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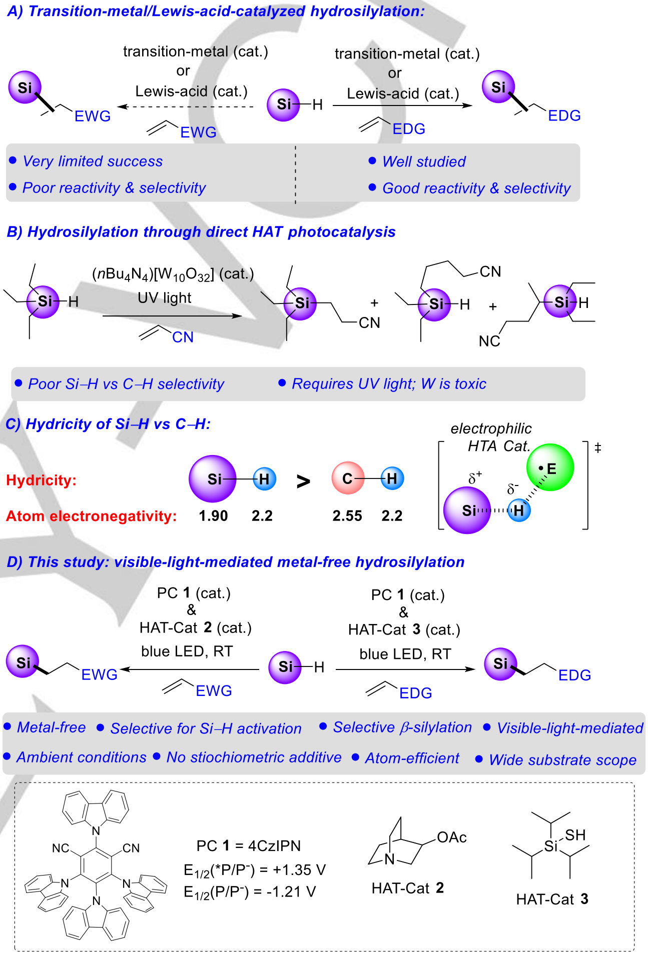
Visible-Light-Mediated Metal-Free Hydrosilylation of Alkenes through Selective Hydrogen Atom Transfer for Si–H Activation

Rong Zhou,[a,b] Yi Yiing Goh,[a] Haiwang Liu,[a] Hairong Tao,[c] Lihua Li,[a] and Jie Wu*[a]

Abstract: Although developments on the transition-metal-catalyzed hydrosilylation of alkenes have achieved great progress over the past several decades, metal-free hydrosilylation is still rare and highly desirable. Herein, we report a convenient visible-light-driven metal-free hydrosilylation of both electron-deficient and electron-rich alkenes via selective hydrogen atom transfer for Si–H activation. By the synergistic combination of an organo-photocatalyst 4CzIPN and quinuclidin-3-yl acetate catalyst, the hydrosilylation of electron-deficient alkenes exclusively occurred with Si–H activation. Additionally, the hydrosilylation of electron-rich alkenes was achieved by merging photoredox and polarity-reversal catalysis.

Organosilanes are versatile intermediates or products in medicinal chemistry and material science. The hydrosilylation of alkenes, a 100% atom-efficient transformation, represents one of the most important reactions in the silicone industry.[1] The direct activation of Si–H bonds for subsequent hydrosilylation has been effectively accomplished through the use of Speier's or Karstedt's platinum catalysts in industrial-scale manufacturing.[2] Intensive efforts in this research field have led to the discovery of earth-abundant metals, such as iron, nickel, and cobalt, as effective hydrosilylation catalysts.[3,4] In addition, recent advances have shown that Lewis acid catalysts, especially electron-deficient boranes, can also catalyze hydrosilylations in a rare-metal-free manner (Scheme 1A).[5] Nevertheless, successful examples have been mostly limited to electron-rich alkenes, as these catalysts generally show poor reactivity and selectivity toward electron-deficient alkenes (α- vs β-adducts, 1,2- vs 1,4-addition).[6] To the best of our knowledge, a practical methodology for effective catalytic hydrosilylation of both electron-deficient and electron-rich alkenes has not been realized, particularly in a metal-free manner.

