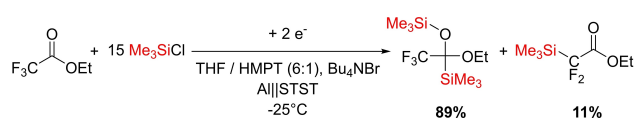
**Scheme 13.** Selective silylation of ethyl trifluoroacetate to the respective ethyltrimethylsilyl ketal (STST = stainless steel).[140]

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conversion of starting material could be increased from the non-mediated 13% to 98%, with very good isolated yield for the silylated anisole (Scheme 14). This technique further allowed the successful reductive coupling of haloaryls, halopyridines and halofurans with chlorosilanes to organofunctional silanes.[99] However, the mediator system faces its limitations when the reduction potentials of mediator and substrate compete, i.e. by NO_2-substituted aryls.

The use of easily reducible organic substrates that show high stabilization of the resulting carbanion, such as allyl,[53–55] benzyl,[53] vinyl,[54,55] and some aryl systems,[54,55] allows the avoidance of additional stabilizing components such as Mg^{2+} or HMPT at high current densities of up to 75 mA/cm². Redox mediators for selective silylation and even the sacrificial anode technique can be omitted for these substrates. Instead of the oxidized metal, the solvent DMF scavenges the oxidized chloride, unless substrates without electron-withdrawing groups are used in an undivided cell. Product chlorination occurs in this case (Scheme 15, a). However, high amounts of applied charge are needed for the conversion, especially in the undivided cell (Scheme 15, b), indicating side reactions of the chlorinated electrolyte. In contrast, Pons and co-workers,[49]
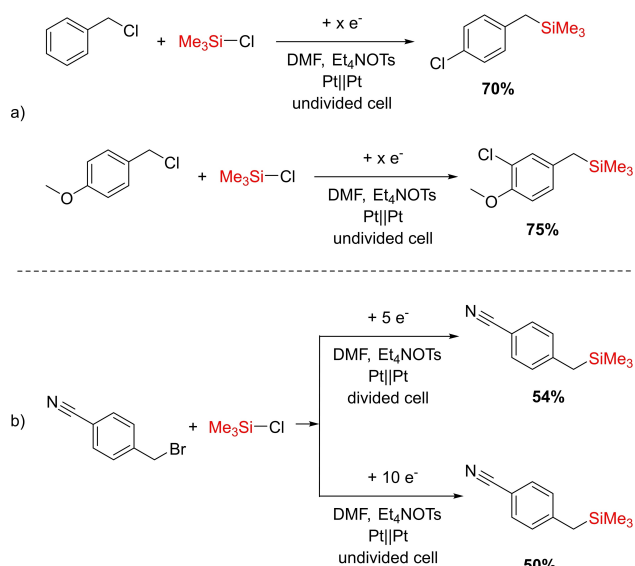
were able to show silylation of benzyl halides without chlorination as a side reaction with a lower amount of charge using the sacrificial anode technique. As Kawabata and co-workers demonstrated,[54,55] in addition to the use of organic halides, acetoxy, carbonate or sulfone compounds are conceivable for the formation of carbanions, although with lower yields. However, chloro- and hydrochlorosilanes are the sole possible nucleophile traps for the desired conversion so far.

Grogger and co-workers,[57] achieved the formation of further organofunctional silanes starting from hydrochlorosilanes via the Mg sacrificial anode technique. However, due to the equilibration reaction of hydrochlorosilanes by tetraalkylammonium cations as mentioned earlier (Scheme 2, b), a suitable supporting electrolyte needs to be used. The 2:1 mixture of LiCl and $MgCl_2$ in THF represents an interesting special case here. The conductivity is increased by a factor of 100 compared to the individual components, due to ion aggregation with the low dissociating $MgCl_2$, shifting equation 5 to the right:

$$Li^+ + MgCl_2 \leftrightarrow [ClMgClLi^+] \tag{5}$$

Suppression of the equilibration reaction is achieved. Further the conversion of the alkoxysilane $Me_2Si(OMe)_2$ as nucleophile trap could be successfully conducted for different organic halides. However, a Grignard effect for organic bromides results in significantly lower necessary applied charges.
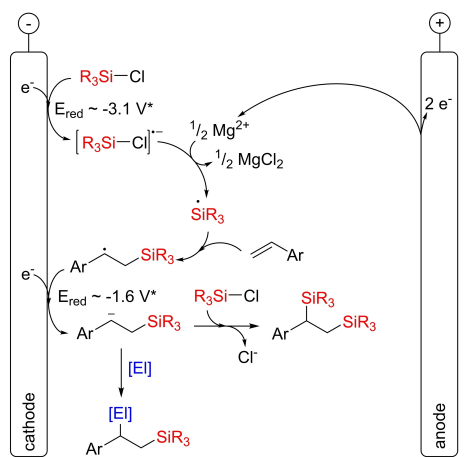
Leaving the realm of nucleophilic trapping functionality of chlorosilanes, the situation is reversed. In the presence of an organic unsaturated hydrocarbon, the reduction takes place at the halosilane, being subsequently trapped by the unsaturated hydrocarbon species. As Ohno and co-workers demonstrated,[89] via this reductive pathway the β-silylation of different aryl acrylates, nitriles and ketones could be achieved in yields up to 79% (Scheme 16). The use of sacrificial anodes, especially Mg is mandatory for the conversion. This indicates a necessity of the stabilization of the silyl intermediate by suitable cations like Mg^{2+}.

However, no mechanistic details were unraveled at that time. In this regard, Lin and co-workers,[88] have recently published an exciting mechanistic elucidation. By using alkenes and alkynes as unsaturated hydrocarbon species for the

Scheme 14. Ni(0) redox mediator for the reductive conversion of halobenzenes as p-bromoanisole and Me_2SiCl_2, generating higher conversion and yield (STST = stainless steel).[99]

Scheme 15. Silylation of benzylic halides: a) chlorination of the product as side reaction in absence of a sacrificial anode in an undivided cell,[53] b) high applied charge needed for the conversion in absence of a sacrificial anode in an undivided cell.[53]

R = H: 79%
R = OMe:79%
R = Me: 76%
R = Cl: 70%

R = 1-Naphthyl: 34%
R = 2-Naphthyl: 48%
R = 2-Furyl: 72%
R = 2-Thienyl: 59%
R = 3-Thienyl: 60%

