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Electrifying synthesis of organosilicon compounds – from electrosynthesis to electrocatalysis

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Occasionally, a synthetic strategy is developed that seems to be a game changer. Not long ago, mechanochemistry or ionic liquids were intensively explored to afford organosilicon compounds. These and other approaches still offer benefits and influence the development of this field. Electrochemistry is currently a new synthetic strategy. Despite its long history, electrosynthesis or electrocatalysis have not become routine procedures in the synthesis of organosilicons. One may justifiably ask why. Accessibility and reproducibility are one of the challenges of electrochemical approaches. However, recent developments in the field of electrified organic synthesis have provided new insights and allowed electrochemistry to become an approachable tool. In this perspective article, several notable contributions to the electrochemical synthesis of organosilicon compounds are highlighted.

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Looking at organic chemistry we notice a tremendous growth of interest in the development of novel electrochemical methodologies. Ackermann,^{1–4} Baran,^{5–8} Lin,^{9,10} Mei,^{11–13} Waldvogel^{14–16} and many other eminent scientists have proverbially brought electrosynthesis/electrocatalysis to light by turning it into a perfectly working synthetic tool.^{17–32} This, in turn, has many implications for the development of materials chemistry. By linking these two factors – synthesis and applications – one can bring to mind organosilicon chemistry.^{33–35} Especially, the synthetically produced silicones (siloxanes), which can be considered milestones for modern-day industry. Moreover, the organosilicons themselves are useful intermediates allowing the synthesis of very complex molecules.^{36–39}

Until we look at the recent development in the field, one should always pay attention to previous studies (Fig. 1).^{40–43} Most of the pioneering electrochemical transformations of organosilicons were developed in the 1970s and 1980s. However, despite valuable conclusions, the above-mentioned investigations were not noticed with due diligence by the audience. In 1976, Litscher and Hengge developed a new method for the facile synthesis of disilanes from chlorosilanes (Fig. 1, A).⁴⁴ It is worth noting, that the formation of Si–Si bonds is challenging by catalytic methods (due to the strong thermodynamic force for Si–O–Si bond formation).⁴⁵ In 1985, Shono *et al.* described an electroreductive silylation of allylic and benzylic halides (Fig. 1, B).⁴⁶ At the same time, Yoshida and coworkers reported a series of electrochemical studies giving

insights into the formation of the C–Si bond (Fig. 1, C), and its further cleavage.^{47–49}

In general, the generation of silyl radical intermediates seems to play an important role during the synthesis of targeted products. Speaking of which, the silyl radicals can be generated in several ways (Fig. 2).^{50–56}

The most obvious one is the peroxide-promoted radical formation *via* the homolyses process (thermal or photochemical), and subsequent hydrogen-atom abstraction from hydrosilanes (Fig. 2, a).⁵⁰ On the other hand, hydrogen-atom transfer (HAT) can be achieved by using photoredox catalysis.⁵¹ Here, two main operative modes are involved based on the use of direct HAT photocatalysts (Fig. 2, b) or indirect photocatalysis requiring additional mediators (Fig. 2, c). Silyl radicals can be also derived from the cleavage of Si–Y bonds (where Y = Si, B, O, P, Se, *etc.*), *via* single electron transfer (SET), however, there is a limited variety of readily available species, and their preparation prolongs the whole procedure (Fig. 2, d).^{57,58} A few years ago, Grubbs and coworkers developed a base-promoted silylation of C–H bonds suggesting a radical addition-dehydrogenation process (Fig. 2, e).^{59,60} Lastly, there are electrochemically induced silyl radicals. Here, the use of redox mediators enables the generation of silyl radicals and further anodic oxidation processes (Fig. 2, f), whilst commercially available chlorosilanes can proceed with the formation of silyl radicals in the 1e[−] regime *via* cathodic reduction (Fig. 2, g). All of the above-mentioned approaches have their benefits and drawbacks. Considering a period of increasing society's awareness in terms of sustainable developments and risks arising from irresponsible resource management, scientists pay more and more attention to the development of greener synthetic solutions.^{61–63} Electrochemical approaches in this regard are

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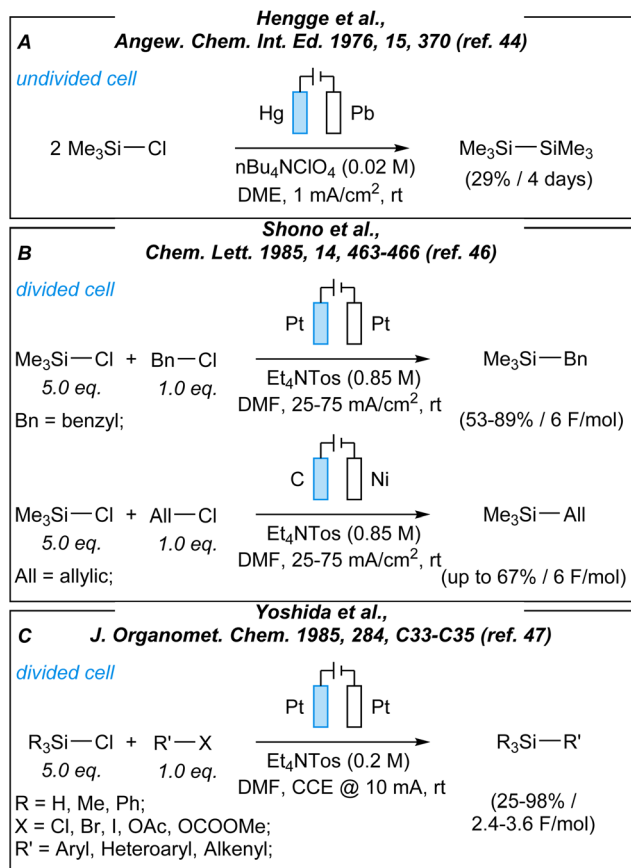



