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# Oligosilanes as Silyl Radical Precursors through Oxidative Si–Si Bond Cleavage using Redox Catalysis

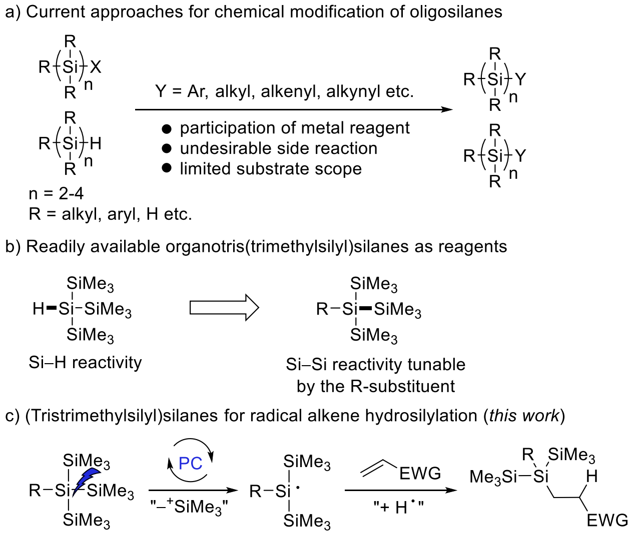
Xiaoye Yu, Maximilian Lübbesmeyer, and Armido Studer*

**Abstract:** Oligosilanes are of great interest in the fields of organic photonics and electronics. In this communication, a highly efficient visible-light-mediated hydrosilylation of electron-deficient alkenes through cleavage of a trimethylsilyl-polysilanyl Si–Si bond is explored. These reactions smoothly occur on readily available organo(tristrimethylsilyl)silanes and other oligosilanes in the presence of an $Ir^{III}$-based photo-redox catalyst under visible light irradiation. Silyl radicals are generated through single electron oxidation of the oligosilane assisted by the solvent. The introduced method exhibits broad substrate scope and high functional group tolerance with respect to the organo(tristrimethylsilyl)silane and alkene components, enabling the construction of functionalized trisilanes. In addition, this catalytic system can be also applied to highly strained bicyclo[1.1.0]butanes as silyl radical acceptors.

Oligosilanes are a class of compounds containing Si–Si bonds that have attracted considerable attention given their unique electronic and photophysical properties.[1] Early syntheses of oligosilane derivatives which can be traced back to the 1920s were achieved by reaction of dichlorodiphenylsilane with sodium.[2] However, these compounds remained fairly unexplored mainly due to their poor characterization until around 1975 when polysilane homopolymers were started to be investigated in more detail.[1a,3] Considering material properties, installation of additional functionalities to the oligosilane backbone is of importance. In this regard, oligosilanyl halides[3, 4] and oligosilanyl hydrides[3] have been identified as substrates for modification of oligosilanes through reductive couplings,[1a] Lewis acid-catalyzed transformations[5], radical processes[6] or transition metal metal-catalyzed reactions (Scheme 1a)[7]. However, these methods show limited applicability due to their relatively harsh conditions that lead to competing Si–Si bond cleavage. In this context, it is highly desirable to develop synthetic methods which allow to efficiently install diverse functional groups on the silicon backbone in oligosilanes using readily available silanyl precursors.

As a special class of oligosilanes, organotris(trimethylsilyl)silanes have gained great interests over the past decades and $(TMS)_3SiH$ as a commercially available reagent has found particular attention.[6] $(TMS)_3SiH$ not only serves as a radical chain reducing reagent in defunctionalizations, but can also be used in hydrosilylations and as a mediator of other radical reactions.[8] The chemistry of the parent $(TMS)_3SiH$ mainly relies on the reactive Si–H bond and derivatives therefrom are not well investigated in synthesis.[9] Considering $(TMS)_3SiR$ (R = alkyl and aryl[10]) as reagents, the Si–Si-bond will become the reactive entity and the readily varied substituent R should allow tuning the reactivity of such organotris(trimethylsilyl)silanes, which in turn could greatly enrich available silanyl precursors (Scheme 1b). Indeed, oligosilanes can undergo photolysis of a Si–Si bond, albeit only under ultraviolet irradiation,[11] limiting the practical application of this approach in synthesis. Other Si–Si bond-breaking reactions in disilanes rely on the participation of a transition metal complex,[12a] alkali and alkaline earth metal salts[12b,c] or strong Brønsted acid[12d]. Therefore, the development of a mild and practical method for Si–Si bond cleavage in oligosilanes is still demanded.