Dramatic developments in photocatalysis have occurred over the past decade, which have enabled previously inaccessible transformations.[7] Other than single-electron transfer (SET) and energy transfer, hydrogen atom transfer (HAT) is frequently involved in photocatalysis, offering enormous opportunities for C–H activations.[8] In the context of HAT, polarity plays a vital role to enable selective hydrogen atom abstraction beyond the control of the relative bond dissociation energies (BDEs).[9]



Scheme 1. Hydrosilylation of alkenes.

The Fagnoni and Ravelli group recently disclosed an elegant hydrosilylation of electron-poor alkenes through the use of tetrabutylammonium decatungstate as a direct HAT catalyst under UV light (310 nm) irradiation.[10] Notably, a mixture of Si–H and C–H activation products were obtained with trialkylsilanes (Scheme 1B), likely due to the similar BDEs of Si–H and C–H in trialkylsilanes.[11] As silicon is more electro-positive than carbon (electronegativity 1.90 vs 2.55 on the Pauling scale), Si–H bonds are generally more hydridic than C–H bonds. We speculated that by incorporating a highly electrophilic HAT catalyst, such as the quinuclidinium radical cation applied by MacMillan,[12] the Si–H bond should be selectively activated in the presence of multiple C–H bonds with similar bond strengths, therefore realizing selective hydrosilylation (Scheme 1C). Herein we reported the first visible-light-driven hydrosilylation of both electron-deficient and electron-rich alkenes in a metal-free manner (Scheme 1D).

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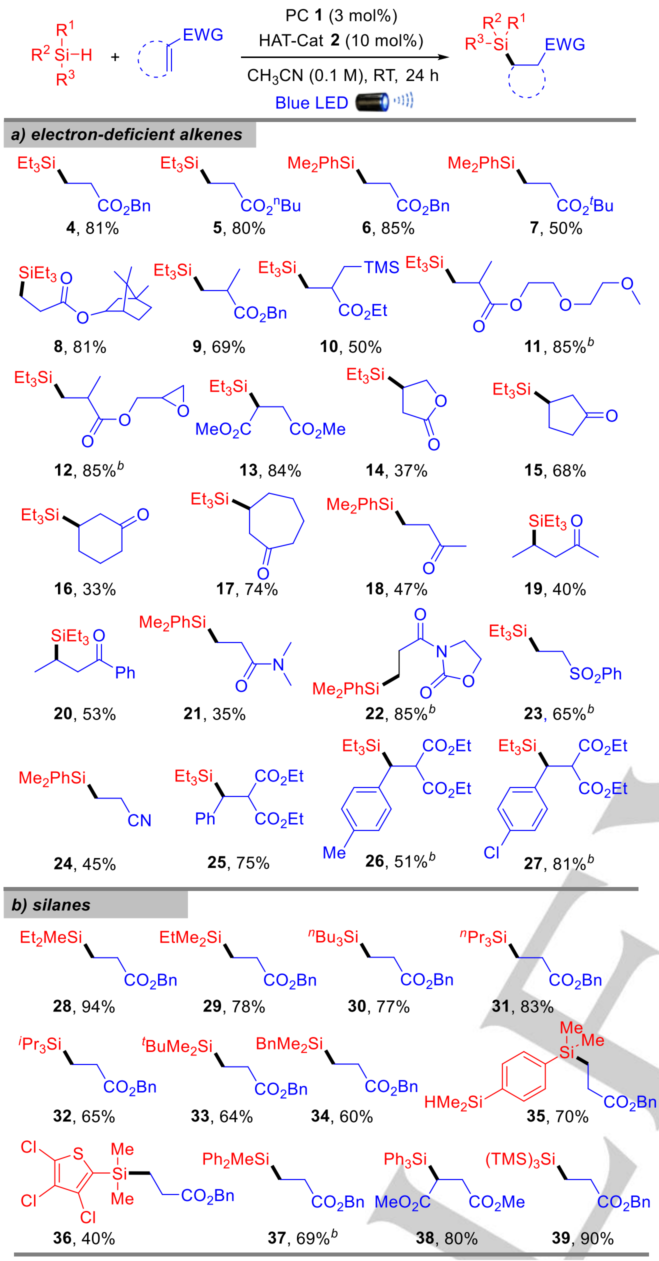