Fig. 1 Previous developments concerning electrochemical transformations of organosilicons.

at a forefront of such a policy, by setting the stage for molecular synthesis with unique levels of resource economy (e.g., chemicals, wastes, energy, etc.).⁶⁴ The cathodic reduction, indeed, benefits from readily available chlorosilanes and the absence of additional mediators. However, the anodic oxidation process requires additional mediators, the use of limited hydrosilanes or their precursors. Nevertheless, novel electro-mediated methodologies seem to lead to fascinating new reactions, whereas the full potential of paired electro-synthetic approaches will hopefully be uncovered in the near future.²²

This short perspective will mainly focus on the recent developments in the electrochemical synthesis of organosilicon compounds. It aims to explain the significance of these developments, provide a critical look at this subject, and identify further challenges. Five recent articles (2020–2022) were selected and the features of these solutions will be discussed with an appropriate description of mechanistic studies and their usefulness.

In 2020, Lin and coworkers described the synthesis of a wide range of organosilicon compounds *via* electro-synthesis.⁶⁵ For the disilylation of alkenes (Fig. 3), the authors used the following combination: Mg anode (sacrificial), graphite cathode, CCE @ 10 mA, and TBAClO₄ as the electrolyte.

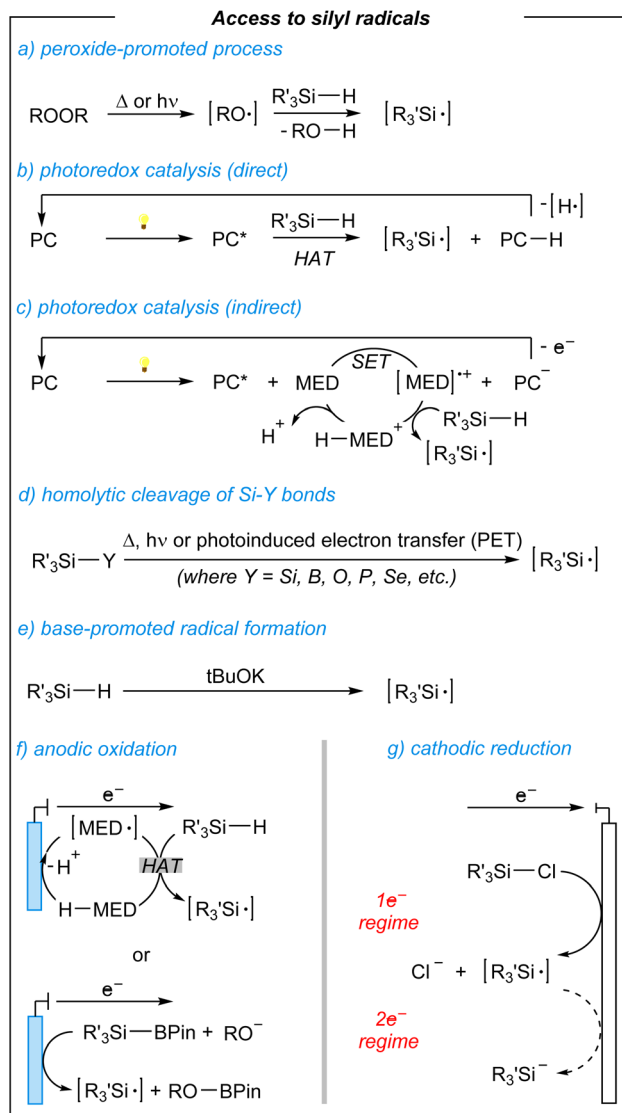


Fig. 2 Overview of general ways for the generation of silyl radicals.

Upon the investigation of the reaction scope, several styrenes, vinylboronates, and vinyl-N-heterocycles were efficiently disilylated at rt, in moderate to very good yields (45–93%). Moreover, the authors performed analogues digermylation, and used other chlorosilanes than chlorotrimethylsilane such as chlorodimethylsilane, chloropentamethyldisilane and chlorotriethylsilane. Among the unreactive or less reactive (and less selective) reagents, one can mention β-methylstyrene, styrenes with strong electron-withdrawing groups, 3-vinylpyridine, allylbenzene, cyclooctene (alkene substrates), as well as dichlorosilanes, chlorotert-butyl dimethylsilane and chlorodimethylphenylsilane (chlorosilanes). Meanwhile, a silyl radical pathway was proposed. The authors conducted detailed mechanistic studies by performing several electroanalytical experiments. The reaction system involved three species that could be reduced at the cathode – chlorosilane, alkene, and magnesium cation (Mg²⁺). The last one was excluded since



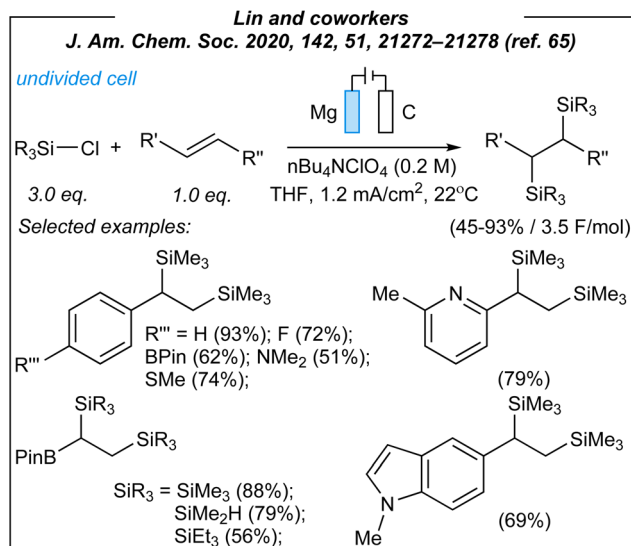


Fig. 3 Disilylation of alkenes *via* electroreductive activation.

magnesium (Mg^0 , electrogenerated or as a powder) gave no product under the optimized conditions. Moreover, the electrolysis performed in a divided cell led to the desired product. Then, cyclic voltammetry experiments suggested the reduction of chlorosilane prior to the alkene. The plausible mechanism is depicted in Fig. 4.