Recently, visible-light-mediated photoredox catalysis[13] has been successfully applied to silyl radical generation. Along these lines, photo-mediated SET, HAT and energy transfer processes have been developed starting with Si–H compounds.[14] In an elegant study, Uchiyama and coworkers recently disclosed photoinduced decarboxylation of silacarboxylic acids via a SET process for silyl radical generation.[14d] Inspired by these works and our interests in Si-radical chemistry,[15] we envisioned that silyl radicals could be formed via oxidative trimethylsilyl-polysilanyl bond cleavage under visible light irradiation using a photocatalyst (PC) in a controlled way, enabling the radical hydrosilylation of alkenes for the preparation of various 2,2-difunctionalized trisilanes (Scheme 1c).



Scheme 1. Functionalization of oligosilanes.

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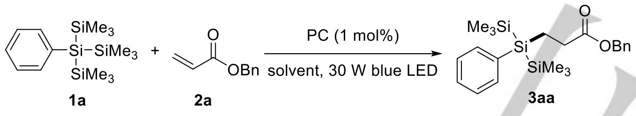
We commenced our study by exploring the hydrosilylation of phenyltris(trimethylsilyl)silane (**1a**) with benzyl acrylate (**2a**, 1.5 equiv) under blue LED irradiation in the presence of a PC (1 mol%). MeOH was initially selected as the solvent (0.1 M) since it should be able to assist the oxidative Si−Si σ-bond cleavage and will further act as the proton donor. Upon using $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ as PC under blue LED irradiation (30 W), the desired hydrosilylation product **3aa** was formed, albeit in a low yield (10%, Table 1, entry 1). Yield was slightly improved upon switching to $[Ir(dF(CF_3)ppy)_2(5,5'\text{-}d(CF_3)bpy)]PF_6$ as the PC that is known to be a stronger oxidant in its excited state ($E^{III*/II}$ = +1.30 V vs. $Fc^+$/Fc in MeCN) (Table 1, entry 2-3).[16] We further examined a series of solvents and as expected non-protic solvents such as $CHCl_3$, DMF and $CH_3CN$ provided worse results (Table 1, entry 4-6). Pleasingly, HFIP proved more effective delivering **3aa** in 40% isolated yield (Table 1, entry 7).[16] The yield could be further increased to 48% upon running the reaction at higher concentration (Table 1, entry 8, 0.2 M). Next, photocatalyst loading was increased (3 mol%) and a measurable improvement was achieved (55%, Table 1, entry 9). 2 equivalents of the acceptor **2a** turned out to be optimal, affording **3aa** with 65% yield (Table 1, entry 10). Careful exclusion of air by freeze-pump-thaw degassing further improved the result (72%, Table 1, entry 11). Finally, control experiments demonstrated the necessity of each of the key reaction components, and no product formation was observed in the absence of either photocatalyst or light irradiation (Table 1, entry 12 and 13).