R = CN: 70%
R = COMe:68%

77%

Scheme 16. Silylation of unsaturated hydrocarbon species by the reduction of chlorosilanes via the Mg sacrificial anode technique (STST = stainless steel).[89]

trapping reaction of reduced silyl intermediates, a wide range of mono- and disilylated products could be obtained. High tolerance towards functional groups as boronates, tertiary amines, thioethers, alcohols and ketones, was reported by the described technique. Although they used a different type of electrolyte system (THF/Bu$_4$NClO$_4$) compared to the work of Ohno and co-workers (DMF/Bu$_4$NBr),[89] the subsequent silylation of unsaturated hydrocarbons with the use of sacrificial anode materials is similar. In their investigation, they clarified that the reaction originates from the chlorosilane. Substrate activation with Mg could be excluded by current-less conditions in the presence of Mg powder. According to the CV data, the potential of the alkene is a significant 0.7 V more negative compared to the cathodic potential of the chlorosilane. Supported by density functional theory (DFT) calculations and radical probe experiments based on the ring opening of a vinyl cyclopropane, the cathodic generation of silyl radicals with Mg assisted cleavage of Cl$^-$ is proposed (Scheme 17). It is assumed that the presence of alkenes or alkynes results in a scavenging reaction of the silyl radical prior to any further reduction to the anion, as observed for the Si–Si bond formation. After the scavenging, a second reduction generates the anionic species. This leads to the subsequent mono- or disilylated product, depending on the availability of further electrophilic species

(El). With weakly acidic substrates, allowing the cleavage of protons as El, such as MeCN, the anionic intermediate is hydrosilylated. Cyclic substrates containing Si–Si bonds could be obtained in high yields by using dichlorooligosilanes, via the "back biting" reaction, referring to the Si–Si bond formation of polysilanes (Scheme 8, c pathway I). The non-appearance of Si–Si bond cleavage in these cases demonstrates the wide range of applicable species.

In a similar work, Kunai and co-workers,[95] studied the addition of dichlorosilanes to an excess of dienes. By the use of a copper sacrificial anode, they generated the respective silacyclopent-3-enes in various electrolyte systems, including THF/Bu$_4$NClO$_4$ as used by Lin and co-workers.[88] Demonstrated by CV studies, the reduction takes place at the dichlorosilane with the diene serving as a trapping reagent. However, they assumed the formation of a silyl anion via two-electron reduction with consecutive ring formation. Given the mechanistic details of Lin and co-workers,[88] it is very likely that the reduction of dichlorosilanes also proceeds via a comparable radical pathway. Presumably, the corresponding silyl radical is scavenged by the diene in this case. Subsequently, reduction to the anion and consecutive ring closure by nucleophilic attack on the electrophilic silane occurs. However, formation of a copolymer via nucleophilic attack at another dichlorosilane was mentioned.

Comparable studies were also conducted by Jouikov and co-workers.[106] Here, Me$_3$SiCl was reduced in the presence of phenylacetylene. CV studies again show that the reduction should occur at the chlorosilane. In this case, the reduction potentials of the two substrates are very close, less than 0.1 V, suggesting a possible additional anionic course. Based on studies of Si–Si bond formation, it is believed that a silyl radical would be immediately further reduced to the corresponding anion. However, experiments in a potentiostatic driven ECE type flow cell (Scheme 18), which allows reduction to the anion and subsequent oxidation to the radical, show that the substrate stoichiometry is crucial for the resulting product. With an excess of chlorosilane, mainly the disilylated product is

Scheme 17. Proposed reaction mechanism of the silylation of unsaturated hydrocarbon species by the reduction of chlorosilanes by Lin and co-workers (top, El = electrophilic species; *vs. SCE), reaction equation, conditions, and yield range of some relevant representatives of the electrochemical conversion (bottom, Bpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl, TIPS = triisopropylsilyl).[88]

Scheme 18. Setup of the ECE type flow cell, to allow radical formation via the potentiostatic driven reduction and subsequent oxidation of substrates by Jouikov and co-workers (P$_1$, P$_2$ = potentiostat; R$_1$, R$_2$ = reference electrode; D = insulating porous diaphragm; C$_1$, C$_2$ = counter electrode; W$_1$, W$_2$ = working electrode).[106]

ChemElectroChem

Review
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obtained. Here, the reaction is assumed to proceed via radical addition to the triple bond, which is consistent with the results of Lin and co-workers.[88] However, if the stoichiometry is changed to a higher amount of alkyne, competition by the anionic route is supposed.

Another exciting publication by Jouikov and co-workers,[142] describes the combination of 2,2'-bipyridine (bipy) complexation of chlorosilanes with the trapping strategy using reactive C=C double bonds. Bipy as an adduct forms a hexacoordinated state with monochlorosilanes (Scheme 19) and chlorogermanes.[143] This results in a redox mediated type of reductive conversion, shifting the reduction potential of bipy by more than 1.0 V into the less negative regime. Electrochemical reduction generates the corresponding radical anion of the complex, which was detected by ESR spectroscopy. After cleavage of chloride, the silyl radical is released from the complex, allowing bipy to be available again for the coordination of monochlorosilanes. In the further course, the silyl radical can be trapped either by α-phenyl-N-t-butyl-nitrone (PBN) to the stable spin adduct, or by reactive C=C double bonds of the glassy carbon (GC) cathode. In the absence of PBN, this results in silylation of the GC surface with a chemically and mechanically stable coating, leading to surface passivation. Thus, the easy and hydrolysis-stable coating of carbon materials can be achieved.

3.1.3. Further reductive Si bond formation

In addition to the Si–Si and Si–C bond formation, further bond types can be obtained via the reductive reaction pathway. These are addressed considerably less frequently in literature and are briefly outlined below. **Si–Ge** bond formation can be achieved via the reduction of halogermanes in the presence of halosilanes, as mentioned earlier. The reaction occurs at cathodic potentials, which allow the reduction via the radical to the anion (Scheme 4, c). The respective germyl anion leads to nucleophilic attack at the halosilane, forming a Si–Ge bond. A variety of Si–Ge bonds,[58,87,110,126] including polymeric products,[56,58,86,87,126] have been achieved in the past via the sacrificial anode technique.

Si–S and **Si–Se** bonds can be obtained in analogy to the discussed nucleophile trapping technique used for Si–C bond formation. As shown by Jouikov and co-workers,[104] the cathodic reduction of a dichalcogenide, e.g. PhSSPh or PhSeSePh, leads to the respective chalcogenide anion (Scheme 20, a). Acting as a strong nucleophile, Si-chalcogenide
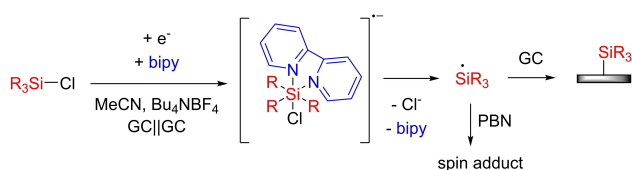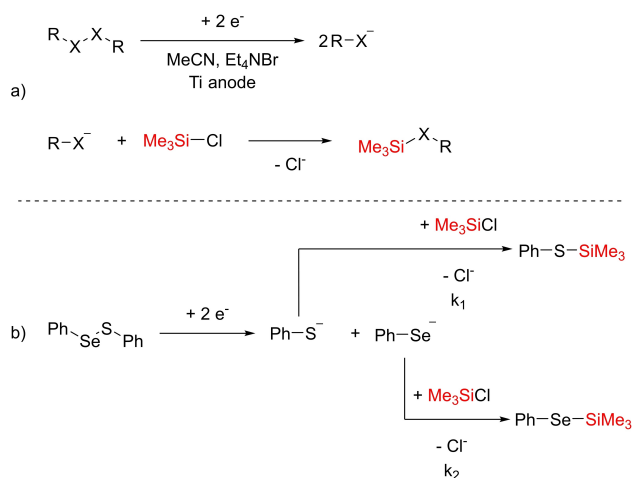
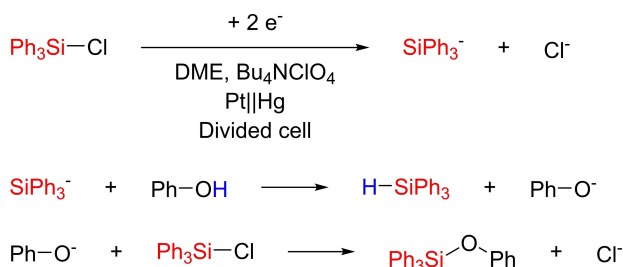