Next, considering the plausible mechanism of this electroreductive process, the authors envisaged a completely novel methodology for the formation of silacycles (Fig. 5). Thus, several tethered silanes including dichlorodi-, tri- and tetrasilanes, as well as dichlorodisiloxane and 1,2-bis(chlorodimethylsilyl)ethane were utilized as the substrates under the same conditions. As the result, seven new silacycles (five- and

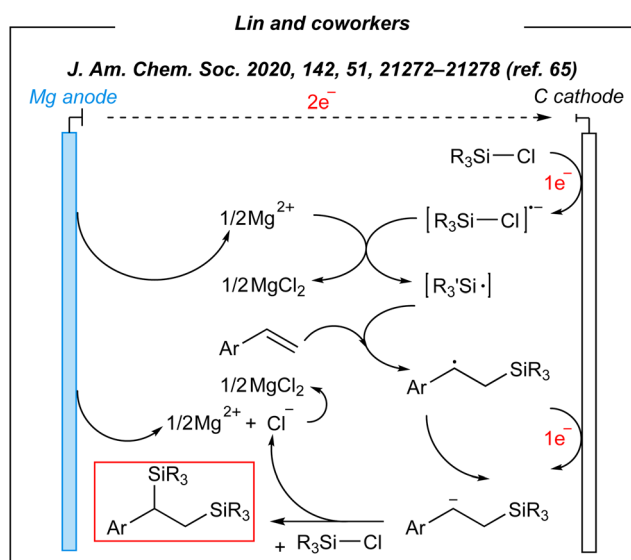


Fig. 4 Plausible mechanism for the disilylation of alkenes under electrochemical conditions.

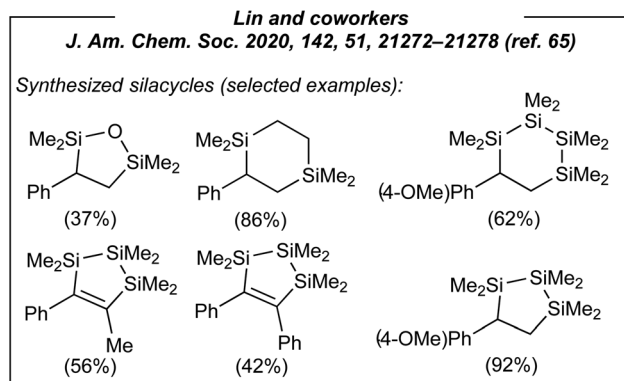


Fig. 5 Selected silacycles obtained *via* electroinduced disilylation of alkenes with tethered dichlorosilyl derivative.

six-membered ones) were obtained in good yields up to 92%. Subsequently, the authors again showed how important is to understand the nature of the process. After the synthesis of the above-mentioned silacycles, the portfolio of the products was extended to monosilylated alkanes (*via* formal hydrosilylation) and allylsilanes. In the case of the former, acetonitrile was used as both solvent and the hydrogen source (Fig. 6). In the latter case, the introduction of a leaving group in β -position to the carbanion intermediate was required.

Finally, Lin demonstrated the derivatization of the obtained organosilicon products to a variety of structurally diverse compounds *via* known transformations including fluorination, oxidation, and Fleming–Tamao oxidation.⁶⁶

To sum up, Lin and coworkers reported a novel methodology for the construction of sp^3 C–Si moieties, induced by electricity. Firstly, they used chlorosilanes. This group of silicon compounds is the most numerous on the commercial

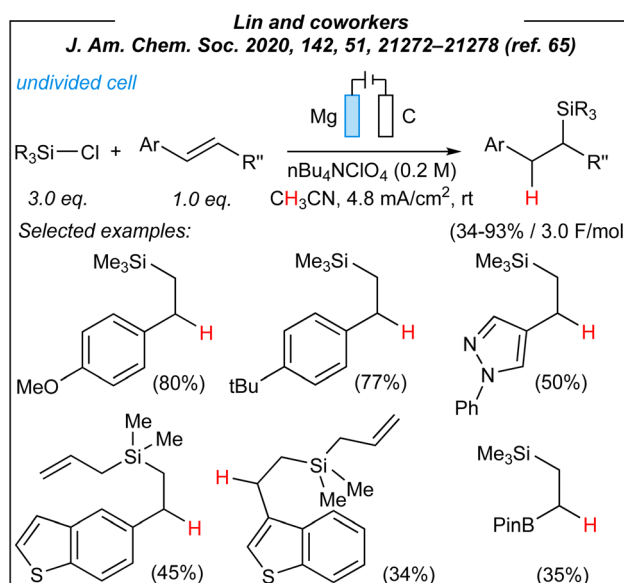


Fig. 6 Hydrosilylation of alkenes *via* electroreductive activation.



