

An Electroreductive Approach to Silyl Radical Chemistry via Strong Si–Cl Bond Activation

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ABSTRACT: The construction of C(sp³)–Si bonds is important in synthetic, medicinal, and materials chemistry. In this context, reactions mediated by silyl radicals have become increasingly attractive but methods for accessing these intermediates remain limited. We present a new strategy for silyl radical generation via electroreduction of readily available chlorosilanes. At highly biased potentials, electrochemistry grants access to silyl radicals through energetically uphill reductive cleavage of strong Si–Cl bonds. This strategy proved to be general in various alkene silylation reactions including disilylation, hydrosilylation, and allylic silylation under simple and transition-metal-free conditions.

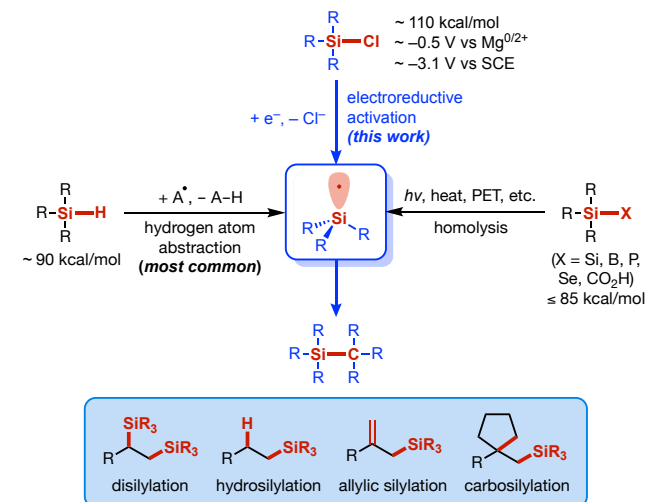
Organosilicon compounds find widespread use in many aspects of modern chemistry. For example, organosilanes are extensively used in chemical synthesis in classic reactions such as the Fleming-Tamao, Hosomi-Sakurai, and Hiyama coupling reactions.¹ Further, incorporation of Si in pharmaceuticals can improve their potency and pharmacokinetics.² Organosilanes have also been extensively studied as lubricants, adhesives, and other polymer materials.^{1a} As such, new and efficient approaches to the synthesis of organosilanes remain highly desirable. In this context, pathways involving the addition of silyl radicals to unsaturated C–C bonds constitute an attractive strategy,³ and recent developments in this direction have led to mild and selective ways to construct Si–C bonds.⁴ Silyl radicals are predominantly generated via hydrogen-atom abstraction from hydrosilanes induced by peroxides⁵ or photoredox catalysts⁶ (Scheme 1A). While these methods have provided innovative transformations, the reliance on hydrosilanes as silyl radical sources are met with several salient challenges, including the limited variety of readily available hydrosilanes and the strongly reducing conditions required for their preparation.⁷ Alternative methods for generating silyl radicals are available but limited to the use of esoteric precursors with labile Si–X bonds (X = Si,⁸ B,⁹ P,¹⁰ etc.¹¹).

We envision an alternative and potentially general method for the generation of silyl radicals by means of reductive activation of chlorosilanes. Chlorosilanes are among the most readily available reagents for organic synthesis.^{7a} Currently, chlorosilanes are predominantly employed as an electrophile to form Si–O¹² and Si–C¹³ bonds in the 2e[−] regime (Scheme 1B). These reactions are thermodynamically favorable owing to the formation of strong chemical bonds or the use of potent organometallic agents. In stark contrast, the use of chlorosilanes as radical silylating agents in the 1e[−] regime has yet to be explored. We reasoned that by applying a sufficiently reducing potential, chlorosilanes could undergo single-electron reduction and fragmentation, giving rise to polarity-reversed nucleophilic silyl radicals. Traditionally, this chemistry has been inaccessible due to the challenging reduction required of the strong Si–Cl bonds (*ca.* −0.5 V vs Mg^{0/2+}, BDE ~ 110 kcal/mol). Electrochemistry is capable of driving reactions far from equilibrium under highly biased potentials, often exceeding the limits of traditional chemical oxidants or reductants.¹⁴ Indeed, early studies showed that electroreduction of chlorosilanes is possible toward the