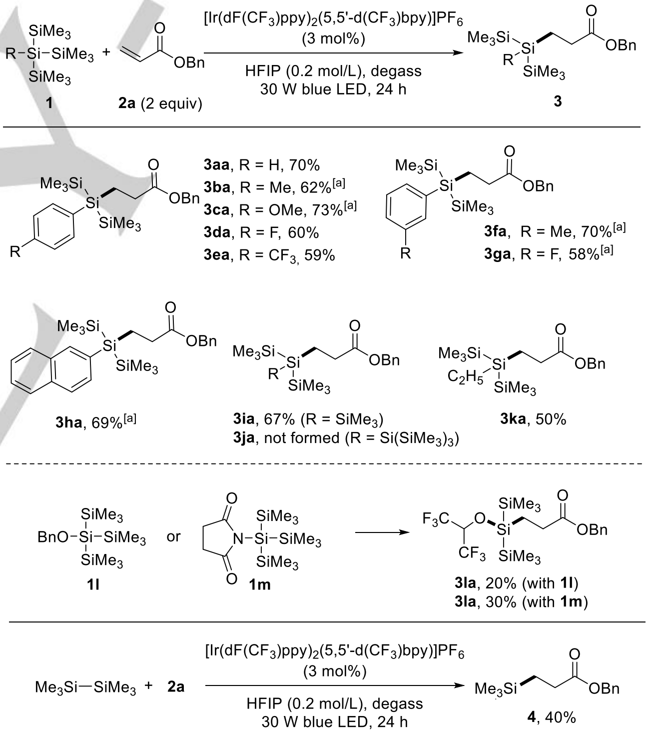
**Table 1.** Reaction optimization.[a]



| Entry | PC | Solvent | Yield [%][b] |
|---|---|---|---|
| 1 | $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ | MeOH | 10 |
| 2 | $[Ir(dF(CF_3)ppy)_2(5,5'\text{-}d(CF_3)bpy)]PF_6$ | MeOH | 26 |
| 3 | $[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$ | MeOH | 23 |
| 4 | $[Ir(dF(CF_3)ppy)_2(5,5'\text{-}d(CF_3)bpy)]PF_6$ | $CHCl_3$ | trace |
| 5 | $[Ir(dF(CF_3)ppy)_2(5,5'\text{-}d(CF_3)bpy)]PF_6$ | DMF | trace |
| 6 | $[Ir(dF(CF_3)ppy)_2(5,5'\text{-}d(CF_3)bpy)]PF_6$ | $CH_3CN$ | 10 |
| 7 | $[Ir(dF(CF_3)ppy)_2(5,5'\text{-}d(CF_3)bpy)]PF_6$ | HFIP | 40 |
| 8[c] | $[Ir(dF(CF_3)ppy)_2(5,5'\text{-}d(CF_3)bpy)]PF_6$ | HFIP | 48 |
| 9[c,d] | $[Ir(dF(CF_3)ppy)_2(5,5'\text{-}d(CF_3)bpy)]PF_6$ | HFIP | 55 |
| 10[c,d,e] | $[Ir(dF(CF_3)ppy)_2(5,5'\text{-}d(CF_3)bpy)]PF_6$ | HFIP | 65 |
| 11[c,d,e,f] | $[Ir(dF(CF_3)ppy)_2(5,5'\text{-}d(CF_3)bpy)]PF_6$ | HFIP | 72 |
| 12[c,d,e,f,g] | $[Ir(dF(CF_3)ppy)_2(5,5'\text{-}d(CF_3)bpy)]PF_6$ | HFIP | No reaction |
| 13[c,d,e,f,h] | $[Ir(dF(CF_3)ppy)_2(5,5'\text{-}d(CF_3)bpy)]PF_6$ | HFIP | No reaction |

[a] Reaction conditions: **1a** (0.10 mmol), **2a** (0.15 mmol) and PC (1 mol%) in solvent (1 mL) at rt under irradiation of 30 W blue LEDs for 12 h. [b] Isolated yields. [c] 0.5 mL HFIP. [d] 3 mol% PC. [e] Ratio of **1a** and **2a** is 1:2. [f] degassing. [g] Without visible light irradiation. [h] Without photocatalyst. bpy = 2,2'-bipyridyl. ppy = 2-phenylpyridine. Bn = benzyl group. HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol. DMF = *N*,*N*-dimethylformamide.