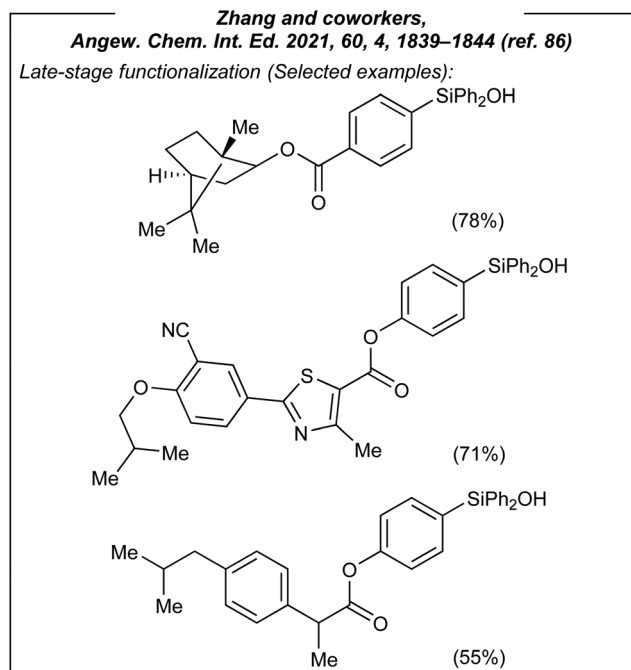


Fig. 8 Selected biorelevant compounds obtained *via* electroinduced hydrolysis of Si–H bonds.

as dichloromethane and dimethylformamide were ineffective solvents in this process, whilst acetonitrile, known for stabilizing silyl cations,⁸⁷ ensured the best conversion. The plausible mechanism is depicted in Fig. 9.

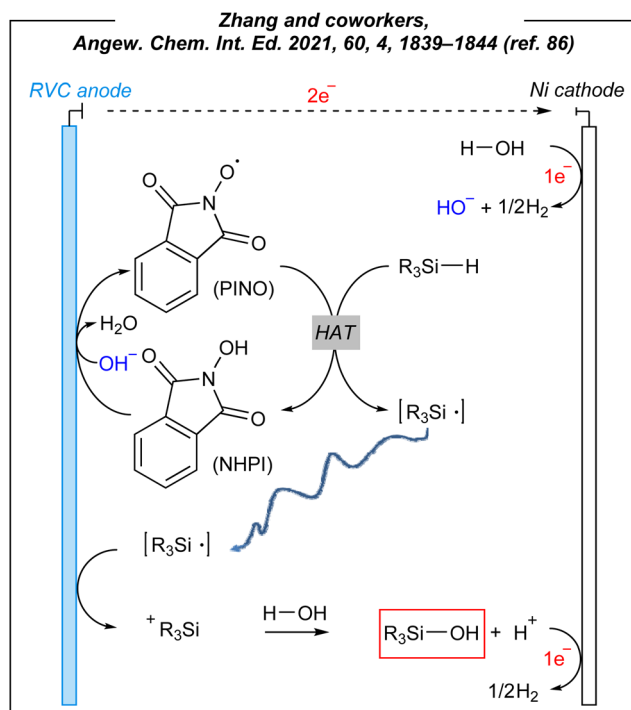


Fig. 9 Plausible mechanism for the hydrolysis of hydrosilanes under electrochemical conditions.

To sum up, Zhang and coworkers reported a novel methodology for the construction of O–Si moieties, induced by electricity. First of all, the authors used hydrosilanes as the substrates. Unlike chlorosilanes, SiH-containing molecules are less sensitive and lead to non-corrosive byproducts. However, they are not as readily available as halosilanes, which serve as the first-choice substrates in conventional methods.⁸⁸ Indeed, chlorosilanes readily undergo hydrolysis to give corrosive HCl (usually trapped by amine bases) and silanols. Unfortunately, the chemoselectivity of these transformations is generally low, whereas silanols can easily undergo condensation to disiloxanes. Zhang's approach gives access to both types of silanols, these easily available from chlorosilanes (*e.g.*, triisopropylsilanol), and those difficult to be conventionally produced with good selectivity (*e.g.*, SiMe₂-containing silanols). What is more, the authors performed the challenging hydrolysis of silyl-derived biorelevant compounds, which contain sensitive functional groups. Furthermore, in the vast majority of cases, the conversion of Si–H to Si–OH moieties requires the use of stoichiometric oxidants and/or expensive transition metal catalysts.^{39,89} Thus, the electrochemical approach seems to be a very significant alternative to known procedures utilizing hydrosilanes as the substrates. The authors performed also pioneering alcoholysis reactions leading to alkoxy silanes under electrochemical conditions. In the past, several sustainable methods were developed,^{39,90–93} but this electroinduced approach might be interesting in the case of the compounds with sensitive groups. Furthermore, the electrochemical system consists of an RVC anode and a nickel cathode. Both are classified as not so expensive. Similarly to Lin,⁶⁵ the Zhang group used an IKA® ElectraSyn 2.0, which ensures the reproducibility of the obtained results. In addition, what is equally important, the authors tested the reaction under electricity-free (as well as mediator-free and catalyst-free) conditions to show the necessity of electroinduced synthesis. This is a very important aspect, whereas some processes can be performed *via* uncatalyzed reactions or without additional terms and conditions.^{94–96} In conclusion, the electrochemical hydrolysis reported by Zhang and coworkers is an interesting alternative to conventional stoichiometric or catalytic methods, and despite some limitations (*e.g.*, stoichiometric amounts of HAT mediator, moderate yields, *etc.*), it can be considered as a useful synthetic approach.