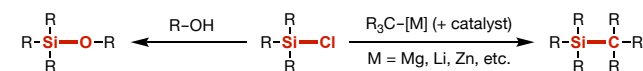
formation of dimeric and polymeric silanes (Scheme 1C).¹⁵ However, these reactions are proposed to undergo a silyl-anion pathway and are limited to Si–Si coupling. In this work, we employed a combination of synthetic and mechanistic tools to establish the electroreductive activation of chlorosilanes as a new and general strategy for the discovery of new radical silylation chemistry.

Scheme 1. Background information.

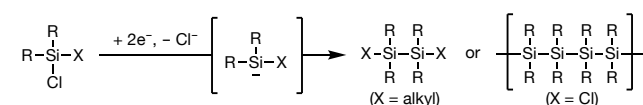
A. Strategies for accessing silyl radicals in organic synthesis



B. Canonical reactivity of chlorosilanes as silyl cation precursors (2e[−] regime)



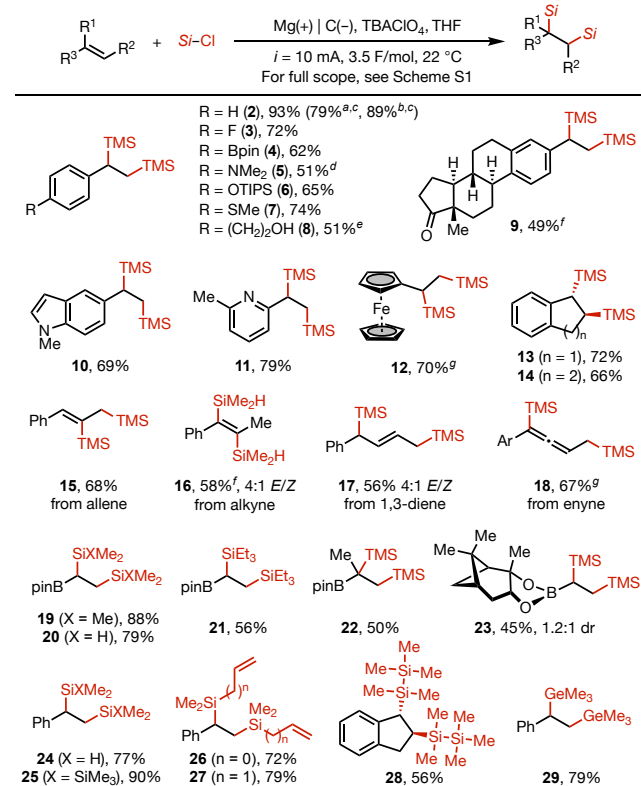
C. Prior art: electro-dimerization and polymerization of chlorosilanes (2e[−] regime)



We focused our initial exploration on the development of an electroreductive alkene silylation reaction and discovered that the electrolysis of a mixture of TMSCl and styrene (**1**) in THF led to the formation of vicinal disilane **2** (Schemes 2 and S1).¹⁶ Recently, Oesterich reported an elegant example of alkene disilylation via

silylium catalysis; however, the reaction scope is currently limited to the installation of TMS groups using TMS–TMS.¹⁷ A combination of TBAClO₄ as the electrolyte, a magnesium sacrificial anode, and a graphite cathode provided the optimal 94% yield under a constant current of 10 mA (cathodic potential ~ -0.85 V vs. Mg^{0/2+}). Notably, even TMSOAc with a very strong Si–O bond (120–140 kcal/mol) can be activated, resulting in 31% yield. Using TBA(TFSI) as the electrolyte instead of TBAClO₄ attained comparable reactivity (77%). This electrochemical protocol is easily scaled to 5 mmol without increasing solvent volume.