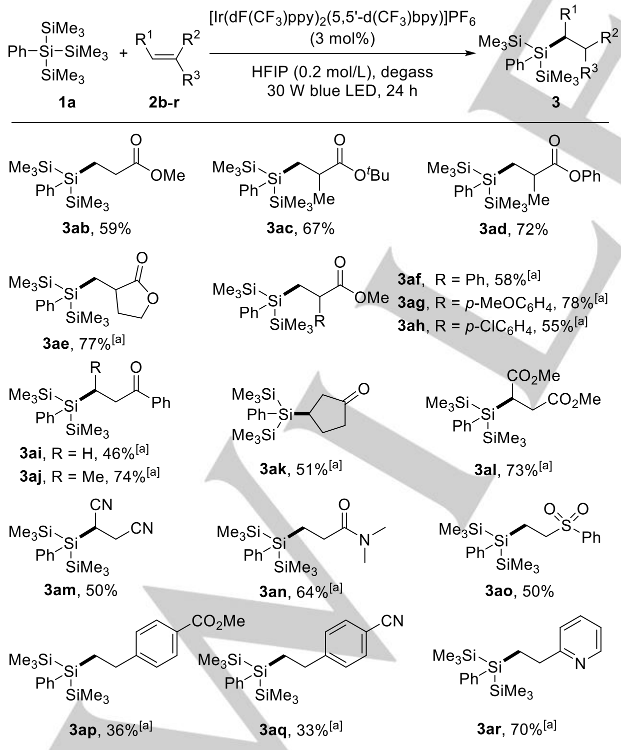
With the optimal conditions identified, we next explored the scope by reacting a range of differently substituted tris(trimethylsilyl)silanes and benzyl acrylate on a 0.2 mmol scale (Scheme 2). The reaction appears to be tolerant of various aryltris-(trimethylsilyl)silanes. Along with **3aa**, a series of aryltris-(trimethylsilyl)silanes bearing electron-donating (Me, OMe) or electron-withdrawing (F, $CF_3$) groups at the *para*-position of the phenyl ring gave good yields of the desired hydrosilylation products **3ba-ea** (59-73%). Moreover, *meta*-substituted substrates were also compatible with the expected products **3fa** and **3ga** being isolated in 70% and 58% yield, respectively. 2-Naphthyltris-(trimethylsilyl)silane **1h** reacted with **2a** in acceptable yield (**3ha**, 69%). Furthermore, commercially available tetrakis(trimethylsilyl)silane **1i** engaged in the reaction to provide the corresponding product **3ia** in good yield. However, with hexakis(trimethylsilyl)disilane as the Si-radical precursor, product **3ja** was not observed and the starting persilylated disilane could be recovered. Notably, when the ethyl substituted tris(trimethylsilyl)silane was used, the corresponding product **3ka** was obtained with 50% yield showing that an aryl group at the central silicon is not required. The O- and N-substituted



**Scheme 2.** Reaction of various oligosilanes with **2a**. Conditions: **1** (0.2 mmol, 1.0 equiv), **2a** (0.4 mmol, 2.0 equiv, 64.8 mg) and $[Ir(dF(CF_3)ppy)_2(5,5'\text{-}d(CF_3)bpy)]PF_6$ (3 mol%) in HFIP (1 mL), rt, 24 h, degassing, 30 W blue LED. Yields given correspond to isolated products. [a] Ratio of **1** and **2a** is 2:1. bpy = 2,2'-bipyridyl. ppy = 2-phenylpyridine. Bn = benzyl group. HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol.

tris(trimethylsilyl)silanes **1l** and **1m** both provided product **3la** in 20 and 30% yield, respectively. Since **1l** and **1m** turned out to be stable toward HFIP, **3la** was formed from the targeted products by reaction with HFIP. Interestingly, commercial hexamethyldisilane could also be used as $Me_3Si$-radical precursor and **4** was isolated in 40% yield.