In 2021, He and coworkers reported the radical 1,2-silyl-functionalization of alkenes under electrochemical conditions.⁹⁷ For the silyl-oxygenation process (Fig. 10), the authors used the following combination: graphite anode, platinum cathode, CCE @ 3 mA, NHPI as HAT mediator (1.2 eq.), and LiClO₄ as the electrolyte. Upon the investigation of the reaction scope, several hydrosilanes (including secondary and tertiary ones) were matched with electron-deficient alkenes and different *N*-oxyl species. In most cases, that was a combination of triphenylsilanes, acrylonitrile, and NHPI. As the result, several β-silyl-cyanohydrines were obtained with moderate to good yields. Moreover, He demonstrated that acrylates, vinyl phenyl sulfone, and vinyl phenyl ketone are also suitable



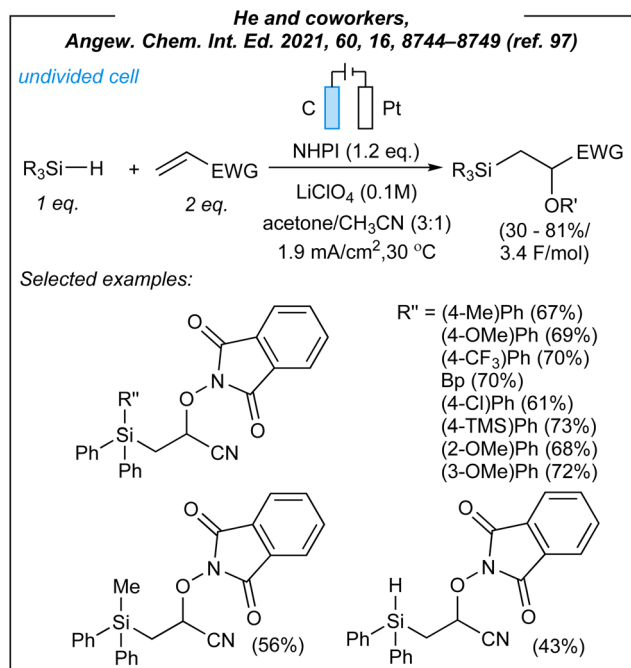


Fig. 10 Radical 1,2-silylfunctionalization of alkenes under electrochemical conditions.

alkene partners, whilst styrene and vinyl ether more or less gave no product. Furthermore, tertiary and secondary germanes were also reactive under these electrochemical conditions, giving β -germyl-cyanohydrins in moderate yields (33–60%). Finally, the described protocol was scaled up to a 5 mmol scale yielding 72% (1.71 g) of 2-((1,3-dioxoisindolin-2-yl)oxy)-3-(triphenylsilyl)propanenitrile. This once again makes it clear that the proposed methodology has significant application potential. Next, the authors demonstrated the derivatization of the obtained β -silyl-cyanohydrins to a variety of structurally diverse compounds *via* transformations of all three functional groups found in the mentioned scaffold.

Thus, it was shown that Si–H group can be efficiently converted to Si–OH moiety in the presence of oxidant and rhenium catalyst (however, it would be interesting to check previously mentioned Zhang's electrochemical conditions to perform this reaction under catalyst-free and external oxidant-free conditions). Moreover, it was demonstrated that nitrile as well as *N*-oxyl groups can be efficiently transformed into other functions such as tetrazoles and α -aminoxy derivatives respectively.

To gain mechanistic insights into these electroinduced reactions, the authors conducted some preliminary experiments and suggested a plausible mechanism (Fig. 11). A radical clock experiment was carried out giving the ring-opening product in 28% yield. This experiment implied that the radical pathway is operative. It is well-known the direct anodic oxidation of hydrosilanes is very difficult due to the high redox potential of Si–H bonds. The CV studies confirmed these presumptions, showing that oxidation of NHPI to PINO

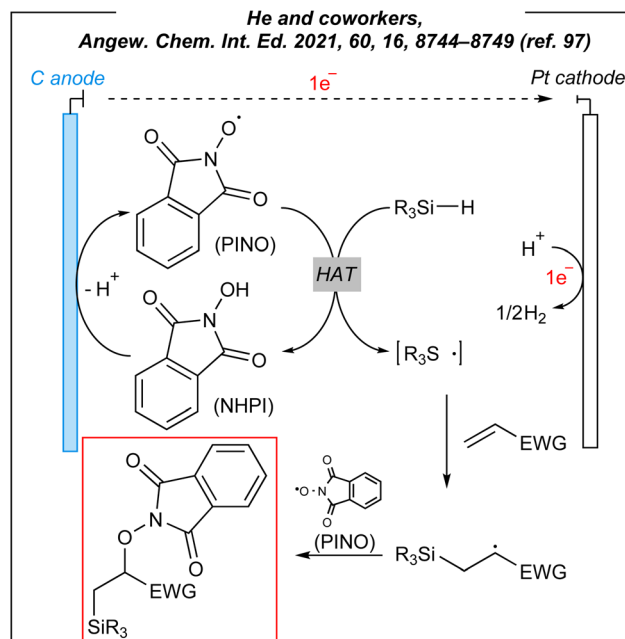


Fig. 11 Plausible mechanism for the 1,2-silylfunctionalization.

should be favoured. As the result, the PINO radical abstracts the hydrogen atom from the Si–H bond of hydrosilanes. The formed silyl radicals are subsequently added to the alkene substrate giving silyl alkyl radical, which is followed by the radical–radical coupling between the latter ones with *N*-oxyl species to give 1,2-silyl-oxygenation products (Fig. 11).