Scheme 2. Electroreductive disilylation of alkenes.



Reaction conditions: 1.0 mmol alkene, 3.0 equiv chlorosilane, 0.2 M TBAClO₄ in 9 mL THF, electrolysis at 22 °C under a constant current of 10 mA (current density = 1.2 mA/cm²) until 3.5 F total charge is passed. ^a2 equiv TMSCl. ^b5 mmol scale. ^cYield determined by ¹H NMR using 1,3,5-trimethoxybenzene as internal standard. ^d5.0 F total charge. ^eTMSCl = 4.0 equiv, 4.0 F total charge. ^fTMSCl = 4.0 equiv, 2.2 F total charge. ^g2.2 F total charge. Abbreviations: TBA, tetrabutylammonium; TMS, trimethylsilyl.

We subsequently evaluated the scope and functional group compatibility of our electroreductive strategy in the context of the disilylation reaction. Various functionalities that are potentially sensitive to chemical redox agents, such as boronate (**4**), tertiary amine (**5**), thioether (**7**), alcohol (**8**), and ketone (**9**) were preserved. Several electron-deficient and electron-rich heterocycles (**10–11**) and ferrocene (**12**) were also compatible with the reaction conditions. We also investigated other types of π -systems such as allenes (**15**), internal alkynes (**16**), conjugated dienes (**17**), and enynes (**18**) to generate a range of allyl and vinyl silanes, which could be further derivatized using cross-coupling and allylation reactions. Moreover, vinyl boronates proved to be suitable substrates, providing products (**19–23**) with *gem*-(B,Si) substitution, which are versatile functional groups in organic synthesis.¹⁸ Simple aliphatic olefins can also react with electrogenerated silyl radicals but suffer from lower reactivity and chemoselectivity likely due to the

lack of anion-stabilizing substituents (Scheme S17). An initial solution to this issue was obtained using information gleaned from mechanistic analysis (*vide infra*).

A diverse array of chlorosilanes proved to be effective for the construction of value-added organosilanes (**24–29**). In particular, dimethylsilane (**24**), vinyltrimethylsilane (**26**), and allyltrimethylsilane (**27**) led to products that could be used as monomers for silicon-containing polymers.¹⁹ Furthermore, the incorporation of disilane groups vicinally to an alkene (**25**, **28**) demonstrated the potential utility of this reaction for the preparation of parallel single-molecular silicon wires for materials and electronic applications.²⁰ Chlorotrimethylgermane could also react to furnish product **29**. The success and limitation of our reaction scope piqued our interest in investigating the reaction mechanism with the objective of expanding the reactivity to other synthetically useful transformations.

The electrochemical disilylation is comprised of three components that can be reduced at the cathode—the alkene, chlorosilane, and anodically generated Mg²⁺. The reduction of each of these components could contribute to the observed disilylation (Scheme S6). For example, electrogenerated Mg⁰ could activate either styrene²¹ or TMSCl to form magnesiated nucleophiles prior to C–Si formation. Alternatively, cathodic reduction of styrene could lead to a radical anion that initiates the disilylation. Finally, the direct reduction of TMSCl followed by mesolytic Si–Cl cleavage could produce TMS[•] prior to its addition to the alkene (Scheme 1A).

A series of electroanalytical experiments, multivariate linear regression (MLR) analyses, and density functional theory (DFT) calculations lent strong support to the silyl radical pathway and provided more insights into the reaction mechanism. First, control experiments using either Mg powder (Table 1, entry 1) or electrogenerated Mg⁰ (entries 2–4) gave no conversion. We also carried out divided-cell electrolysis that separates the cathodic disilylation reaction from oxidation of the sacrificial anode. Using either Mg or Zn as the anode (entries 5–6), moderate yield of **2** was observed. The low yields were due to sluggish reaction caused by high cell resistance. These experiments led us to exclude reaction pathways involving electrogeneration of Mg⁰.

