

Special
Issue

Recent Developments in the Photo-Mediated Generation of Silyl Radicals and Their Application in Organic Synthesis

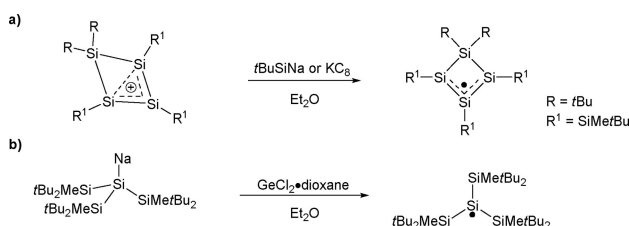
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Silicon radicals play important roles in diverse areas of organic synthesis and material science. With the rapid development of photocatalysis over the past decades, photochemistry may potentially serve as an appealing approach for the generation

of silyl radicals. This Minireview will focus on recent photo-mediated generation of silyl radicals in the area of organic synthesis.

1. Introduction

Organosilanes are versatile intermediates and products in medicinal chemistry and material science. Silicon centered radicals are known as silyl radical bearing an unpaired electron on the silicon atom.^[1] A vast amount of reports with silyl radicals has been published since the late 1940s, and was mainly speculated through spectroscopic characterization as the intermediate in hydrosilylation of alkenes.^[2] The first stable and isolatable silyl radical was presented by Sekiguchi and co-workers in 2001 (Scheme 1a).^[3] In the following year, the same



Scheme 1. Generation of the first stable and isolatable silyl radicals.^[3,4]

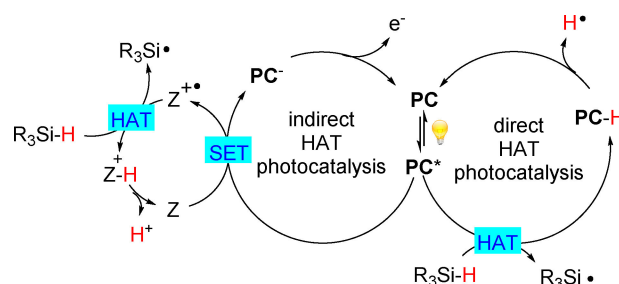
research group reported the first air stable silyl radical without stabilization by conjugation with π -bonds (Scheme 1b).^[4] Silyl radical plays an important role in diverse areas of material and polymer science and industry.^[5] On the other hand, significant developments have been achieved in photochemistry over the past decade, which have enabled previously impossible transformations.^[6–12] Apart from single electron transfer (SET) and energy transfer, hydrogen atom transfer (HAT) is frequently involved in photocatalysis, offering enormous opportunities for C–H activation.^[13–16] In analogy to carbon, photochemistry may potentially serve as an appealing approach for the generation of silyl radicals.^[17] For instance, the photolysis of Si–Si bond is feasible but has no practical application in synthesis yet.^[18] To

the best of our knowledge, there is no recent review on photo generation of silyl radicals with or without the aid of catalysts. In line with our recent work on visible-light mediated metal-free hydrosilylation,^[19] this mini review seeks to showcase the recent development on photo-mediated generation of silyl radicals and their application in organic synthesis.

2. Photo-Mediated Generation of Silyl Radicals

2.1. Formation of Silyl Radicals from Silicon Hydrides

Hydrogen atom transfer (HAT) has been frequently involved in photocatalysis, which can activate substrates without the limitation of redox potentials. The use of HAT strategy can provide a convenient and straightforward way to activate silicon hydride (Si–H) for silyl radical generation. HAT catalysis can be achieved in three general pathways upon light irradiation.^[13] The first straightforward strategy is the use of activated photocatalyst as a direct HAT catalyst to abstract a H atom from the substrate (Scheme 2). The HAT catalyst is then



Scheme 2. Typical reaction mechanism for direct and indirect HAT photocatalysis to generate silyl radicals.

regenerated through a reverse hydrogen atom transfer (RHAT) via hydrogen abstraction by generated intermediates.^[20] For instance, photo-excited carbonyl compounds, e.g. aromatic ketones with an $n-\pi^*$ triplet state, can act as direct HAT photocatalysts for silyl radical generation, due to an unpaired electron on oxygen at the excited state.^[21] However, the limited