We continued the studies by exploring the scope with respect to the alkene component using **1a** as the silyl donor (Scheme 3). As expected, reaction worked with methyl acrylate (**2b**) to afford **3ab** in 59% yield. Moreover, *tert*-butyl methacrylate (**2c**), phenyl methacrylate (**2d**) and the γ-butyrolactone **2e** were found to be effective acceptors to give the desired products **3ac**-**ae** in good yields. 2-Aryl acrylates bearing different substituents at the aryl group (H, OMe, Cl) engaged in the cascade to furnish **3af-ah** in moderate to good yields (55-78%). However, phenyl vinyl ketone (**2i**) provided a significantly lower yield (**3ai**, 46%). Gratifyingly, when a methyl group was introduced into the β-position of **2i**, reaction proceeded well to deliver **3aj** in good yield (74%). The hydrosilylation was successfully applied to the cyclic enone **2k** (**3ak**, 51%). Other electron-deficient alkenes such as dimethyl maleate (**2l**), fumaronitrile (**2m**), acrylamide **2n** and the vinyl sulfone **2o** were eligible acceptors to afford the corresponding hydrosilylation products **3al-ao** in 50-73% yield. It should be noted that electron-deficient styrene derivatives **2p** and **2q** engaged in this transformation, albeit products **3ap** and **3aq** were isolated in low yields and a large amount of starting materials remained unreacted. For styrene, only traces of product were identified. Hence, reaction only works for styrene derivatives leading to electrophilic-type benzylic radicals. Indeed, 2-vinylpyridine **2r** provided **3ar** in 70% isolated yield.

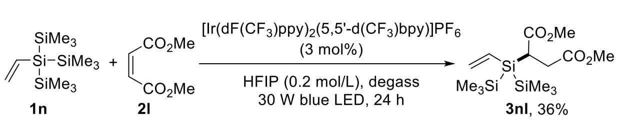


**Scheme 3.** Reaction of **1a** with various alkenes. Conditions: **1a** (0.2 mmol, 1.0 equiv, 65.0 mg), **2** (0.4 mmol, 2.0 equiv) and $[Ir(dF(CF_3)ppy)_2(5,5'\text{-}d(CF_3)bpy)]PF_6$ (3 mol%) in HFIP (1 mL), rt, 24 h, degassing, 30 W blue LED. Yields given correspond to isolated products. [a] Ratio of **1a** and **2** is 2:1. bpy = 2,2'-bipyridyl. ppy = 2-phenylpyridine. Bn = benzyl group. HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol.

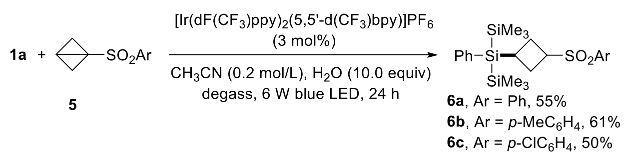
It is worth mentioning that vinyltris(trimethylsilyl)silane **1n** was applicable to this reaction when using dimethyl maleate **2l** as the acceptor, delivering the product **3nl** with moderate yield (Scheme 4a, 36%). Reaction of the nucleophilic Si-radical derived from **1n** occurred chemoselectively at the electrophilic double bond of **2l** and reaction with the benzyl acrylate **2a** as acceptor was not observed. In view of reactivity of the silyl radical with respect to dehalogenation, we added 1 equivalent of n-hexyl bromide or cyclohexyl bromide to the standard reaction conditions. Under these conditions, only a trace amount of the product **3aa** was obtained with the starting phenyltris(trimethylsilyl)silane **1a** mostly remained unreacted. These experiments show that the Si-radical derived from **1a** preferably reacts with alkyl bromides instead of engaging in the conjugate addition. Unfortunately, the Giese-type addition of the alkyl bromides with **2a** did not work under these conditions, as checked by GCMS-analysis. To further explore the potential of this methodology, we attempted to apply our strategy to highly reactive bicyclo[1.1.0]butanes (BCBs) as Si-radical acceptors.[17] Of note, radical additions to the central C−C bond of BCBs are well established for the preparation of functionalized cyclobutanes.[18] Gratifyingly, simple modification of our optimized reaction conditions allowed the rapid access of 1,3-disubstituted cyclobutanes (see the Supporting Information for optimization). As shown in Scheme 4b, BCBs bearing an activating aryl sulfonyl substituent reacted with **1a** to the corresponding products **6a-c** in good yields (50-61%) with 1:1-diastereoselectivity.

Finally, we could show that the trisilane products can act as silyl donors in a renewed redox neutral hydrosilylation. This was documented by the reaction of trisilane **3am** with **2a** under our standard conditions which afforded the disilane **7** in moderate yield (Scheme 4c).