Table 1. Control experiments.

Entry	Conditions	NMR yield (%)
1	No electrical input. 1, TMSCl, Mg powder TBAClO ₄ , THF, 12 h, 22 °C	<1% (1 recovered)
2	Mg(+) C(–), TBAClO ₄ , THF, <i>i</i> = 10 mA, 2 F then, add 1 and TMSCl, 12 h, 22 °C	<1% (1 recovered)
3	1, Mg(+) C(–), TBAClO ₄ , THF, <i>i</i> = 10 mA, 2 F then, add TMSCl, 12 h, 22 °C	<1% (1 consumed)
4	TMSCl, Mg(+) C(–), TBAClO ₄ , THF, <i>i</i> = 10 mA, 2 F then, add 1, 12 h, 22 °C	<1% (1 recovered)
5	Mg(+) C(–) (divided cell), TBAClO ₄ , THF <i>U</i> _{cell} = 31 V, <i>E</i> _c ~ -0.5 to -0.9 V, 12 h, 22 °C	38% (1 recovered)
6	Zn(+) C(–) (divided cell), TBAClO ₄ , THF <i>U</i> _{cell} = 31 V, <i>E</i> _c ~ -0.5 to -0.9 V, 12 h, 22 °C	35% (1 recovered)

Cyclic voltammetry studies revealed that onset potential for the reduction of TMSCl (*ca.* -0.5 V) is higher than that of styrene (*ca.* -1.2 V).²² Meanwhile, the cathodic potential of a standard disilylation

reaction was measured to vary between -0.7 to -1.0 V. Controlled potential electrolysis at -0.7 V and -1.0 V (Table S3) produced nearly identical reaction yield to standard conditions, supporting the notion that TMSCl, not styrene, is reduced in the predominant pathway. Notably, a current enhancement was observed for the reduction of TMSCl upon addition of Mg^{2+} , indicating that while Mg^{2+} is not required, it facilitates the reduction of TMSCl likely by binding to the leaving Cl^- .

Having established the mechanism of initiation via TMSCl reduction, we subsequently employed structure-activity relationship studies using various substituted styrenes to probe the mechanism of the first C–Si bond formation. Attempts to correlate relative rates with either Hammett parameter (σ) or radical stability parameter (σ^*)²³ alone were unsuccessful ($R^2 < 0.65$; Figure S16). Thus, a two-parameter MLR model was developed (Figure 1), which shows that both electronic property of the alkene *and* stability of the ensuing benzylic radical influence the reaction rate.^{24,25} These results are consistent with the formation of the first C–Si bond proceeding via addition of a nucleophilic silyl radical to the alkene, which is also the rate-determining chemical step (RDCS) of the reaction. ¹³C kinetic isotope effect experiments provided additional support for this hypothesis (Scheme S19–20).

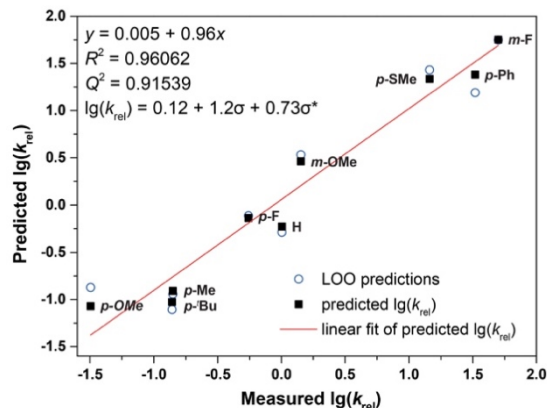


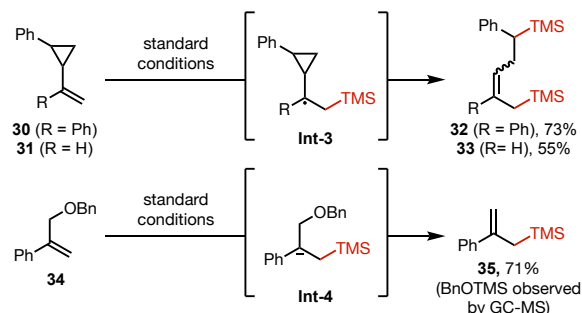
Figure 1. Multivariate linear regression analysis.