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pool of available photocatalysts able to perform direct HAT⁽¹⁴⁾ is generally restricted to families of aromatic ketones,^[22] polyoxometalates (especially decatungstate anion [W₁₀O₃₂]⁴⁻),^[23] and others such as uranyl cation^[24] [UO₂]²⁺ and recently established xanthenes dyes such as eosin Y.^[20]

The second mode proceeds via indirect HAT photocatalysis (Scheme 2), where the excited photocatalyst activates another species **Z** through a SET process, thereby generating a radical species. Subsequently, radical **Z** can abstract hydrogen from Si–H to deliver a silyl radical. This species **Z** may either be added in a stoichiometric amount where it is consumed in the process, or behave catalytically, resulting in a dual-catalytic system.^[25] The last strategy, proton-coupled electron transfer (PCET) involves concerted transfer of an electron and a proton.^[26] The mode of direct HAT catalysis represents the most reagent and redox-economical method among the three pathways, as indirect HAT photocatalysis and PCET processes require the use of other additives prior to the desired radical generation.

The use of photoredox catalysis via HAT process enables the generation of silyl radical from Si–H bonds. In contrast, it is difficult to activate Si–H (except for (Me₃Si)₃Si–H) using conventional initiators such as 2,2-azobis (2-methylpropanitrile), AIBN or Et₃B. In addition, the widely used tin reagent to generate silyl radical is not desired from an environment standpoint and it is difficult to remove organotin impurities from the products after reactions.^[27] The trend of Si–H bond strength progressively increases with the replacement of H atom on SiH₄ by carbon atoms (Table 1), as the more electronegative carbon atom will

Silane (R ₃ Si–H)	BDE [kJ mol ⁻¹]	Silane (R ₃ Si–H)	BDE [kJ mol ⁻¹]
H ₃ Si–H	383 ± 8	PhSiH ₂ –H	377 ± 8
MeSiH ₂ –H	386 ± 12	PhMeSiH–H	382 ± 12
Me ₂ SiH–H	392	Me ₂ SiSiMe ₂ –H	381
Me ₃ Si–H	397.4	(Me ₃ Si) ₃ Si–H	351.5
Et ₃ Si–H	398	(MeS) ₃ Si–H	364

cause the central silicon to become more electron withdrawing.^[28]

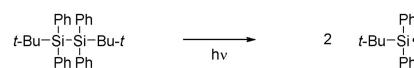


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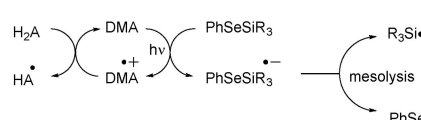
2.2. Formation of Silyl Radicals from Si–M Reagents (M = Si, Se, B, O)

In 1997, Matsumoto demonstrated that silyl radical could be derived from the homolytic cleavage of sterically hindered Si–Si bonds (Scheme 3a).^[29] The bulky substituent on the disilane

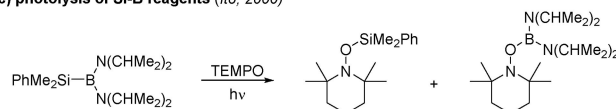
a) homolytic Si–Si bond cleavage (Matsumoto, 1997)



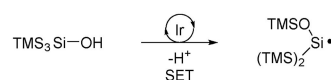
b) mesolysis of Se–Si reagents (Pandey, 1998)



c) photolysis of Si–B reagents (Ito, 2000)



d) silanol migration (Macmillan, 2018)



Scheme 3. Generation of silyl radicals using Si–M reagents (M = Si, Se, B, O).^[29–32]

prevents 1,3-Si shift to the ortho-position of the aryl group. These silyl radicals were obtained from the lowest excited triplet state and are the major products in polar solvents such as acetonitrile. In the following year, the Pandey group reported an efficient strategy to generate silyl radicals based on the photo mesolysis of selenium reagent PhSeSiR₃, using 9,10-dimethoxyanthracene (DMA) as an electron donor and ascorbic acid as a co-oxidant to generate PhSeSiR₃[•], followed by mesolysis to give the R₃Si[•] radical and PhSe⁻ anion (Scheme 3b).^[30] In 2000, the Ito group described the use of bulky substituents on boron in organosiliconboranes, e.g., R₃SiB[N(CHMe₂)₂]₂, to generate a pair of silyl and boryl radicals by photolysis, where both radical species could be quantitatively trapped by TEMPO (Scheme 3c).^[31] Control experiments re-