Scheme 20. Reductive silylation of dichalcogenides via the generation of strong chalcogenide nucleophiles (X=S, Se):[104] a) silylation via nucleophilic bond formation by chalcogenide anions, b) kinetic investigations showing the favored Si–Se bond formation due to higher nucleophilicity.

bonds can be formed in high yields. They further investigated reaction kinetics regarding the type of chalcogenide. By the use of PhSSePh as the substrate in large excess, concentration of both species can be neglected, and the order of reaction is similar (Scheme 20, b). By chromatographic observation of the conversion, they concluded that the PhSe$^-$ anion is the stronger nucleophile, achieving one order of magnitude faster Si bond formation for k_2 (Scheme 20, b). This is probably due to the bigger ion size, leading to the disfavoring of π-conjugation with the Ph-group and subsequent higher negative charge localization at Se$^-$.

Si-H bond formation can be achieved via the reduction of chlorosilanes in the presence of an H-donor. In some cases, the electrolyte solvent, such as DME,[48] or MeCN,[41] can be the source of protons and is used as the H-donor, generating electrolytic side reactions. In other cases, the H-donor, e.g. phenol,[110] or a diol,[144] is added as a substrate to provide protons in the course of the reaction. However, especially in the case of phenol, the formation of equimolar amounts of Si-O bonds occurs, due to the formation of PhO$^-$ by proton abstraction. PhO$^-$ represents a nucleophile, being trapped by available chlorosilanes to form the corresponding siloxane (Scheme 21). This reaction is electrochemically directed, as the phenol does not react with Ph$_3$SiCl at room temperature.

Si–O bond formation via reductive conversion has also been addressed in literature. However, the respective reaction pathways are considered special cases which are briefly described in the following. As reported by Jouikov and co-workers,[27,145–148] by electrochemical reduction of oxygen in different aprotic electrolytes, presumably the superoxide anion can be generated as a strong nucleophile in a divided cell. In the presence of reactive dichlorosilanes,[27,145–147] and dialkoxysilanes,[27,146–148] trapping of the above anion occurs, forming the highly reactive silanone intermediate R$_2$Si=O. If short-chain (cyclo)siloxanes are present as trapping reagents, extension of these frameworks occurs (Scheme 22). In the

Scheme 19. Electrochemical generation of detectable silyl radical anions via bipy coordination and subsequent silylation of unsaturated C=C bonds at the glassy carbon (GC) cathode surface.[142]

ChemElectroChem

Review

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Scheme 21. Formation of equimolar amounts of siloxane and hydrosilane in the electrochemical conversion of chlorosilane with phenol.[110]
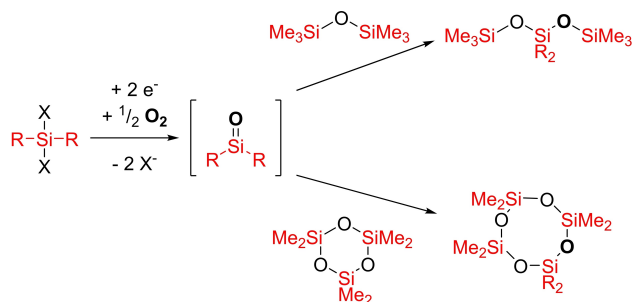
Scheme 22. Electrochemical conversion of chloro- and alkoxysilanes to silanones via the reactive superoxide intermediate as suggested by Jouikov and co-workers (X = Cl, OAlkyl).[27,145–147]

absence of these species, the silanone reacts with itself to form cyclic siloxanes, being available for further Si–O elongation.

Another special case involves the reduction of O_2 in the presence of CO_2, resulting in the formation of the reactive $C_2O_6^{2-}$.[149] By addition of monochlorosilanes, silylcarboxylic acids are obtained, dichlorosilanes are converted to cyclic siloxanes. However, the electrochemical conversion occurs here only for the preparation of the precursor molecule $C_2O_6^{2-}$, further silylation can be achieved via current-less conditions.

A further example of Si–O bond formation is the preparation of silyl enol ethers by electrochemically generated bases (EGBs).[150] Reduction of 2-pyrrolidone as a pre-base using the Mg sacrificial anode technique yields the Mg-stabilized base at temperatures of −75 °C. Addition of a ketone forms the Mg enolate, which is further trapped by an excess of Me3SiCl. Here again, the electrochemical reduction is not applied for silylation, but for the preparation of the reactive precursor. The synthesis of silyl ethers is comparable,[151] with aldehydes and ketones serving as EGBs via reduction to the alkoxide anion. In this case, initial amounts of 0.05–0.5 F are sufficient, due to a catalytic cycle, generating the silyl ether compound.

In another special case, Me3SiCl serves as a promoter for the hydrocoupling of α,β-unsaturated esters with aldehydes and ketones.[108] While the role of the chlorosilane is not clarified, an activation of the carbonyl compounds is suspected.

Si–Fe bonds could be prepared by the Mg sacrificial electrode technique.[152–154] In this process, cyclopentadienyl iron(II) dicarbonyl dimers (Fp2) are reduced in the presence of chlorosilanes as nucleophile trapping agents in a THF/Bu4NBr electrolyte (Scheme 23). While the respective substrates con-
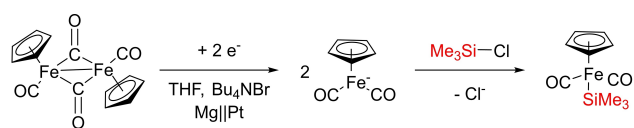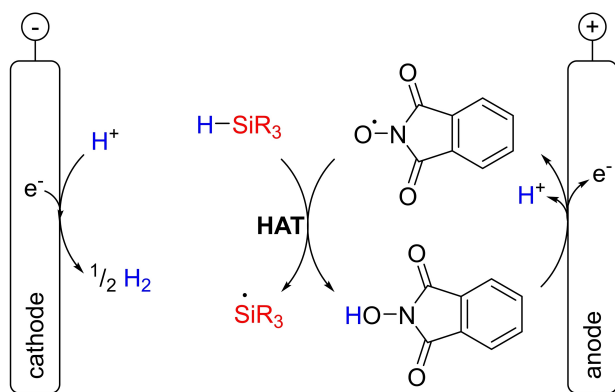

Scheme 23. Electrochemical Si–Fe bond formation via the generation of a strong Fp⁻ nucleophile being trapped by the chlorosilane.[152–154]

taining Si–Fe bonds could be isolated and crystallized, the reaction is shown to proceed slowly even in the current-less state, suggesting Grignard-type contribution in the reaction.