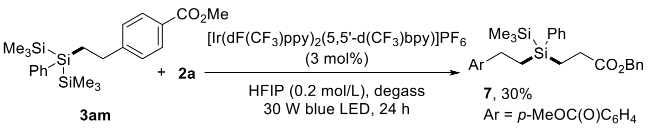
a) Vinyltris(trimethylsilyl)silane as Si-radical precursor[a]



b) Addition of silyl radicals to strained bicyclic acceptors[b]



c) Renewed hydrosilylation with trisilane **3am**[c]

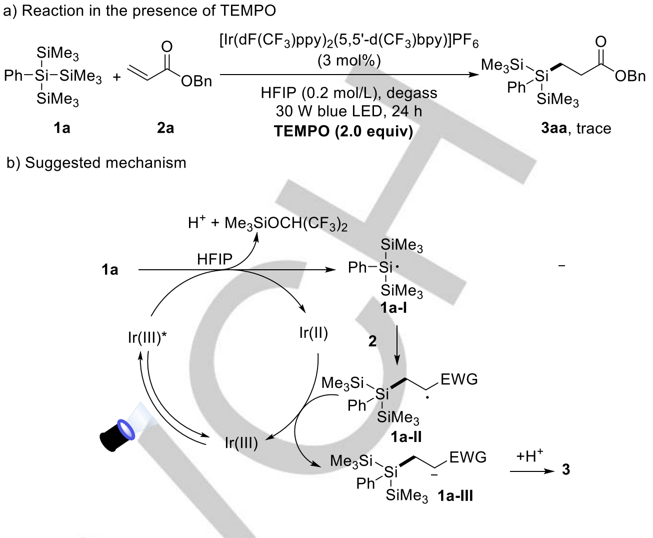


**Scheme 4.** Synthetic utility. a) Reaction condition: **1n** (0.4 mmol, 2.0 equiv), **2l** (0.2 mmol, 1.0 equiv) and $[Ir(dF(CF_3)ppy)_2(5,5'\text{-}d(CF_3)bpy)]PF_6$ (3 mol%) in HFIP (1 mL), rt, 24 h, degassing, 30 W blue LED. b) Reaction condition: **1a** (0.15

mmol, 1.0 equiv, 48.7 mg), **5** (0.1 mmol, 1.0 equiv), $H_2O$ (1.0 mmol, 10 equiv) and $[Ir(dF(CF_3)ppy)_2(5,5'\text{-}d(CF_3)bpy)]PF_6$ (3 mol%) in $CH_3CN$ (0.5 mL), rt, 24 h, degassing, 6 W blue LED. *dr* = 1:1. c) Reaction condition: **3am** (0.2 mmol, 2.0 equiv, 65.0 mg), **2a** (0.1 mmol, 1.0 equiv) and $[Ir(dF(CF_3)ppy)_2(5,5'\text{-}d(CF_3)bpy)]PF_6$ (3 mol%) in HFIP (0.5 mL), rt, 24 h, degassing, 30 W blue LED.

To gain insights into the mechanism, some additional experiments were carried out. Formation of product **3aa** was largely suppressed in the presence of TEMPO (Scheme 5a). Stern−Volmer quenching experiments revealed that phenyltris(trimethylsilyl)silane **1a** with the assistance of HFIP could efficiently quench the excited photocatalyst while substrate **2a** did not quench the excited state of the photocatalyst. The importance of HFIP for oxidation of **1a** was supported by the fact that no quenching of the excited photocatalyst was observed with **1a** in $CH_3CN$. Moreover, for **1b** bearing the electron-donating para-methyl group a small decrease in the emission intensity was measured as compared to the parent **1a**. The para-fluoro substituent (see **1d**) did not show a large effect and a similar quenching efficiency as with **1a** was measured. These results are in accordance with cyclic voltammetry experiments. The tris(trimethylsilyl)silanes **1a**, **1b**, and **1d** are irreversibly oxidized anodically. The oxidation is observed as a superposition of two consecutive oxidation processes. The first process that is relevant in the context of this study is observed at peak potentials of approx. 1.0 V, 0.9 V, and 1.1 V versus $Fc/Fc^+$ in HFIP, respectively, reflecting the electronic characteristics of the phenyl substituents (see SI for detailed information). In contrast, a significantly higher peak potential of approx. 1.4 V versus $Fc/Fc^+$ was determined for **1a** in $CH_3CN$. Oxidation of the tris(trimethylsilyl)silanes by the excited state photocatalyst ($E_{Ir(II)/^*Ir(III)}$ = 1.30 V versus $Fc/Fc^+$ in $CH_3CN$)[19a] is, thus, thermodynamically favored in HFIP only.