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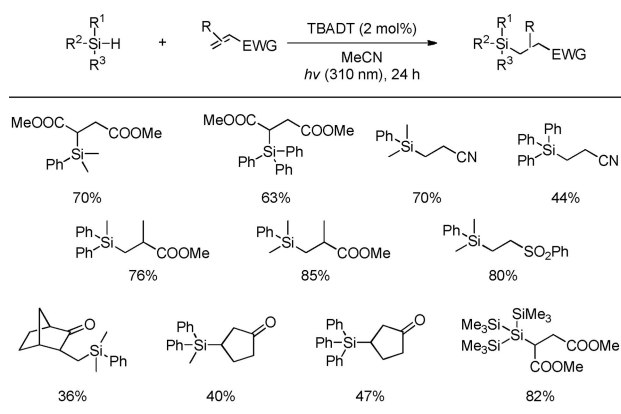
vealed that homolysis occurred only after irradiation with a high-pressure mercury lamp. These organosiliconborane reagents were thermally stable without decomposition even at 180 °C. In 2018, the Macmillan group reported an unprecedented silyl radical generation from tris-(trimethylsilyl) silanol by a SET process with photo excited Ir photocatalyst. The silanol underwent silyl migration upon oxidation and deprotonation to yield relevant silyl radical, and in turn could abstract bromide from an aryl bromide, generating an aryl radical (Scheme 3d).^[32]

3. Hydrosilylation via Photo-Generated Silyl Radicals

3.1. Hydrosilylation of Alkenes via Direct HAT Photocatalysis

The hydrosilylation of alkenes represents one of the most important reactions in the silicon industry.^[33] The transformation proceeds via a 100% atom-efficient. Speier and Karstedt have demonstrated the use of platinum catalysts for direct Si-H bond activation in hydrosilylation, and has been employed in industrial-scale manufacturing.^[34] Intensive research in hydrosilylation have led to the discovery of other effective catalysts such as earth-abundant Fe, Ni, and Co metals.^[35–42] In addition, recent advancement demonstrated the metal-free hydrosilylation using electron-deficient borane Lewis acid catalysts.^[43]

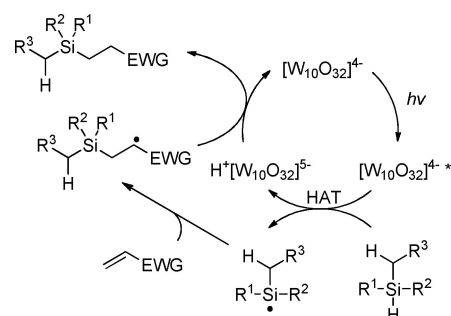
In 2015, Fagnoni, Ravelli, and co-workers disclosed an elegant hydrosilylation of electron-deficient alkenes through the use of tetrabutylammonium decatungstate (TBADT, (nBu₄N)₄[W₁₀O₃₂]) as a direct HAT photocatalyst under UV light (310 nm) irradiation.^[44] TBADT has been employed as a photocatalyst to generate silyl radicals to induce polymerization.^[45] TBADT-catalyzed hydrosilylation with arylsilanes were successfully applied to phenyl vinyl sulfone, methyl methacrylate and acrylonitrile, with respective yields above 85%. The representative substrates were shown in Scheme 4. This transformation



Scheme 4. TBADT-catalyzed hydrosilylation of electron-deficient olefins.^[44]

was amendable to scale-up using the continuous flow reactor equipped with UV-transparent PTFE tubing wrapped around water-cooled well apparatus. Reactivity was increased under continuous-flow conditions, with reaction time decreasing from 24 h to 3 h, with comparable yields as batch conditions.

The mechanistic evaluation of TBADT-catalyzed hydrosilylation (Scheme 5) included laser flash photolysis (LFP) experi-