[a] For typical conditions, see the Supplementary Materials. Isolated yields obtained from batch reactors. [b] Results obtained from SFMT reactors.

Scheme 2 Scope of metal-free hydrosilylation of electron-deficient alkenes.[a]

Our study was commenced by evaluating the photo-promoted hydrosilylation of benzyl acrylate with triethylsilane under blue LED irradiation (λmax = 470 nm). After careful investigation of various photocatalysts and solvents (Table S1, Supplementary Materials), the combination of a catalytic amount of organo photocatalyst 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN) **1**[13] and quinuclidin-3-yl acetate **2** in acetonitrile (MeCN) was found to provide the best result, isolating hydrosilylation product **4** in 81% yield. Remarkably, compared to Fagnoni and Ravelli's study,[10] only the hydrosilylation product was obtained without any C–H activation byproducts detected, highlighting the effectiveness of the electrophilic quinuclidinium radical cation HAT catalyst for the selective Si–H activation. Changing the photocatalyst to Ir[dF(CF_3)ppy]$_2$(dtbpy)PF_6, which has a similar redox potential as that of 4CzIPN, delivered a comparable result. Other photocatalysts including Ir(ppy)$_2$(dtbpy)$_3PF_6$, Ir(ppy)$_3$, Ru(bpy)$_3Cl_2$, and eosin Y, failed to afford the desired product. Among the range of solvents examined, MeCN resulted in the best reactivity. Finally, no hydrosilylation product was detected in the absence of either photocatalyst **1**, quinuclidinium catalyst **2**, or light, demonstrating the need for all these components.

Adopting the optimal metal-free conditions, we sought to investigate the generality of this hydrosilylation. Our recently developed "stop-flow" micro-tubing (SFMT) reactor was applied in reactions where conversions were low in batch reactors due to its enhanced light penetration efficiency.[14] Employing Et_3SiH and Me_2PhSiH as two representative silane reagents, a diverse range of electron-deficient alkenes were examined. As depicted in Scheme 2a, acrylates with different steric and electronic properties were well tolerated (**4**-**12**), with functionalities including silane (**10**), ether (**11**), and epoxide (**12**). Dimethyl maleates and lactones were also viable substrates, readily affording the corresponding hydrosilylation products in 84% and 37% yields, respectively (**13** and **14**). Cyclic enones with different ring sizes (**15**-**17**) and acyclic enones with either alkyl or aryl substituents (**18**-**20**) were all accommodated. Furthermore, the hydrosilylation was successfully applied to other types of electron-deficient alkenes such as acryamides (**21** and **22**), vinyl sulfone (**23**), acrylonitrile (**24**), and methylene-malonates (**25**-**27**). Notably, activated C–H bonds adjacent to heteroatoms, such as α-oxy (**11** and **12**), α-nitro (**21** and **22**), and α-silyl (**10**) C–H bonds were well tolerated in this selective Si–H activation protocol. Experiments probing silane scope using benzyl acrylate (Scheme 2b) illustrated that a series of trialkylsilanes with different sizes uneventfully underwent the hydrosilylation to deliver products **28**-**34** in moderate to excellent yields. Notably, only mono-hydrosilylation product **35** was obtained with *p*-phenylenebis(dimethylsilane). The incorporation of heteroaryl (**36**) or phenyl (**37** and **38**) substituents in the silane were all feasible. Tris(trimethylsilyl)silane gave product **39** in excellent yield, likely due to the enhanced stability of the super-silyl radical intermediate.