Further experiments using radical and anion probe substrates support a radical-polar crossover mechanism for the formation of the second C–Si bond (Scheme 3). First, vinyl cyclopropane **30/31** underwent rupture of the three-membered ring, suggesting the intermediacy of radical **Int-3**. In addition, allylether **34** was converted to allylsilane **35**, thereby supporting the formation of benzylic anion **Int-4** that triggers the elimination of the BnO leaving group. **Int-4** is likely generated in a second cathodic reduction event from the corresponding radical intermediate.

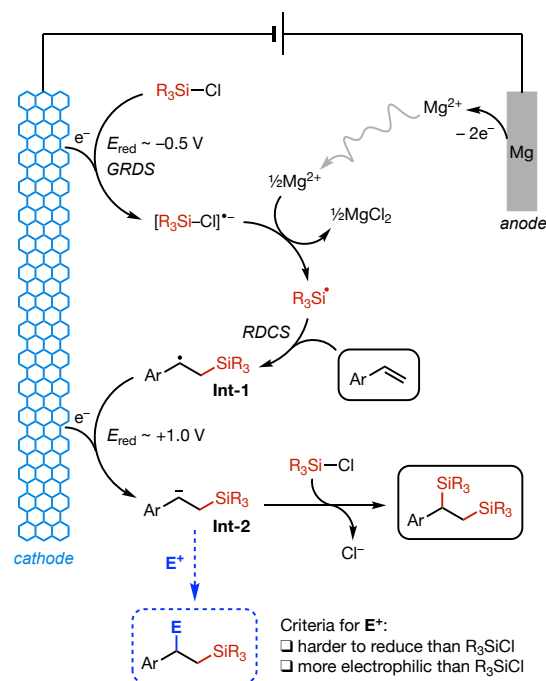
The slow kinetics of TMSCl reduction as shown in the CV suggests that it is the global rate-determining step (GRDS). This hypothesis was supported by kinetic measurements, which showed that the reaction displays a zero-order dependence on the reactant concentration and first-order dependence on the current applied (Figure S12–15). The overall reaction thus proceeds through an electrochemical-chemical-electrochemical-chemical (ECEC) mechanism,²⁶ which allows for the installation of the vicinal C–Si bonds via a radical-polar crossover pathway (Scheme 4). We also considered an alternative mechanism wherein the $2e^-$ -reduction of TMSCl generates TMS^- and initiates the disilylation (Scheme

1C);^{15,27} however, this pathway is unlikely based on experimental and theoretical data.²⁸

Scheme 3. Radical and anion probe experiments.