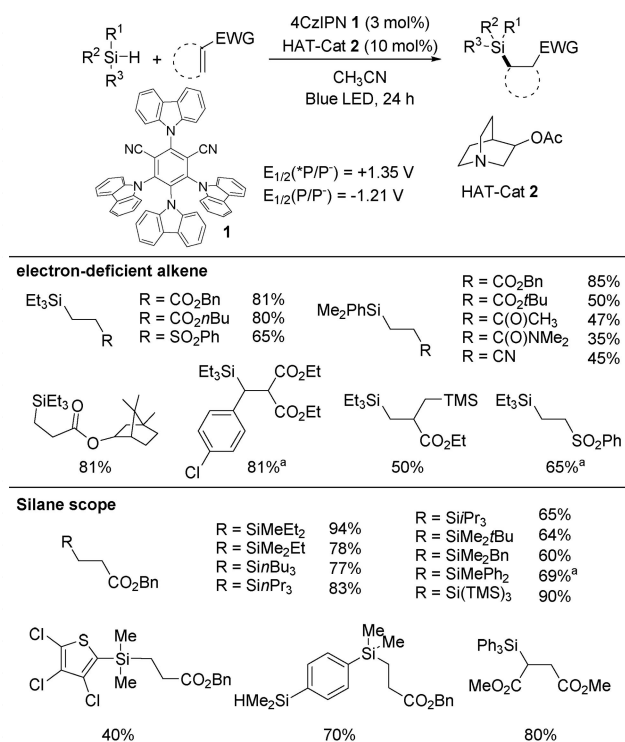


Scheme 5. Proposed mechanism for TBADT-catalyzed hydrosilylation.

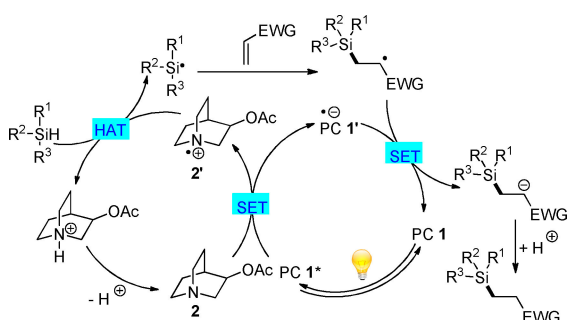
ments and steady-state EPR spectroscopy in the presence of a spin trap. LFP experiments supported the HAT mechanism, in which the detection of persistent absorption at 780 nm attributed to [HW₁₀O₃₂]⁴⁻ species. Excited TBADT behaves similarly to photo-excited ketones (triplet benzophenone) in reaction with silanes, but was a more efficient catalyst for Si-H bond activation. EPR trapping experiments with nitrene indicated the present of Si-centered radicals.

3.2. Hydrosilylation of Alkenes via Indirect HAT Photocatalysis

In 2017, Wu group demonstrated the visible-light mediated metal free hydrosilylation of both electron-deficient and electron-rich alkenes.^[19] The hydrosilylation of electron-deficient alkenes was accomplished through Si-H activation by merging organophotocatalyst 1,2,3,5-tetrakis (carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN) and quinuclidinium HAT catalyst (Scheme 6). Hydrosilylation product was obtained using trialkyl silanes without any C-H activation by-products, highlighting the effectiveness of this electron-deficient HAT catalyst for the selective Si-H activation. A plausible mechanism for hydrosilylation of electron-deficient alkenes was proposed (Scheme 7) based on several control experiments, including radical scavenging, Stern-Volmer quenching studies, deuterium-labeling experiments, light on/off experiments and quantum yield calculation. The catalytic cycle was initiated by SET of HAT catalyst 2 to light-activated photocatalyst 1* to afford the reduced photocatalyst 1' and amine radical cation 2'. This radical cation would then selectively abstract a hydrogen atom from hydridic Si-H bond to deliver a silyl radical. Subsequent addition to electron deficient olefin and reduction by photocatalyst 1', followed by another HAT from protonated 2' achieves the final hydrosilylated product.



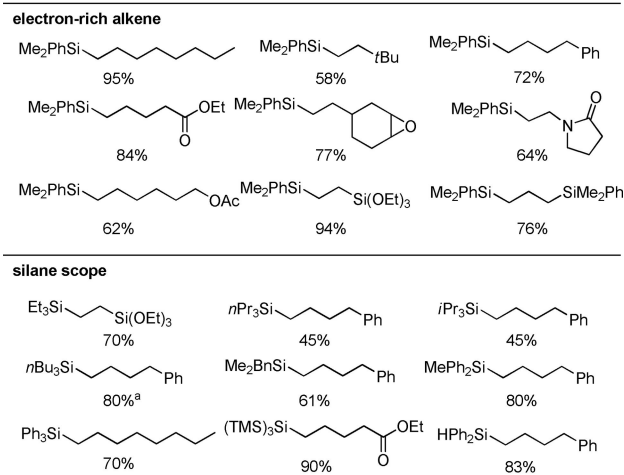
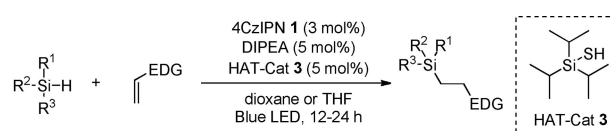
Scheme 6. Representative scope of metal-free hydrosilylation of electron-deficient alkenes. [a] Reactions carried out in stop-flow microtubing (SFMT) reactors.^[19]