3.2. Anodic conversion

The anodic oxidation of silanes takes up a special role in literature. In contrast to the strongly electrophilic character of halosilanes, the desired bonds cannot be formed in the anodic conversion in the same diversity as is accessible for halosilanes by generating a nucleophile and subsequent trapping. Depending on the reaction conditions, oxidative conversion can be initiated via either the cationic or radical reaction pathway. Since hydrosilanes as starting compounds usually exhibit high oxidation potentials,[69,155] direct oxidation corresponds to relatively harsh reaction conditions that limits functional group tolerance, generating high reactive and strong electrophilic silyl cations.[156] Together with the more expensive and narrower range of available substrates compared to chlorosilanes, the electrochemical oxidation of hydrosilanes has been scarcely studied for a long time. This results in a much smaller number of publications on the subject compared to the cathodic conversion of halosilanes. However, the anodic approach to organosilanes is important from both a structural and technical point of view, due to the possible elimination of sacrificial anodes.[70] The oxidation of organosilanes for the synthesis of organic molecules, by cleavage of a "silyl super proton" is beyond the scope of this review and has been addressed in other work.[24,25]

In recent years, mediated strategies have developed in addition to the direct oxidation technique,[157] and have been adopted to the hydrosilane mediation. Here, oxidation of a mediator substrate, for example N-hydroxyphthalimide (NHPI), generates a reactive radical species in this case phthalimido-N-oxyl (PINO) (Scheme 24). By a hydrogen atom transfer (HAT) reaction with a hydrosilane, the silyl radical can thus be generated under mild reaction conditions, which in the further process either initiates a radical reaction or is itself oxidized to the cation due to the shift of the oxidation potential. While the purely radical reaction pathway has already been highlighted in a recent review,[35] synthetic tricks and electrochemical techniques that allow both radical and cationic conversion starting from hydrosilanes are presented below.

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Scheme 24. NHPI/PINO mediated electrochemical oxidative transformation of hydrosilanes to silylradicals.[69,72,155]

3.2.1. Si-Si bond formation

The foundation for the oxidative Si–Si bond formation was laid by Kunai and co-workers in 1993.[60] They investigated the conversion towards disilanes starting from hydrosilanes in a DME/Bu$_4$NClO$_4$ electrolyte at platinum electrodes. In their work they demonstrated that hydrosilanes such as Me$_2$PhSiH can be oxidized at a GC anode at high potentials of 2.2 V vs. SCE. Presumably, the silyl cation is formed via a 2-electron oxidation and stabilized by the perchlorate anion of the supporting electrolyte (Scheme 25). Diffusion of the stabilized intermediate to the cathode and subsequent reduction is possible. The backwards reduction, probably to the silyl radical allows the corresponding dimerization (Scheme 25, **I**). Direct conversion to the corresponding disilane occurred in a yield of only 7.0% with an applied charge of 4.4 F. Parallel to the desired reduction, decomposition of the perchlorate supporting electrolyte anion is also possible (Scheme 25, **II**), resulting in the formation of the corresponding disiloxane in 15% yield. To increase the yield of the disilane, chlorination of the silyl cation by CuCl and CuCl$_2$ was investigated, leading to the corresponding chlorosilane in high yields up to 95% (Scheme 25, **III**). As a coupled one-pot reaction with formation of the chlorosilane and subsequent dimerization, 48% of the disilane could be prepared
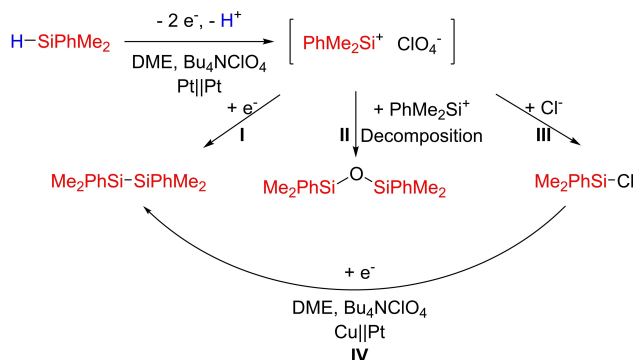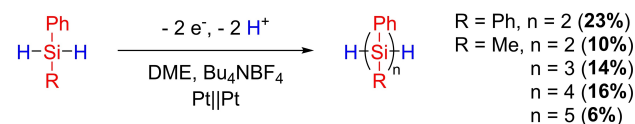
(Scheme 25, **IV**). However, for the corresponding conversion, the sacrificial anode technique based on Cu was necessary.

In recent studies,[61] Waldvogel and co-workers have demonstrated that the amount of charge required for Si–Si bond formation can be more than halved. The reaction of Kunai and co-workers is based on the presence of a silyl cation species which generates a Si–Si bond via subsequent reduction. By the addition of the strongly Lewis acidic borane B(C$_6$F$_5$)$_3$, the generation of a stabilized, activated silyl intermediate as silicon electrophile was sought, as has fundamentally expanded organic chemistry in recent years.[158] In the absence of coordinating substrates such as the supporting electrolyte, hydride abstraction can generate these silyl cationic intermediates, as a reactive species (Scheme 26, a).[159–161] In the presence of coordinating substrates such as the perchlorate anion, the formation of a silyl cation and borohydride has not yet been clearly confirmed by CV studies. However, CV measurements of the borohydride are difficult in the absence of suitable substrates due to the nature of the equilibrium, lying on the side of the non-activated hydrosilane.[162] However, a clear influence on the course of the reaction in the synthesis can be shown. Thus, the amount of charge necessary to generate 7% of the disilane decreases by more than half to 2.0 F by adding catalytic amounts of borane (Scheme 26, b). While the desired product could not be generated in high yield, this study demonstrates the potential use of Lewis acidic boranes for the electrochemical conversion of hydrosilanes.