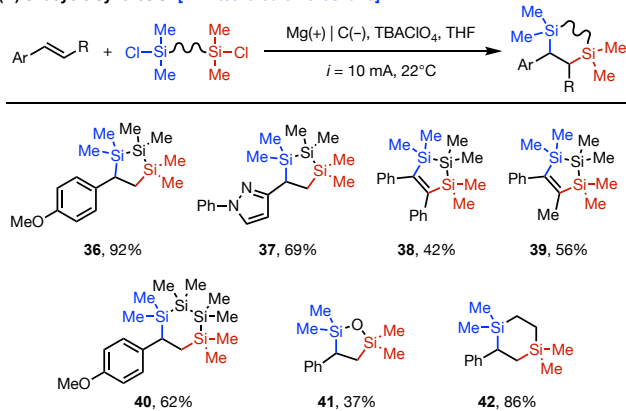
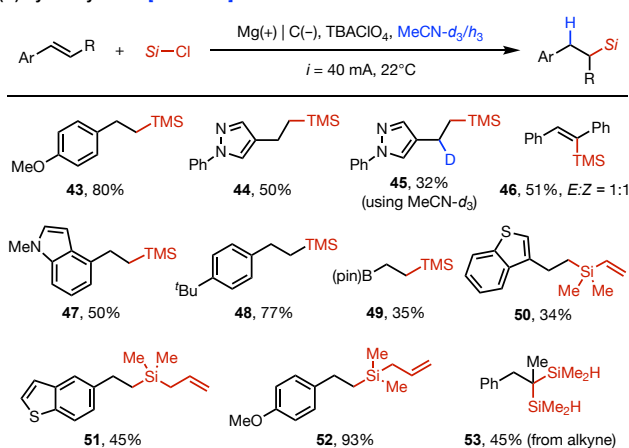
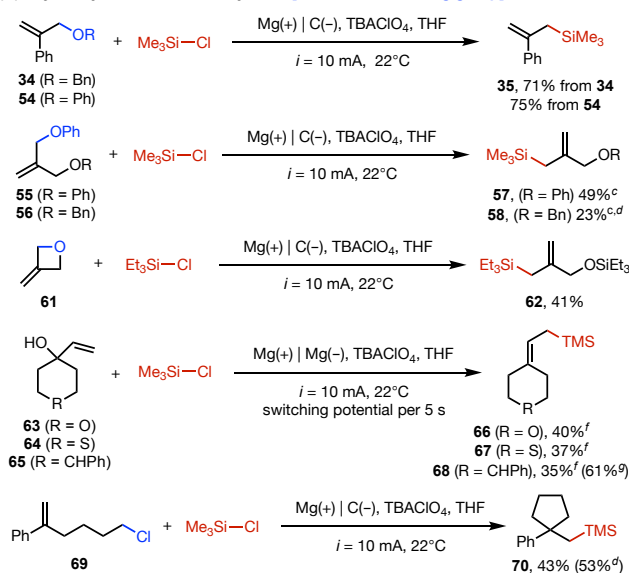


Scheme 4. Proposed mechanism.



The proposed mechanism led us to envision that a variety of other reactions could be realized under the same mechanistic manifold (Scheme 4, blue dashed arrow). Specifically, given that the two Si–C bonds are formed via distinct radical and polar mechanisms, we reasoned that the introduction of another electrophilic species (E^+), which is less likely to reduce than chlorosilanes but easier to react with a carbanion, could lead to selective new transformations. To test our hypothesis, we first applied this strategy to synthesize silacycles from dichlorodisilanes (Scheme 5A). In this case, the reduction of the second Si–Cl unit should be slower than the first, but intramolecular ring closure should be favored over intermolecular substitution. Silacycles are valuable motifs in the field of materials sciences as it can modulate the photophysical and electrical properties of compounds.^{29,30} However, no general synthetic methods are available for these building blocks with limited examples relying on potent reductants such as Li. Using our strategy, a suite of 5- and 6-membered silacycles were prepared without cleaving weak Si–Si bonds (**36–42**).

Scheme 5. Mechanism-guided discovery of new silylation reactions

(A) Silacycle synthesis^a [E⁺ = tethered chlorosilane]**(B) Hydrosilylation^b [E⁺ = H⁺/D⁺]****(C) Allylic silylation and carbosilylation [E⁺ = tethered leaving group]**