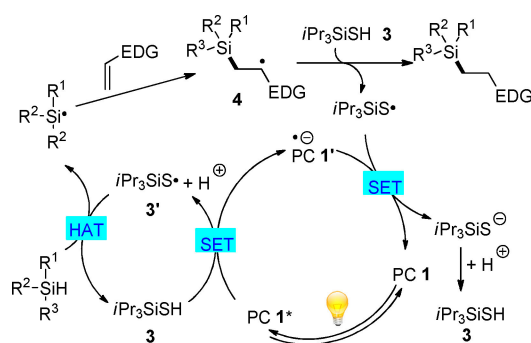
Scheme 7. Plausible mechanism for the hydrosilylation of electron-poor alkenes.^[19]

Hydrosilylation of electron-rich alkenes was also demonstrated and accomplished through the combination of 4CzIPN organophotocatalyst, *N,N*-diisopropylethylamine (DIPEA), and triisopropylsilanethiol under blue LED irradiation via dual photoredox and polarity-reversal catalysis (Scheme 8).

A plausible mechanism for the hydrosilylation of electron-rich alkenes (Scheme 9) was initiated by a SET event between excited photocatalyst 1* and HAT catalyst 3 in the presence of a catalytic amount of base (DIPEA), presumably to deprotonate and facilitate the generation of thiyl radical 3'. This thiyl radical, 3' would then undergo a HAT process with the hydridic Si–H bond to deliver a silyl radical which would subsequently add to electron rich alkenes to deliver radical 4. A polarity matched HAT process between 4 and 3 would generate the final hydrosilylation product. The BDE difference between the S–H



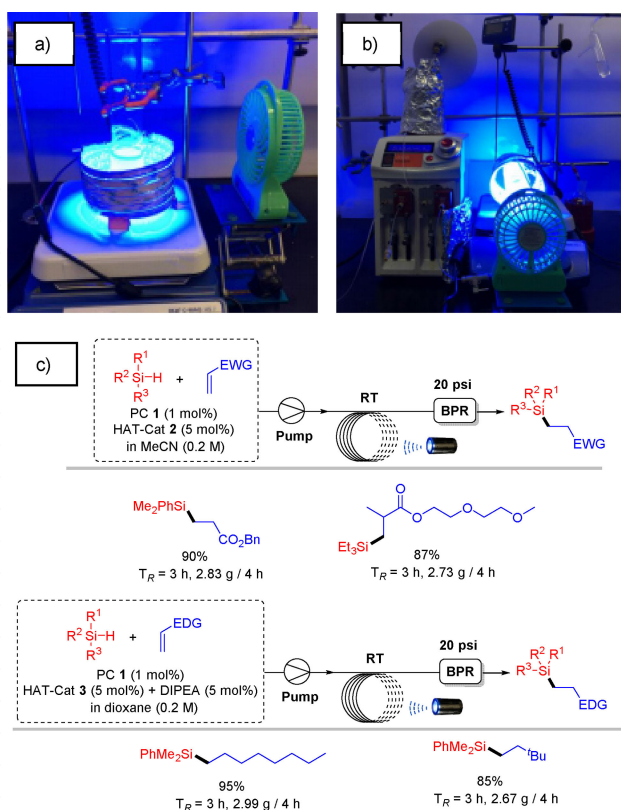
Scheme 8. Representative scope of metal-free hydrosilylation of electron-rich alkenes. [a] Reactions carried out in SFMT reactors.^[19]



Scheme 9. Plausible mechanism for hydrosilylation of electron-rich alkenes.^[19]

bond of 3 (S–H BDE=88.2 kcal/mol) and the C–H bond α to the electron-donating group of the hydrosilylation product (C–H BDE=93.2 kcal/mol) indicated the HAT was feasible. Thus thiol 3 behaved as a polarity-reversal catalyst to enable the transformation.^[46] However, the authors cannot exclude the possibility of a chain process with quick termination triggered by HAT between the radical of HAT catalyst 3 and the silane.