Analogue to the synthesis of oligosilanes via the reductive reaction pathway with the use of dichlorosilanes, the oxidative process is accessible via the choice of dihydrosilanes, as Kimata and co-workers have shown.[71,163] Oxidation of MePhSiH$_2$ at a platinum anode yields a mixture of short-chain oligosilanes with Si–Si chain lengths of 2–5 as products. The use of the sterically more challenging Ph$_2$SiH$_2$ results exclusively in the formation of the dimer with 23% (Scheme 27). Unfortunately,
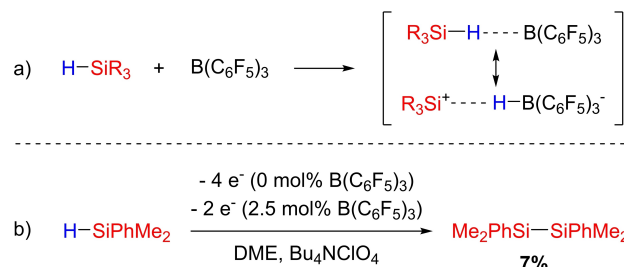
Scheme 26. The use of the Lewis acidic borane B(C$_6$F$_5$)$_3$: a) for the activation of hydrosilanes,[159–161] b) for the electrochemical conversion of hydrosilanes.[61]
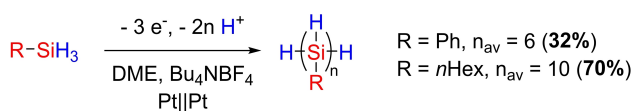

Scheme 25. Electrochemical oxidative conversion of hydrosilanes via the stabilized silyl cation to the disilane (**I**, **IV**), disiloxane (**II**) or chlorosilane (**III**).[60]

Scheme 27. Oxidative conversion of dihydrosilanes to di- and oligo-silanes.[71,163]

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no further mechanistic studies were conducted. The formation of radical cations is assumed, but the cathodic access by the undivided cell could allow an analogous course as in the case of Kunai and co-workers.[60]
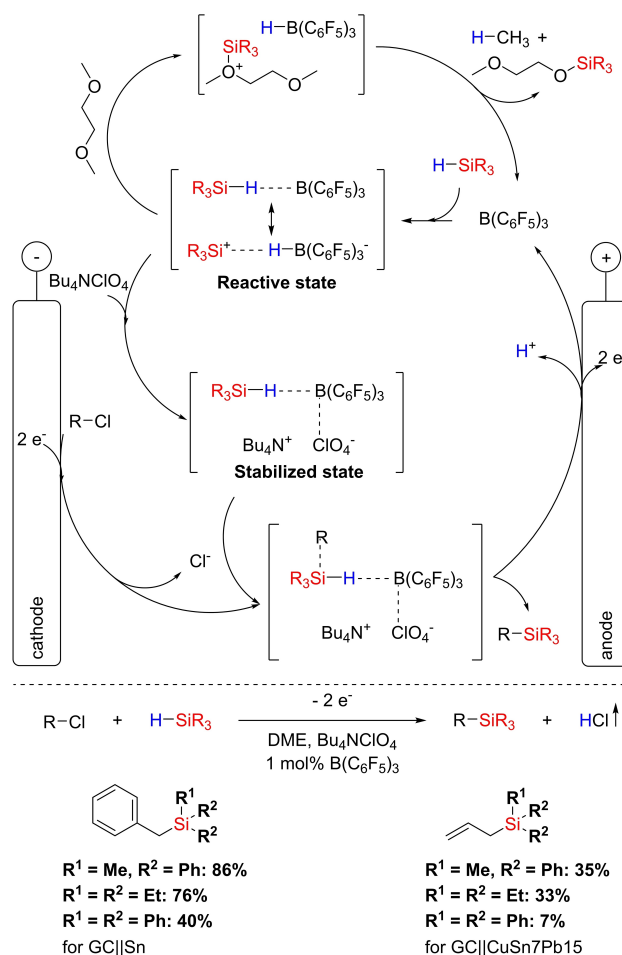
To further increase the Si–Si chain length during the oxidative conversion of hydrosilanes, it is necessary to switch to trihydrosilanes, as Kimata and co-workers have demonstrated.[71] Due to the lower steric requirements, the use of PhSiH$_3$ and HexSiH$_3$ allows the formation of average chain lengths of 6 and 10, respectively, enabling molecular weights to exceed 3 kDa (Scheme 28). However, linear oligosilanes and polysilanes are still obtained with the use of trihydrosilanes. Network structures, as known for the reductive pathway, are not formed via the oxidative reaction route. Similarly, higher chain lengths have not yet been formed via the described method. This fact can be explained by the high oxidation potential of the Si–H bond compared to the Si–Si bond. Analog to the reduction potential of Si–Si bonds, the oxidation potential decreases into the lower anodic regime with increasing chain length.[164] This fact is intensified by aryl groups compared to alkyl groups. If the oxidation potentials of Si–H and Si–Si bonds compete, the Si–Si bond is cleaved in a concurrent reaction, limiting the absolute chain length. Here again, a radical cation is assumed to be the intermediate of synthesis in the undivided cell.

3.2.2. Si-C bond formation

In contrast to the reductive Si–C bond formation via chlorosilanes as substrates, anodic access via hydrosilanes was hardly known until a few years ago. Only recently possible electrochemical reaction routes for this access have been described. Following the work in Si–Si bond formation,[61] Waldvogel and co-workers established the concept of Lewis acidic boranes as mediators for the conversion to Si–C bonds starting from hydrosilanes and enhancing the yields, i.e. for benzyldi-methylphenylsilane from 12% to 86%.[70] As could be demonstrated in this study, contrary to previous assumptions,[165] the presence of a supporting electrolyte does not prevent the function of the borane by coordination. Rather, the interaction of supporting electrolyte and borane is necessary to stabilize the highly reactive intermediate (Scheme 29). Alternatively, a spontaneous reaction with the solvent DME occurs with the formation of the respective silyl ether. Various supporting electrolytes, such as perchlorates and tetrafluoroborates, have proven suitable for this stabilization. In the electrochemical conversion, the hydrosilane is activated by the addition of borane. In parallel, an organic halide is reduced at the cathode. In a subsequent step, the nucleophilic carbanion formed reacts with the activated,
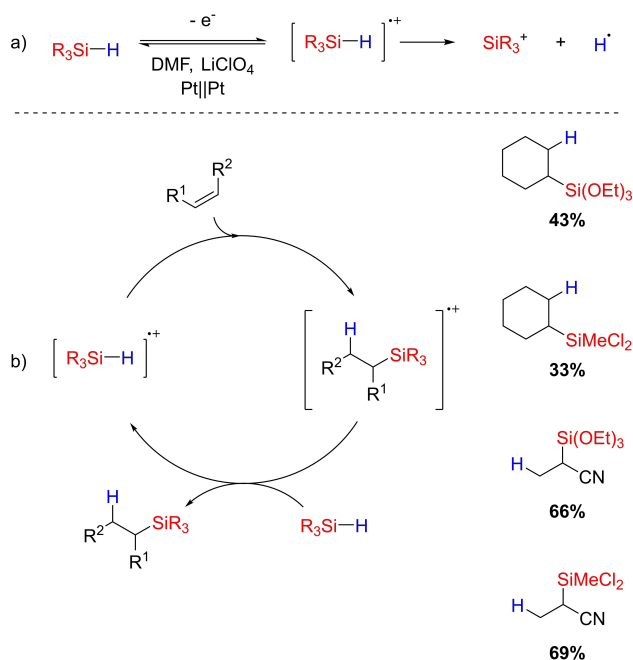