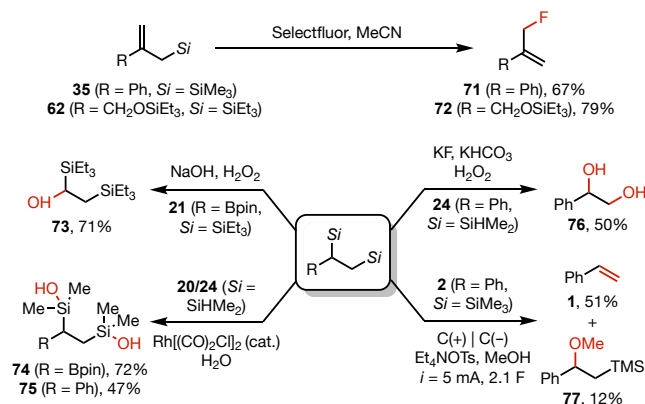
^a0.5 mmol alkene, 1.5 equiv chlorosilane, 0.2 M TBAClO₄ in 4 ml THF. ^b1.0 mmol alkene, 3 equiv chlorosilane, 0.2 M TBAClO₄ in 4 ml THF, electrolysis at a constant current of 40 mA [Mg(+)|C(-)] (current density = 4.8 mA/cm²). ^c2.2 F instead. ^dyield determined by NMR with dibromomethane as an internal standard. ^eTMSCl 4 equiv. ^f0.5 mmol alkene, 0.2 M TBAClO₄ in 4 ml THF, TMSCl 4 equiv, Mg is used for both anode and cathode with 5 s polarity switch interval. ^gyield based on recovered starting material.

Hydrosilylation is an important industrial transformation and traditionally relies on noble metal catalysts in combination with

hydrosilanes. Recent contributions made possible the use of earth-abundant transition-metal³¹ or organic³² catalysts as well as other types of Si reagents.^{11a,33} We envisioned a complementary strategy for transition-metal-free hydrosilylation via electrochemistry by intercepting carbanion **Int-2** with an appropriate proton source.³⁴ Indeed, when weakly acidic acetonitrile was used as the solvent in lieu of THF, hydrosilylation proceeded as the predominant pathway with little competitive disilylation. Thus, a collection of hydrosilylated products were synthesized from conjugated alkenes, alkynes, and chlorosilanes (Scheme 5B). Notably, deuteriosilylation product **45** was obtained using CD₃CN as the solvent.

We also postulated that if a suitable leaving group is positioned β- to the carbanion in intermediate **Int-2**, an elimination event could occur to produce synthetically valuable allylsilanes.³⁵ This hypothesis was first validated in the anion probe experiment and was further expanded to various other substrates (Scheme 5C). Importantly, this system allowed us to expand the scope of electroreductive silylation from conjugated alkenes (**34**, **54**) to simple alkenes (**55–56**, **61**). In addition to allylethers, even allylic alcohols (**63–65**) can be directly used as starting materials presumably via the initial formation of a TMS-ether. We reason that simple alkenes are challenging substrates in the disilylation due largely to the instability of non-conjugated carbanion intermediates, but the vicinity of a leaving group in the radical-polar substitution reaction reduces the necessity for a long-lived carbanion. Our reaction thus provides a new and efficient means to access value-added allylsilanes from readily available allylic ethers³⁶ and alcohols³⁷. This approach was further applied to a cyclization reaction with a tethered leaving group (**69**).

Finally, we demonstrated the derivatization of organosilicon products to a variety of structurally diverse compounds via allylsilane fluorination³⁸, hydrosilane oxidation³⁹, and Tamao-Flemming oxidation (Scheme 6).⁴⁰ Interestingly, electrochemical oxidation returned disilane **2** to styrene **1**, providing a potential protecting group strategy for styrenes.⁴¹

Scheme 6. Product derivatization.

In conclusion, we developed a general electrochemical protocol to access silyl radicals by activating chlorosilanes at deeply reducing potentials and demonstrated its use in Si–C bond forming reactions. We anticipate this operationally simple and modular protocol will enhance the accessibility of a diverse range of organosilanes, and that the general design principle will lead to new non-spontaneous

reactions that are difficult to achieve with traditional chemical methods.

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Notes

The authors declare no competing financial interest.

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