As shown in Scheme 3, a plausible mechanism for the hydrosilylation of electron-deficient alkenes was proposed based on several control experiments. No reaction was detected when adding the radical scavenger TEMPO or hydroquinone, suggesting a radical-based process.[15] The Stern-Volmer quenching studies supported SET from 3-acetoxyquinuclidine (E_p = +1.22 V vs SCE in MeCN)[12b] to the light-activated photocatalyst **1*** [$E_{1/2}$ (*P/P$^-$) = +1.35 V vs SCE in MeCN][13] to afford the reduced photocatalyst **1'** and amine radical cation **I**. No obvious quenching of **1*** was observed by the silane or benzyl acrylate.[15] Due to its high electrophilicity, radical cation **I** would selectively abstract a hydrogen atom from the more hydridic Si–H bond to deliver silyl radical **III**, along with the generation of quinuclidinium cation **II**. Nucleophilic addition of silane radical **III** to an electron-deficient alkene formed a transient radical adduct **IV**. Single-electron reduction of radical adduct **IV** by **1'** [$E_{1/2}$ (P/P$^-$) = -1.21 V vs SCE

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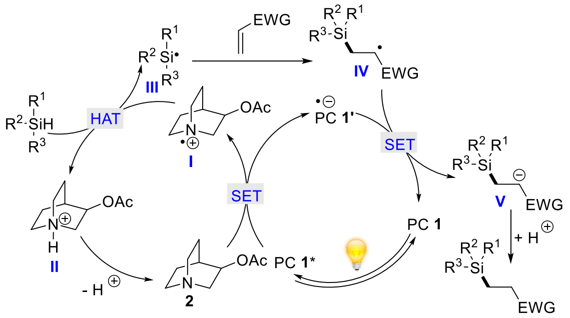
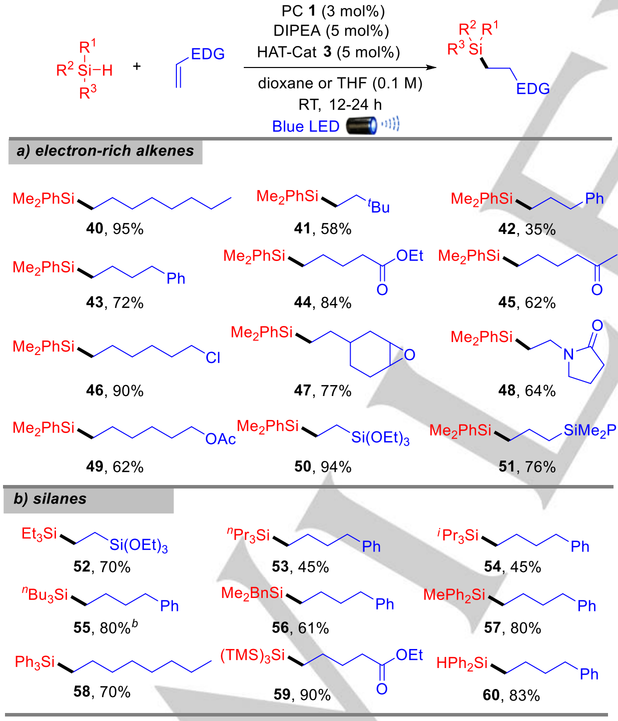
in MeCN][13] afforded the hydrosilylation product after protonation,[14b] while regenerating photocatalyst **1**. The deuterium-labeling experiments indicated that anion **V** would most likely abstract a free proton from solvent.[15] The BDE difference between the N–H bond of the quinuclidinium cation (N^+–H BDE = 100 kcal/mol)[12b] and the C–H bond α to the electron-withdrawing group of the hydrosilylation product (C–H BDE = 85.2 kcal/mol for **4**)[11] indicated that a radical chain process between radical **IV** and cation **II** was unlikely. Furthermore, both the light on/off experiment and the calculated quantum yield (Φ = 0.048) further excluded the possibility of a chain mechanism.[15,16]



Scheme 3. Plausible mechanism for hydrosilylation of electron-poor alkenes.