Based on these results and the fact that both light and photocatalyst are required, we propose a mechanism that is presented in Scheme 5b, exemplified for the reaction with **1a**. The catalytic cycle starts with SET oxidation of **1a** by the excited state photocatalyst $^*$Ir(III), forming the silyl radical **1a-I** and the corresponding reduced Ir(II)-complex. Si-radical generation is likely mediated by HFIP to give $Me_3SiOCH(CF_3)_2$ which is identified as a byproduct. The free Si-radical **1a-I** then adds to the double bond of **2**, generating the adduct carbon radical **1a-II**. Reduction of **1a-II** by the Ir(II)-complex gives the anion **1a-III** with concomitant regeneration of the ground-state Ir(III)-complex,[19b] closing the photocatalytic cycle. As expected, reduction is only possible for electrophilic type radicals **1a-II**. This is well reflected by the styrene series where only the electron-poor pyridine derivative provided a high yield, whereas the parent styrene did not work. Protonation of **1a-III** eventually affords the final product **3**.


a) Reaction in the presence of TEMPO

b) Suggested mechanism

**Scheme 5.** Proposed mechanism.

In summary, we have utilized organo(tristrimethylsilyl)silanes as silyl radical precursors in redox neutral hydrosilylation of electron-deficient alkenes. Diversely substituted silyl radicals are generated as key intermediates through direct activation of a trimethylsilyl-polysilanyl Si−Si bond via single electron oxidation, enabling rapid access to a wide range of functionalized trisilanes. Along with electron-poor alkenes, strained bicyclo[1.1.0]butanes also react as Si-radical acceptors. Notably, sequential double hydrosilylation starting with aryl(tristrimethylsilyl)silanes is also feasible. Considering the broad substrate scope and operationally simple procedure the introduced methodology should find widespread use for the preparation of functionalized oligosilanes.

## Acknowledgements

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**Keywords:** oligosilanes • photocatalysis • single-electron transfer • silyl radicals • hydrosilylation

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## COMMUNICATION

*X. Yu, M. Lübbesmeyer, A. Studer*

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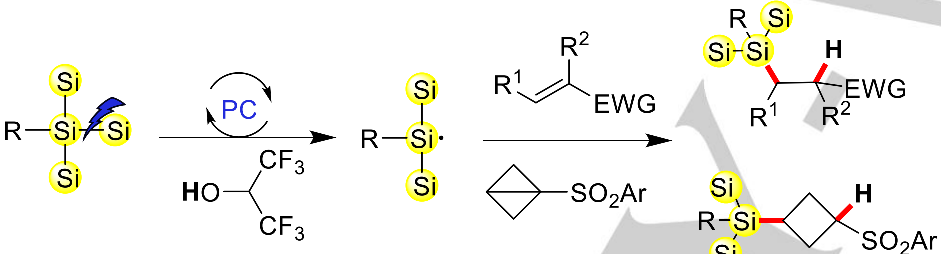
**Oligosilanes as Silyl Radical Precursors through Oxidative Si–Si Bond Cleavage using Redox Catalysis**

Radical hydrosilylation of electron-deficient alkenes through cleavage of a trimethylsilyl-polysilanyl bond has been accomplished. These reactions smoothly occur by direct activation of a trimethylsilyl-polysilanyl bond via single electron oxidation by a redox catalyst assisted by solvent under visible light irradiation. This catalytic strategy could be also applied to the silylation of highly strained bicyclo[1.1.0]butanes.



- broad substrate scope
- high functional-group tolerance
- facile synthesis of substituted oligosilanes