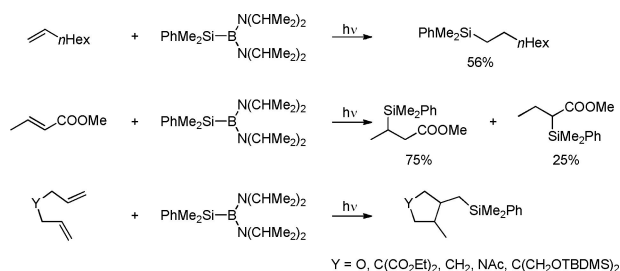
“Stop-flow” micro-tubing (SFMT) reactor was applied to reactions where conversions were low in batch reactors (Scheme 10a).^[47] The synthetic utility of SFMT reactor was further translated to gram scale synthesis of hydrosilylation of both electron-rich and -poor alkenes in continuous-flow reactors (Scheme 10b). Notably, the reaction efficiency was improved in microflow system compared to the batch reactor due to its enhanced light penetration using the microtubing reactor, enabling effective reactions even at lower catalyst loading (1 mol% photocatalyst and 5 mol% HAT catalyst).^[48]



Scheme 10. Reaction setup using a) SFMT reactors, b) continuous flow reactors, and c) gram-scale hydrosilylation schematic in continuous-flow reactors.^[19]

3.3. Hydrosilylation of Alkenes via Organosiliconboranes

The photohomolytic cleavage of Si–B bonds demonstrated by Ito using bis(diisopropylamino) organosilylboranes was able to hydrosilylate both electron-rich and electron-poor olefins and dienes (Scheme 11).^[31] The organoboryl radical, on the other

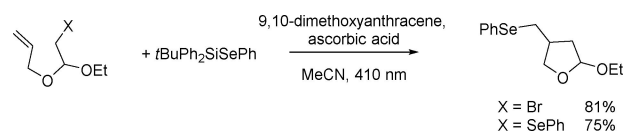


Scheme 11. Scope of hydrosilylation using organosiliconborane reagents.^[31]

hand, may have been simultaneously generated but did not participate in the reaction with olefins, probably due to the steric hindrance.

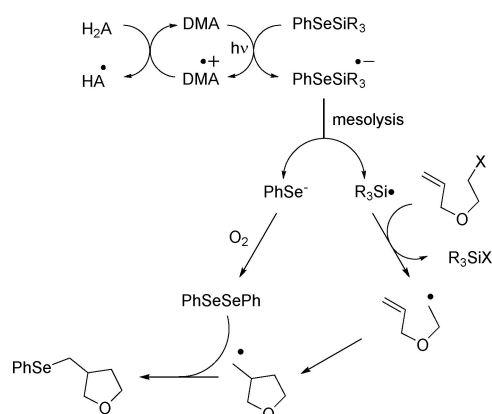
4. Photo-Induced Silyl Radicals to Promote Subsequent Radical Substitution

Silyl radicals can promote free-radical substitution with organohalides to access carbon radicals for cascade transformations.^[49] Two early reports in the late 1990s by the Pandey group showcased the production of silyl radicals via mesolysis of PhSeSiR₃[•] produced by photo-induced electron transfer (PET) under visible-light (410 nm). Starting from a bromide or a selenium compound, the same furanic product could be obtained (Scheme 12).^[50]



Scheme 12. PET reductive activation of PhSeSiR₃.^[50]

In the proposed mechanism (Scheme 13), a solution containing PhSeSiR₃, 9,10-dimethoxyanthracene as an electron

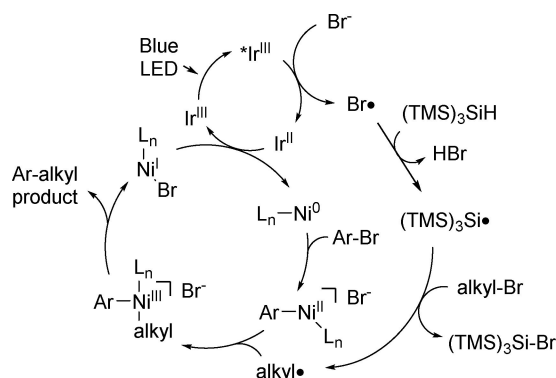


Scheme 13. Plausible mechanism for PET reductive activation of PhSeSiR₃.^[50]

donor and ascorbic acid as a co-oxidant can selectively generate PhSeSiR₃[•] under visible-light irradiation at 410 nm. Further mesolysis provides the R₃Si[•] radical and PhSe[•]. The generated silyl radical is then able to abstract Br or PhSe from the substrate to deliver an alkyl radical intermediate. Subsequent intramolecular ring closing and radical termination by PhSeSePh delivers the furanic product.