[a] For typical conditions, see the Supplementary Materials. Isolated yields were obtained from batch reactors. [b] Results were obtained from SFMT reactors.

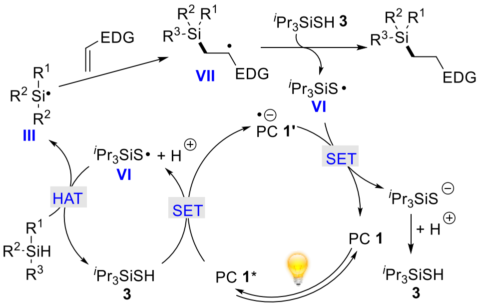
Scheme 4. Scope of metal-free hydrosilylation of electron-rich alkenes.[a]

We next attempted to extend this visible-light-promoted metal-free hydrosilylation protocol to electron-rich alkenes. However, no product was formed with 1-octene under the optimal conditions for electron-deficient alkenes (Table S2, entry 1, Supplementary Materials). Compared to reactions with electron-deficient alkenes, the reason of failure may be that the radical adduct generated from addition of silyl radical **III** to an electron-rich alkene was not oxidative enough to oxidize **1'** to turn over the catalytic cycle. We envisioned that merging the photoredox catalyst with a polarity-reversal catalyst for hydrogen atom abstraction may solve this problem.[9b] Employing dimethylphenylsilane and 1-octene as the model substrates, a series of thiol catalysts,[17] additives, and solvents were examined under the photoredox conditions (Table S2). It was found that the combination of PC **1** (3 mol%), *N*,*N*-diisopropylethylamine (DIPEA, 5 mol%), and triisopropylsilanethiol (5 mol%) in dioxane under blue LED irradiation delivered the hydrosilylation product **40** in excellent yield. Control experiments unveiled that the reaction proceeded smoothly even without DIPEA, albeit with a lower efficiency (60% yield). Changing DIPEA to a catalytic amount of K_2CO_3 also resulted in an efficient transformation (85% yield).

With the optimal conditions, the scope of electron-rich alkenes was investigated (Scheme 4a). A broad range of aliphatic terminal alkenes were shown to be good substrates for this protocol, delivering the corresponding silane products in moderate to excellent yields (**40**-**49**). Functional groups such as ester (**44** and **49**), ketone (**45**), chloride (**46**), epoxide (**47**), and amide (**48**) were well tolerated. Both vinyl silanes and allyl silanes could be applied to introduce disilane products (**50** and **51**). Different silane reagents were examined as well (Scheme 4b). Trialkylsilanes such as triethylsilane, tripropylsilane, triisopropylsilane, tributylsilane, and benzyldimethylsilane all afforded hydrosilylation products in good yields (**52**-**56**). Moreover, the hydrosilylations proceeded smoothly with aryl substituted silanes including diphenylmethylsilane and triphenylsilane (**57** and **58**). Tris(trimethylsilyl)silane resulted in hydrosilylation product **59** in excellent yield. Notably, this protocol could be expanded to secondary silane to give product **60** bearing one Si–H bond.