To sum up, He and coworkers reported a novel methodology for the silyl-oxygenation of activated alkenes, induced by electricity. First of all, the authors used hydrosilanes as the substrates, which is a typical choice for this type of reaction. However, usually, the scope of hydrosilane is limited to triethylsilane or tris(trimethylsilyl)silane, and the conversion of Si–H moieties requires the use of stoichiometric peroxides, traditional transition-metal catalysis or metallaphotocatalysis.^{98–107} Despite some disadvantages, the mentioned approaches are more or less a sustainable way to obtain the desired 1,2-silylfunctionalized products. Here, He's method stands out from others in terms of a wide range of silicon substrates. Furthermore, the electrochemical system consists of a graphite anode and a platinum cathode. The latter is classified as an expensive electrode but also reusable. Similarly to Lin⁶⁵ and Zhang,⁸⁶ He and coworkers again used an IKA® ElectraSyn 2.0, which ensures the reproducibility of the obtained results. In conclusion, the electrochemical 1,2-silylfunctionalization of alkenes reported by He and coworkers is an interesting alternative to other synthetic methods. Despite some limitations in the alkene scope, it can be considered a useful synthetic approach.

In 2021, Han and Jing achieved the synthesis of dibenzosiloles through electrocatalytic sila-Friedel-Crafts reaction.¹⁰⁸ For this process (Fig. 12), the authors used the following combination: RVC anode, platinum cathode, CCE @ 5 mA, NHPI



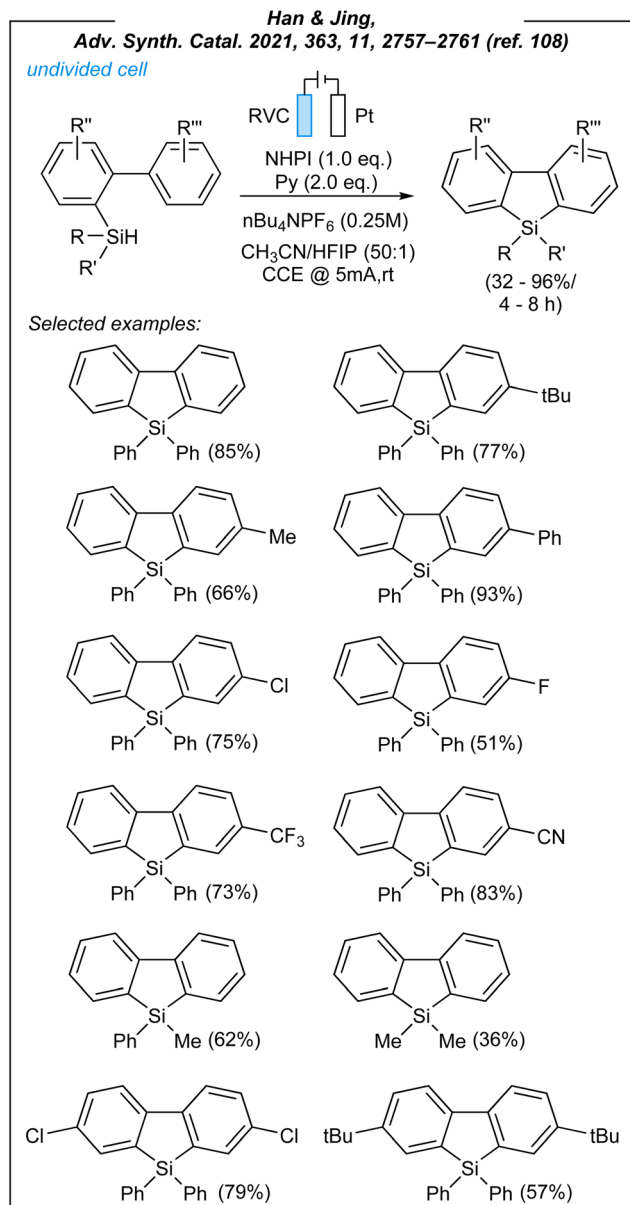


Fig. 12 Electroinduced sila-Friedel-Crafts reaction leading to dibenzosiloles.

as HAT mediator (1.2 eq.), pyridine as an additive (2.0 eq.) and $n\text{Bu}_4\text{NPF}_6$ as the electrolyte. During the optimization studies, several HAT mediators were tested including NHPI (selected), NHSI, quinuclidine, and DABCO. The mediator-free attempt was also carried out and proved the essential role of the HAT-step. Han also demonstrated the necessity of electricity, and that pyridine was the additive of choice. After considerable experimentation, it was also found that $\text{CH}_3\text{CN}/\text{HFIP}$ mixture (50:1) is crucial, and the absence of HFIP (hexafluoroisopropanol) gave inferior results. Upon the investigation of the reaction scope, it was revealed that biaryl-2-yl-diphenylsilanes with both electron-donating groups and electron-withdrawing substituents at the phenyl rings are compatible with the process

conditions, leading to the desired products in moderate to excellent yields (32–96%).

However, in the vast majority of cases, the substrates with activated rings afforded higher yields. It is worth noting that the nature of substituents at silicon atoms is crucial, probably due to stabilization effects. Thus, the best results were obtained for biaryl-2-yl-diphenylsilanes, whilst biaryl-2-yl-methylphenylsilane and biaryl-2-yl-dimethylsilane gave inferior results (62% and 36%, respectively).

The presented reaction system involved a HAT mediator – NHPI, which undergoes deprotonation facilitated by pyridine, and a subsequent anodic oxidation process. As the result, the PINO radical is afforded and it abstracts the hydrogen atom from the Si–H bond of hydrosilane. The formed silyl radical is subsequently oxidized to a silyl cation. The formation of R_3Si^+ species was indirectly confirmed by quenching the cations with water to afford the corresponding silanols (similar to Zhang's procedure). However, under standard conditions, the silyl cations cyclize through sila-Friedel-Crafts reaction. The plausible mechanism is depicted in Fig. 13.