In 2016, the Macmillan group reported a bromine-based HAT process to access silyl radicals for the subsequent activation of alkyl halides for cross-electrophile coupling through the merger of Ir photoredox and Ni catalysis.^[51] The reaction was initiated via single-electron oxidation of bromide, a dissociable ligand on nickel, by photo-excited Ir photocatalyst to deliver the bromine radical. The generated electrophilic bromine radical would then abstract a hydrogen atom from (Me₃Si)₃Si–H to give a silyl radical, which will subsequently

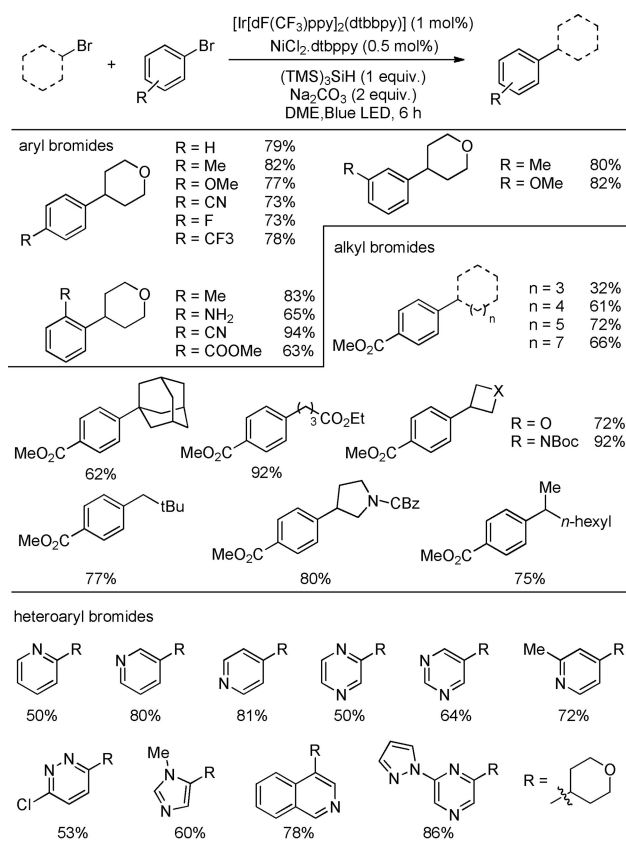
abstract bromine atom from alkyl bromides to provide a nucleophilic alkyl radical and a silyl bromide byproduct. Oxidative capture of the alkyl radical by in situ generated Ni(II) and final reductive elimination will afford the reductive cross-coupling product (Scheme 14). However, the yield decreased



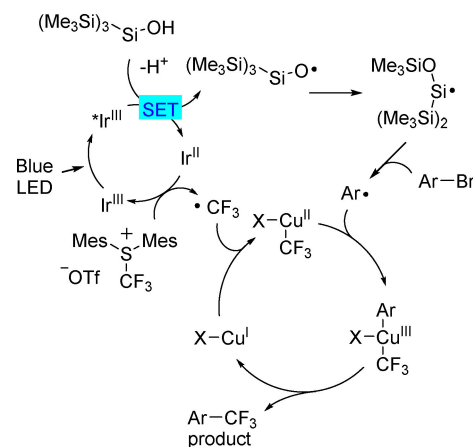
Scheme 14. Mechanism for silyl-mediated C_{sp^3} - C_{sp^2} cross-coupling reactions.^[51]

drastically to 18% when using stronger Si-H bond, such as Me₂(TMS) Si-H. The author observed a correlation between the reaction efficiency and Si-H BDE, where the proposed hydrogen abstraction mechanism is dependent to the BDE of Si-H. The generality of this reaction was demonstrated in Scheme 15 and it was expected that this light-mediated cross-electrophilic coupling will be useful leading toward a large range of medicinal agents and complex molecules.