Scheme 29. Borane mediated electrochemical conversion of hydrosilanes to allyl and benzyl silanes as suggested by Waldvogel and co-workers (top), reaction equation, conditions, and yield range of relevant representatives of the electrochemical conversion (bottom).[70]

higher electrophilic hydrosilane, and Si–C bond formation occurs. The borane mediator is converted back to its initial state via oxidation at the anode to activate a hydrosilane again. At the anodic side, the regeneration of the borane yields protons to react with the cathodically produced chloride ions. Hydrogen chloride is formed and released from the reaction solution. This reaction path eliminates the need for the sacrificial anode technique to obtain a Si–C bond formation in presence of chloride ions. Besides its role as a mediator, the borane additionally serves as a protection against over-oxidation. This is comparable to the protection against over-reduction by metal ions as shown by Pons and co-workers on chlorosilanes.[82] The corresponding allylsilane can only be prepared in the presence of a borane mediator. As reported, allyldimethylphenylsilane is oxidized 0.58 V more readily than the hydrosilane starting material. Addition of the mediator shifts the oxidation potential of the hydrosilane by 0.88 V into the lower anodic regime and consequently prevents oxidation of the product. In addition to B(C$_6$F$_5$)$_3$, BCl$_3$ and BEt$_3$ have proved to be potentially mediators for the conversion of hydrosilanes towards benzyl and allyl functionalities.

Scheme 28. Oxidative conversion of trihydrosilanes to linear oligo- and polysilanes (n_{av} = average chain length).[71]

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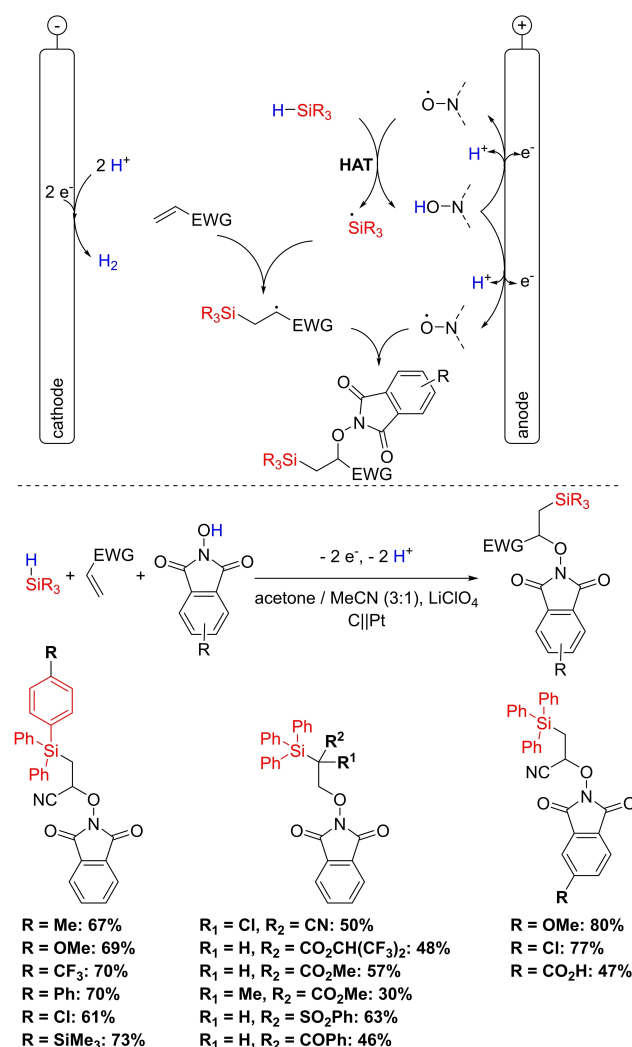Europe**
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Another strategy to form Si–C bonds is the scavenging of radical intermediates by unsaturated hydrocarbons, in analogy to the reductive synthesis of Lin and co-workers.[88] As early as 2000, Berberova reported,[166] that electrochemical hydrosilylation is accessible via the anodic oxidation of hydrosilanes in the presence of C≡C double bonds, as in acrylonitrile and cyclohexene. Direct oxidation of hydrosilanes demonstrated the formation of hydrogen as a radical dimerization product. This indicates a silyl radical cation as intermediate, which reacts in a subsequent reaction step to the silyl cation with elimination of a hydrogen radical (Scheme 30, a). Investigation of the limiting current using a ring-disk electrode allowed the lifetime of the radical cation to be calculated as 0.003 s, exceeding the stability of free radicals in solution. Via a pulsed electrolysis, it was further demonstrated that the hydrosilylation reaction occurring corresponds to a radical chain reaction, with the initiation proceeding electrochemically. The generated silyl radical cation is trapped by the unsaturated hydrocarbon and subsequent oxidation of a further hydrosilane occurs, continuing the process (Scheme 30, b). Only minor initial charge amounts already result in complete hydrosilylation by the emerging reaction. However, it was noted that only small supporting electrolyte cations as Li^+ and Na^+ could be successfully applied, as tetraalkylammonium cations block the anode, preventing the desired hydrosilane oxidation. Recent studies show a possible hydrosilylation of alkynes via the electrochemical reaction pathway.[167] However, the oxidation of Si–B bonds is beyond the scope of our review and has been already discussed elsewhere.[35]

Recent studies by He and co-workers,[69] have shown that the use of a HAT mediator generates a silyl radical that can be scavenged by unsaturated hydrocarbons. Again, small supporting electrolyte cations as Li^+ were beneficial for the desired oxidation. However, a special case is applied by consuming the mediator in the reaction, resulting in silyl-oxygenation of the C≡C double bond rather than hydrosilylation (Scheme 31). NHPI and adjacent structures are oxidized to PINO radical derivatives, generating the silyl radical via a HAT reaction. The C≡C double bond scavenges the silyl radical, resulting in the formation of an α-silyl alkyl radical, which allows the formation of the corresponding C–O bond by trapping another PINO radical derivative. The reduction of hydrogen is described as the cathodic reaction. The radical intermediate was confirmed by (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) and radical clock experiments based on vinyl cyclopropane in analogy to Lin and co-workers.[88] Via this radical three-component reaction, a broad substrate base with diverse hydrosilanes, electron-deficient alkenes, and N-oxyl species could be obtained in high yields.

Scheme 30. Electrochemical oxidation of hydrosilanes:[166] a) formation of the silyl radical cation with subsequent reaction to the silyl cation under the release of hydrogen atom, b) catalytic cycle for the hydrosilylation of alkenes via electrochemical oxidative hydrosilane activation.