To sum up, Han and coworkers reported a novel methodology for the synthesis of dibenzosiloles, induced by electricity. The reaction proceeds *via* cyclization of *in situ* generated silyl cations (*via* sequence: hydrosilane – silyl radical – silyl cation).

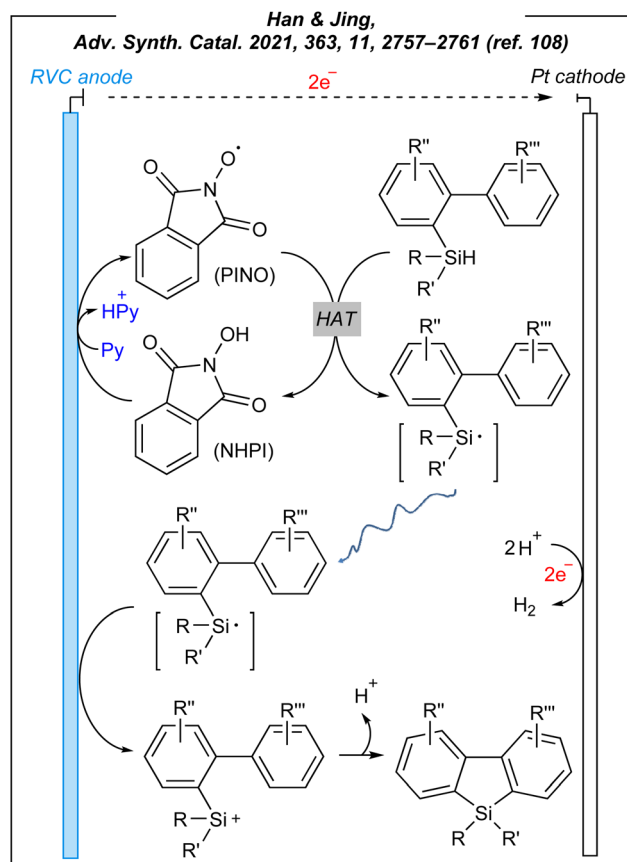


Fig. 13 Plausible mechanism for the electrocatalytic sila-Friedel-Crafts reaction.



The SiH-substituted biaryls are a typical choice for this type of reaction. The authors showed that triarylsilanes give the best results, with a wide range of substituents at biaryl rings. To date, there were four major ways to obtain dibenzosiloles. The conventional coupling between readily available chlorosilane with organometallic derivative has a limited scope and gives the desired products with low yields.^{109,110} Secondly, there are radical approaches usually suffering from harsh conditions and stoichiometric amounts of oxidants.^{111,112} There are also classical dehydrogenative coupling processes employing very expensive transition metal complexes (such as Rh).^{113–115} Finally, the sila-Friedel-Crafts reactions can be performed in the presence of trityl cation¹¹⁶ or cationic Ru-S complexes.^{117,118} Thus, from the synthetic point of view, the electrochemical approach seems to be a sustainable alternative to known procedures (*e.g.*, no TM-catalysts, no external oxidants, *etc.*) Furthermore, the electrochemical system consists of an inexpensive graphite anode and an expensive platinum cathode. The authors used a homemade reactor providing no crucial information about the anode dimensions and the current density. In conclusion, the electrochemical sila-Friedel-Crafts reaction reported by Han and coworkers is an interesting alternative to known synthetic protocols, but it has some limitations in the scope (*e.g.*, mostly the utilization of triarylsilyl derivatives) and supporting information for the users.

Recently, Poisson and coworkers disclosed a novel strategy to carry out hydrosilylation reaction by using the Suginome reagent (PhMe₂Si-Bpin) and alkynes under electrochemical conditions (Fig. 14).¹¹⁹

This article clearly shows how important recent developments in the field were. For the formal hydrosilylation process, the authors used the following combination: stainless steel electrodes (both anode and cathode), CCE @ 10 mA, and *n*Bu₄NCl as the electrolyte. Control experiments showed that a mixture of CH₃CN/CH₃OH (9:1) is crucial to obtain the desired products, and the essential role of electricity was also confirmed. The switch from *n*Bu₄NCl to *n*Bu₄NBF₄ led to lower conversion but slightly better selectivity. Subsequently, the authors investigated the scope of this hydrosilylation approach. A wide range of phenylacetylene derivatives worked efficiently under the reaction conditions. Furthermore, commercial ene-yne derivative also participated effectively in this process, while preserving the ene-functionality untouched. Finally, the authors were able to convert a few biorelevant complex molecules, as well as four internal alkynes.

To gain some mechanistic insights into this electroinduced transformation, the authors conducted some experiments. Firstly, the origin of the hydrogen atom (red colour in Fig. 14) added to the vinyl radicals was examined. Unlike Lin, and despite a lower bond dissociation energy of the C–H bond in CH₃CN molecule, Poisson proposed that CH₃OH serves as the hydrogen source (not CH₃CN). It was confirmed *via* labeling experiments; however, the true nature of this process is still unknown. The plausible mechanism is depicted in Fig. 15.