In 2018, the Macmillan group utilized a brilliant strategy to access silyl radicals from silanols for halogen abstraction from aryl bromides to generate aryl radicals, which circumvent the sluggish nature of oxidation addition of aryl bromide in copper catalysis.^[32] Through the combination of copper and photoredox catalysis, a variety of trifluoromethylated arenes were synthesized under mild condition (visible light and room temperature). In the proposed mechanism (Scheme 16), the photo-excited Ir photocatalyst promotes SET with tris-(trimethylsilyl) silanol that rapidly undergoes silyl migration upon oxidation and deprotonation to yield the corresponding silyl radical, which in turn abstracts bromide from aryl bromides, generating the aryl radical intermediate that is intercepted by Cu^{II} to give the Cu^{III} species. The Cu^{II} species is formed via interaction of Cu^I precursor with CF₃ radical generated from SET event of the photocatalyst with the electrophilic CF₃ reagent. Reductive elimination of aryl-Cu^{III}-CF₃ adduct furnishes the trifluoromethylated product outlined in Scheme 17. The use of tris-(trimethylsilyl) silanol other than silane as the silyl radical precursor was crucial, as a significant amount of aryl dehalogenated side products were generated through the HAT process between the in situ generated reactive aryl radical and the silane reagent.



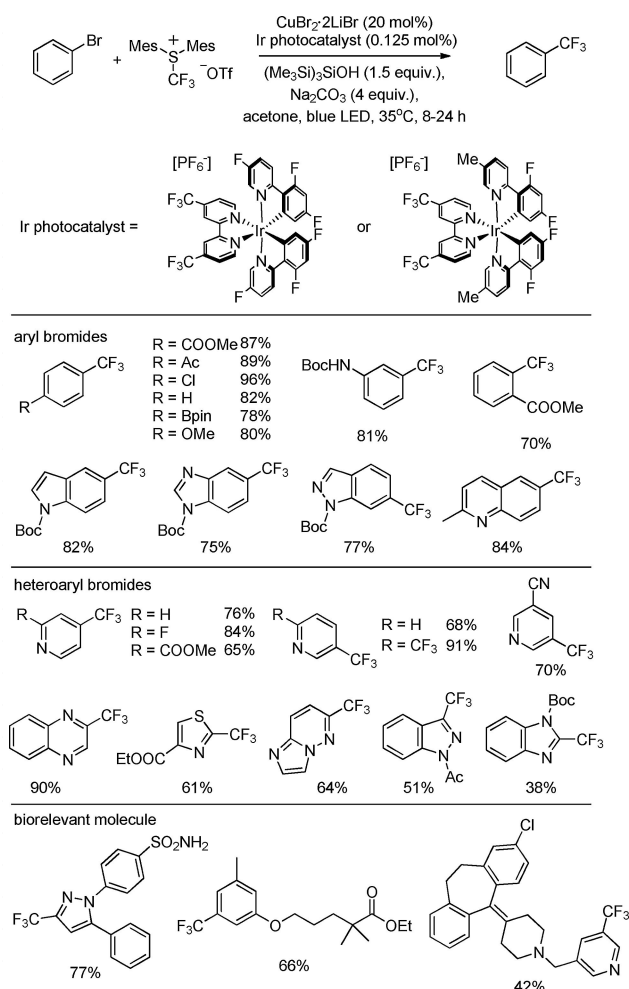
Scheme 15. Representative scope of photoredox silyl-mediated C_{sp^3} - C_{sp^2} cross-coupling reactions.^[51]



Scheme 16. Mechanism for photoredox/copper-catalyzed trifluoromethylation of (hetero)aryl bromides.^[51]

5. Conclusion

Recent development of light-driven generation of silyl radicals and their subsequent applications in organic synthesis were summarized. It is evident that this research field is still at the beginning stage with only limited reports. We anticipate that more research work will emerge accompanying with the rapid development of photochemistry. Photo-mediated SET, HAT, and



Scheme 17. Representative scope of photoredox silyl-mediated copper-catalyzed trifluoromethylation of (hetero) aryl bromides.^[51]

energy transfer processes are all possible strategies to access silyl radicals, enabling green and sustainable protocols to utilize these important intermediates for fine chemical synthesis.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: flow chemistry · hydrogen atom transfer · hydrosilylation · photoredox catalysis · silyl radicals

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