Scheme 31. Electrochemical silyl-oxygenation of activated alkenes via radical mediated HAT reaction with hydrosilanes as suggested by He and co-workers (top, EWG = electron withdrawing group), reaction equation, conditions, and yield range of some relevant representatives of the electrochemical conversion (bottom).[69]

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In addition to the previously described formation of intermolecular Si–C bonds, the electrochemical synthesis of intramolecular Si–C bonds is possible. Recently, Han and co-workers reported,[72] that dibenzosiloles can be obtained via an oxidative HAT reaction of hydrosilanes. Interestingly, the reaction requires the addition of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) to increase the yields above 10%. Furthermore, pyridine is used to deprotonate NHPI to the respective anion, which is electrochemically oxidized to the PINO radical. The direct anodic oxidation seems to be prevented, probably due to the choice of the supporting electrolyte cation. The optimization of the reaction conditions starts with a tetraalkylammonium cation, which has a negative impact by at least partially blocking of the anodic access, as shown in previous studies.[69,166] By using the combination of HFIP and pyridine, the choice of the supporting electrolyte cation is of secondary importance, so that high yields can be achieved for various salt combinations. In this way, the used system circumvents the cationic anode blockage. The silyl radical is first formed by the HAT reaction in the course of the reaction (Scheme 32), analog to the work of He and co-workers,[69] as TEMPO studies show. Further anodic oxidation to the silyl cation occurs in the subsequent step. This silyl cation can be trapped as a silanol by the addition of water. The corresponding dibenzosilole is formed via a sila-Friedel-Crafts reaction with subsequent deprotonation, analogous to silicon electrophiles reported in the organic chemistry.[168]

3.2.3. Further oxidative Si bond formations

In addition to Si–Si and Si–C bond formation, further coupling type reactions exist in the electrochemical oxidative synthesis of silanes, which will be briefly highlighted below. For the use of hydrosilanes as starting material, as is the focus of this review, additional **Si–H** bond formation is not established. However, an anodic route for the conversion to Si–H bonds starting from silicon as a sacrificial anode in hydride salt melts has been reported.[169]

In reference to the reductive synthesis of the **Si–O** bond to silanones, an oxidative approach is known. Via the hydrosilane mediated electrochemical reduction of amides to amines, the respective Si=O bond is formed as a consecutive reaction.[170] PhSiH$_3$ is converted to the silyl radical via a bromide mediator with a HAT reaction. In parallel, the reduction of the amide occurs, to generate the respective Si–C bond via recombination. In the course of the reaction, after [1,2]-brook rearrangement and subsequent oxidation to the silyl cation, the silanone is cleaved, with further conversion of the amide to the amine (Scheme 33).
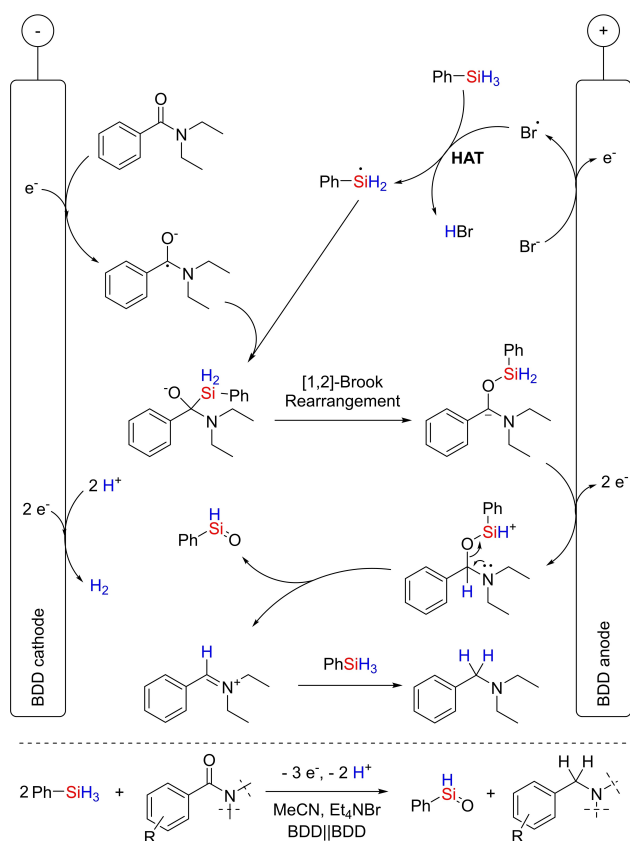
Furthermore, silyl ethers can be prepared via the oxidative reaction pathway.[171] In this case, the oxidation does not start from a hydrosilane, but from easily oxidizable allyl and benzyl silanes. By anodic cleavage of the Si–C bond in an alcohol as electrolyte solvent, such as MeOH, the released silyl cation can be scavenged as the respective silyl ether.

The electrochemical access to silyl ethers and silanols starting from hydrosilanes was recently reported by Zhang and co-workers.[155] In their work, the activation of a hydrosilane via a HAT process plays a central role (Scheme 34). NHPI is oxidized in an anodic conversion to the PINO radical, which is facilitated by the presence of hydroxide ions. These occur in the reaction process due to the reduction of water, being the substrate for silanol formation. The hydroxide ions hence exhibit a comparable facilitating function in the anodic oxidation of NHPI as the HFIP/pyridine system of Han and co-workers.[72] In this study, tetrabutylammonium cations are again used exclusively as supporting electrolytes. After the HAT process, the silyl radical, which was verified by TEMPO trapping experiments, is further electrochemically oxidized to the silyl cation. The silyl cation reacts with water or the corresponding alcohol under the release of protons. The conversion of hydrosilanes to the respective silanols, disilanols and silyl ethers could thus be demonstrated over a broad substrate base. Due to the mild reaction conditions, the functional group tolerance is high, allowing even complex structures to be prepared.