It assumes, that firstly, the methoxide anion reacts with the Suginome reagent to form anionic borate species, which is fol-

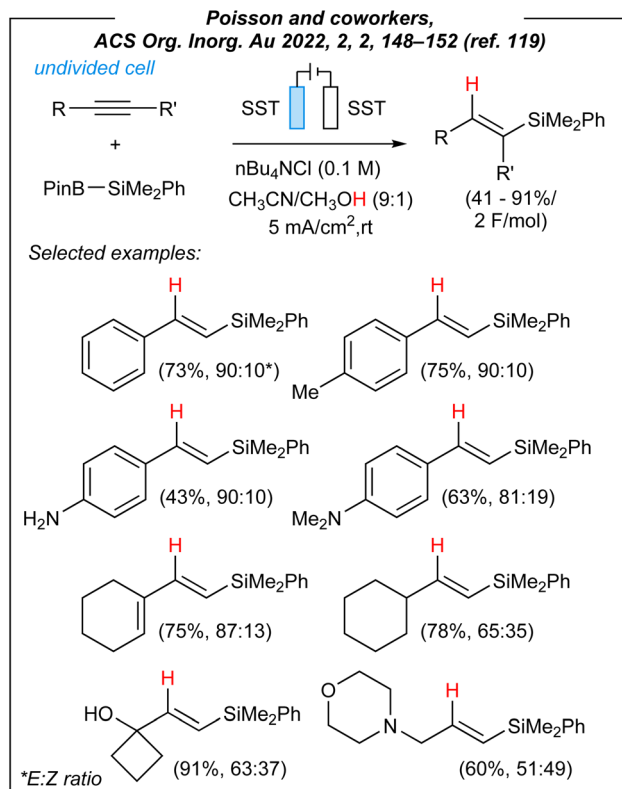


Fig. 14 Hydrosilylation of alkynes under electrochemical conditions.

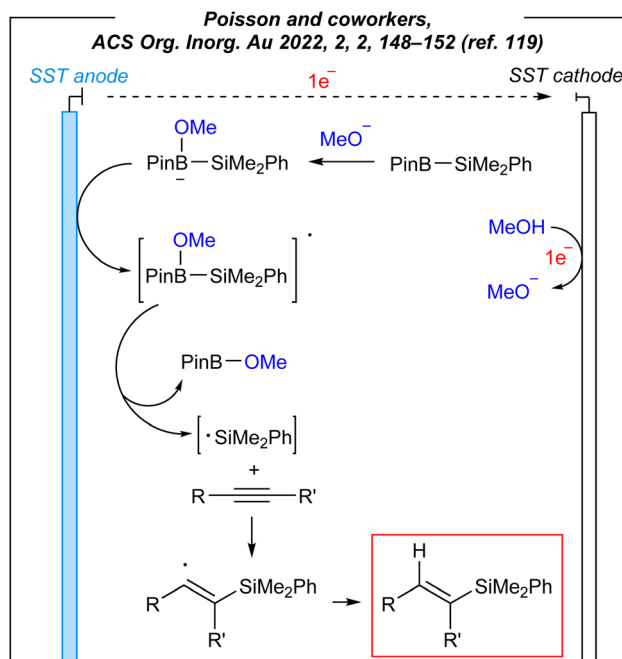


Fig. 15 Plausible mechanism for the electroinduced hydrosilylation.

lowed by the anodic oxidation of the latter to form borate radical species. Their decomposition leads to methoxyboronic acid pinacol ester and silyl radicals. The next step involves a



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nucleophilic silyl radical addition to the alkyne to generate a Si–C bond. The highly reactive vinyl radicals undergo the radical–radical coupling or they abstract the proton from tetra-coordinated boron species (formed from methanol and Suginome reagent).

To sum up, Poisson and coworkers reported a novel methodology for the hydrosilylation of alkynes, induced by electricity. First of all, the authors used only Suginome reagent as the source of silicon (it is worth noting, that recently, the authors disclosed also another interesting application of this compound under electrochemical conditions¹²⁰). The mentioned 2-(dimethylphenylsilyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane is commercially available but quite expensive (Merck – 104€ per 1 g; Gelest – 462.00\$ per 2.5 g). The future expansion of the scope (for other B–Si species) would imply an additional preparation of such precursors. Fortunately, the scope of alkynes includes a wide range of terminal and internal derivatives, giving access to several hydrosilylation products. Of course, there are plenty of methods to achieve Si–H addition to unsaturated bonds.^{34,121–123} However, they involve the use of radical generators or different catalysts (mainly TM-complexes). Therefore, a very important step is searching for an alternative to highly expensive oxidants, as well as catalysts based on platinum or rhodium.^{124–129} Furthermore, in terms of the electrochemical system, the authors used readily available stainless steel electrodes. Similarly to Lin,⁶⁵ Zhang,⁸⁶ and He,⁹⁷ also Poisson and coworkers used an IKA® ElectraSyn 2.0, which ensures the reproducibility of the obtained results. In conclusion, the presented electrochemical hydrosilylation of alkynes is a fresh look at the process of Si–H addition to unsaturated bonds. Despite some limitations (*e.g.*, all reactions limited to the Suginome reagent, the mixture of *E/Z* isomers, *etc.*), it can be considered as one of the pioneering achievements, which should stimulate further development of this field.

The main goal of this perspective was to showcase the diverse synthetic approaches associated with the electroinduced cleavage of Si–H, Si–Cl, and Si–B bonds enabling the synthesis of several organosilicon compounds. These, in turn, create a platform for both known and completely new materials. During the last two years, a significant recent impetus has been gained by the use of electrosynthesis. Notably, this also involved the use of knowledge regarding previous investigations dating back to the 1970s. The major advances had been achieved with the reproducibility and accessibility of the electrochemical approaches. Commercial, standardized equipment such as IKA® ElectraSyn 2.0 may revolutionize the electrochemical synthesis itself. Given the importance of organosilicon compounds for material chemistry, further exciting advances are expected in this constantly-evolving research area. These should address the use of less expensive precursors and additives, the issue of selectivity, and probably the development of electrocatalytic approaches for more challenging transformations. Finally, it is hoped that further achievements will meet the criteria of broadly understood green synthesis, which will ensure the sustainable development of our societies.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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