Mechanistically, as shown in Scheme 5, the hydrosilylation of electron-rich alkenes was initiated with the formation of thiyl radical **VI** via SET between excited photocatalyst **1*** and triisopropylsilanethiol **3** ($E_{1/2}^{ox}$ = +0.28 V vs SCE in MeCN)[15] followed by deprotonation. The Stern-Volmer quenching studies illustrated that **3** could quench the excited catalyst **1***, but both the silane and electron-rich alkene cannot. The presence of a catalytic amount of base (DIPEA or K_2CO_3) presumably promoted the deprotonation first to facilitate the formation of thiyl radical **VI**.[15] The electrophilic thiyl radical **VI** then abstracted a hydrogen atom from the hydridic Si–H bond to deliver silyl radical **III**, along with the regeneration of thiol **3**. Regioselective addition of the silyl radical **III** at the less sterically hindered site of electron-rich alkenes afforded radical adduct **VII**. The nucleophilic radical **VII** would undergo another polarity matched HAT process to generate the hydrosilylation product, accompanying with the formation of thiyl radical **VI**. The BDE difference between the S–H 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 for **40**) indicated the HAT was feasible.[11] Thus thiol **3** behaved as a polarity-reversal catalyst to enable the efficient transformation. However, both the light on/off study and quantum yield measurements (Φ = 0.02)[15] did not support a chain process.[17] The ineffectiveness of several photoredox catalysts with stronger oxidative potentials also indicated that catalyst **1** played roles more than a simple radical initiator.[15] Therefore, other than abstracting a hydrogen atom from silane, the thiyl radical **VI** ($E_{1/2}^{red}$ = -0.82 V vs SCE in MeCN)[15] may preferentially oxidize **1'** [$E_{1/2}$ (P/P$^-$) = -1.21 V vs SCE in MeCN] to regenerate photocatalyst **1** to finish the catalytic cycle. However, at the current stage, we were unable to exclude the possibility of a chain process with quick termination triggered by HAT between radical **VI** and the silane.[16]



Scheme 5. Plausible mechanism for hydrosilylation of electron-rich alkenes.

To further demonstrate the synthetic utility of this methodology, hydrosilylations of electron-rich or electron-poor alkenes were both amenable to scale-up to gram quantities assisted by continuous-flow reactors (Scheme S1, Supplementary Materials). Notably, the continuous micro-flow system showed improved reaction efficiency compared to a batch reactor, enabling effective reactions using a lower catalyst loading (1 mol% **1** and 5 mol% HAT catalyst).[18]

In summary, we developed the first visible-light-mediated metal-free hydrosilylation of both electron-deficient and electron-rich alkenes through the synergistic combination of photoredox and HAT catalysis. By merging the organo-photocatalyst 4CzIPN and HAT catalyst quinuclidin-3-yl acetate, Si–H activations exclusively occurred over C–H activations to achieve the hydrosilylation with electron-deficient alkenes. Additionally, the hydrosilylation of electron-rich alkenes was realized by dual organo photoredox and polarity-reversal catalysis. Both reactions featured merits such as atom- and redox-economy, mild conditions, working efficiently with an extremely broad substrate scope, and easy scaled up by continuous-flow technology. Our study also provides convenient approaches to introduce silicon radicals under visible-light conditions, which will likely find further application for the synthesis of functionalized silicon-containing molecules.

Acknowledgements

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Keywords: metal-free • photocatalysis • hydrosilylation • hydrogen atom transfer • polarity-reversal catalysis

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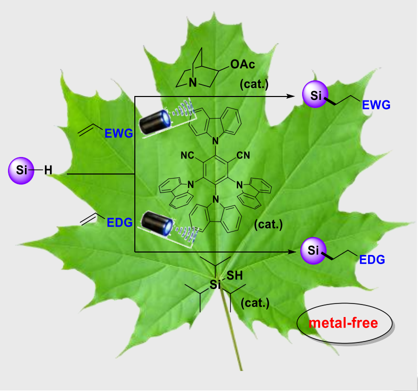
COMMUNICATION

We accomplished a metal-free visible light-driven hydrosilylation of electron-deficient alkenes through the synergistic combination of an organo-photoredox catalyst and a highly electrophilic hydrogen atom transfer catalyst, while the hydrosilylation of electron-rich alkenes was achieved by merging the photocatalyst and a polarity-reversal catalyst.



*Rong Zhou, Yi Yiing Goh, Haiwang Liu, Hairong Tao, Lihua Li, Jie Wu**

Page No. – Page No.

Visible-Light-Mediated Metal-Free Hydrosilylation of Alkenes through Selective Hydrogen Atom Transfer for Si–H Activation