As shown in previous studies,[60,70] **Si–Cl** bond formation starting from hydrosilanes is also possible, but not of economic interest. The corresponding Si–Cl bond can be obtained by
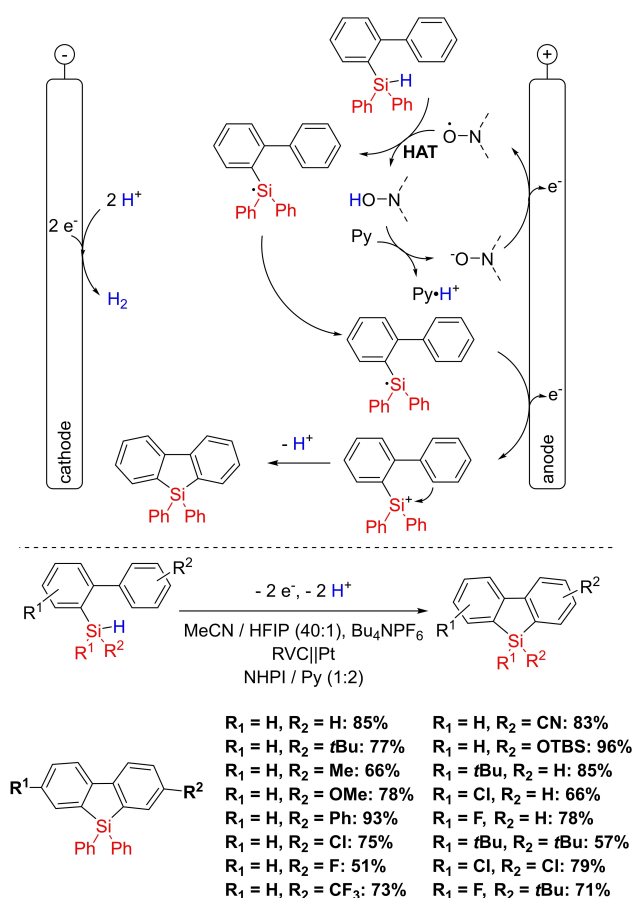
Scheme 32. Electrochemical HAT mediated conversion of hydrosilanes via sila-Friedel-Crafts reaction for the formation of dibenzosiloles as suggested by Han and co-workers (top), reaction equation, conditions, and yield range of some relevant representatives of the electrochemical conversion (bottom, HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol, RVC = reticulated vitreous carbon, Py = pyridine, TBS = t-butyl dimethylsilyloxy).[72]
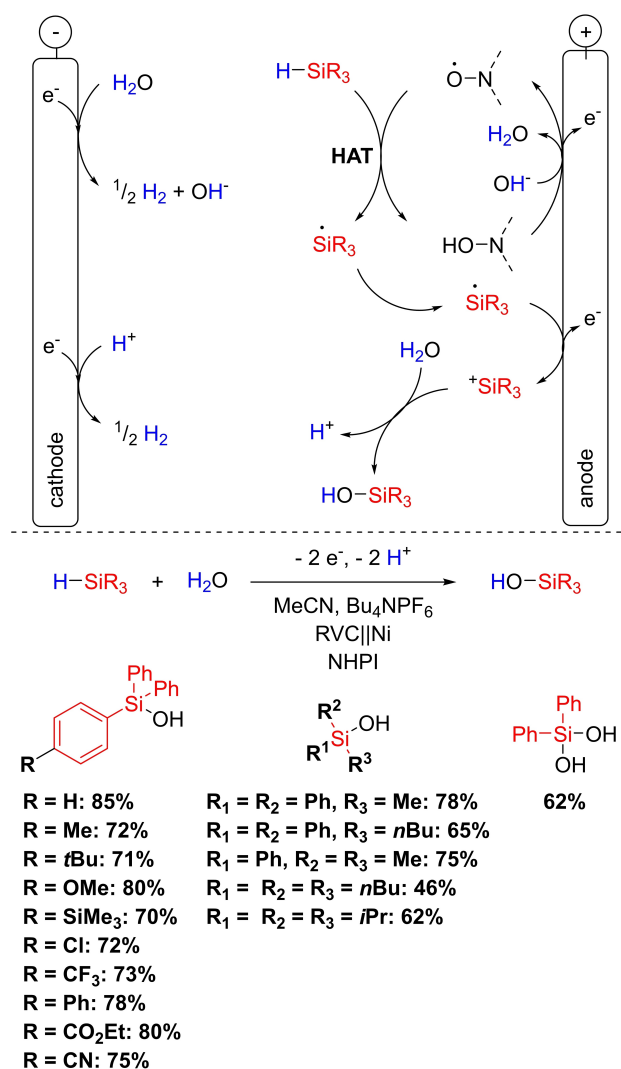
R$_1$ = H, R$_2$ = H: 85%	R$_1$ = H, R$_2$ = CN: 83%
R$_1$ = H, R$_2$ = tBu: 77%	R$_1$ = H, R$_2$ = OTBS: 96%
R$_1$ = H, R$_2$ = Me: 66%	R$_1$ = tBu, R$_2$ = H: 85%
R$_1$ = H, R$_2$ = OMe: 78%	R$_1$ = Cl, R$_2$ = H: 66%
R$_1$ = H, R$_2$ = Ph: 93%	R$_1$ = F, R$_2$ = H: 78%
R$_1$ = H, R$_2$ = Cl: 75%	R$_1$ = tBu, R$_2$ = tBu: 57%
R$_1$ = H, R$_2$ = F: 51%	R$_1$ = Cl, R$_2$ = Cl: 79%
R$_1$ = H, R$_2$ = CF$_3$: 73%	R$_1$ = F, R$_2$ = tBu: 71%

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Scheme 33. Electrochemical conversion of silanes to silanones via a HAT reaction and subsequent oxidation to the silyl cation with consecutive reduction of an amide to an amine as suggested by Chiba and co-workers (top), reaction equation and conditions (bottom, BBD = boron-doped diamond).[170]

Scheme 34. Electrochemical HAT mediated oxidation of hydrosilanes to silanols as suggested by Zhang and co-workers (top), reaction equation, conditions, and yield range of some relevant representatives of the electrochemical conversion (bottom, RVC = reticulated vitreous carbon).[155]

oxidation of hydrosilanes in the presence of free chloride ions. The **Si–F** bond formation has not yet been described starting from hydrosilanes but should proceed analogously to the synthesis of the Si–Cl bond. Starting from tetraalkylsilanes,[46] and cyclosilanes,[172] the Si–F bond formation is described via cleavage of the corresponding Si–C or Si–Si bond in the presence of a fluoride ion. This fluoride ion can be provided, for example, as BF_4^- by the supporting electrolyte.

4. Conclusion

The electrochemical conversion of chlorosilanes and hydrosilanes is a safe and versatile method that has been applied successfully, although depending on a number of parameters. The solvent, supporting electrolyte and substrates require very dry conditions in order to exclude a hydrolysis reaction. Karl-Fischer titration and electroanalytical techniques are suitable for this verification and should be established together with a standardized electrolyte-electrode concept for the CV investigation of chlorosilanes and hydrosilanes for high comparability. Supporting electrolytes can cause stabilization of intermediates as well as exchange and equilibration reactions and should be chosen carefully.

The cathodic conversion of chlorosilanes provides a large number of publications that allow a profound comprehensibility. The reduction proceeds to the anion formation in the absence of appropriate trapping reagents, such as unsaturated hydrocarbons. This results in the generation of a nucleophile, and subsequent bond formation with another chlorosilane. High yields have been described with a variety of substrates via both silyl anions and carbanions. Mediator systems are gaining in importance, making the necessary reduction potentials more readily available. However, the high reactivity of chlorosilanes still leaves a wide field open for more stable mediator systems, yet metal ionic systems i.e., Ni-based ones show promising approaches. Trapping reactions of silyl radicals by unsaturated hydrocarbons further open up new synthetic possibilities and offer additional functionalization possibilities. Nevertheless, concepts for scavenging the cathodically released chloride, besides the mostly used sacrificial anodes, remain to be desired.

Establishing gas anodes, i.e., hydrogen, and facilitating the easy commercial access may be a necessary step.

The oxidative conversion of hydrosilanes still leaves space for new electrochemical approaches. Direct conversion is limited by the high oxidation potential of hydrosilanes and has only been demonstrated on a marginal substrate range with low yields. Both activation by Lewis acid boranes for easier access to bond formation and radical mediated approaches show enormous features for future applications. Due to the mild conditions, a variety of substrate classes, as well as further mediation concepts, are conceivable. In addition, the use of Si–B compounds reveals novel possibilities for the electrochemical oxidative preparation of organosilanes.

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

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