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Copper-catalyzed silylation of activated alkenes by photoinduced ligand-to-metal charge transfer

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Dedicated to Dr. Samir Zard in recognition of his scientific contributions to the fields of radical and organic chemistry

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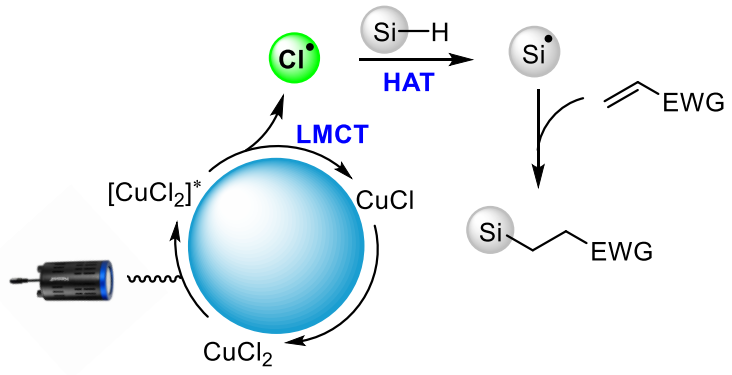
Abstract

A $CuCl_2$-mediated hydrosilylation of activated olefins with hydrosilanes under visible-light irradiation is reported. The photoactive $CuCl_2$ undergoes a ligand to metal charge transfer, generating a chlorine radical, which abstracts an hydrogen from the hydrosilane, forming a silyl radical, which then adds to the activated olefin. The reaction provides the corresponding carbosilanes in generally good yield under practically simple and mild conditions.



Keywords: Hydrosilylation, silyl radical, LMCT, copper, photocatalysis

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Introduction

The hydrosilylation of olefins involves the addition of a silicon-hydrogen (Si-H) bond across the carbon-carbon double bond of an olefin (Figure 1).[1,2,3,4,5] It is a valuable tool to create C-Si bonds and to incorporate silicon moieties onto a hydrocarbon skeleton in an atom economical manner. It is commonly employed in industrial processes for the production of functional materials such as silicone-based polymers,[6] coatings, and adhesives, the resulting organosilanes serving as oils, rubbers, and resins.[2] Hydrosilylation was also found useful for pharmaceutical applications with the incorporation of apolar silicon substituents allowing enhanced bioavailability and for targeted drug delivery. Replacing carbon with silicon in biologically active molecules improves lipophilicity and cell permeability, a strategy known as "silicon switch".[7] It has recently been introduced for surface modification in the preparation of self-assembled monolayers (SAMs) for tailored surface properties and applications in nanotechnology.[8]

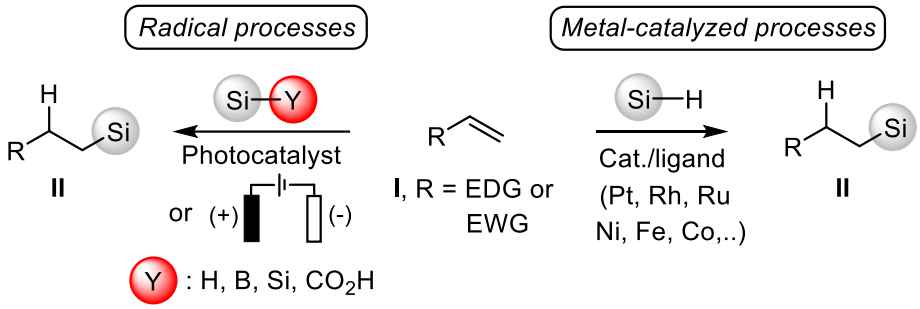
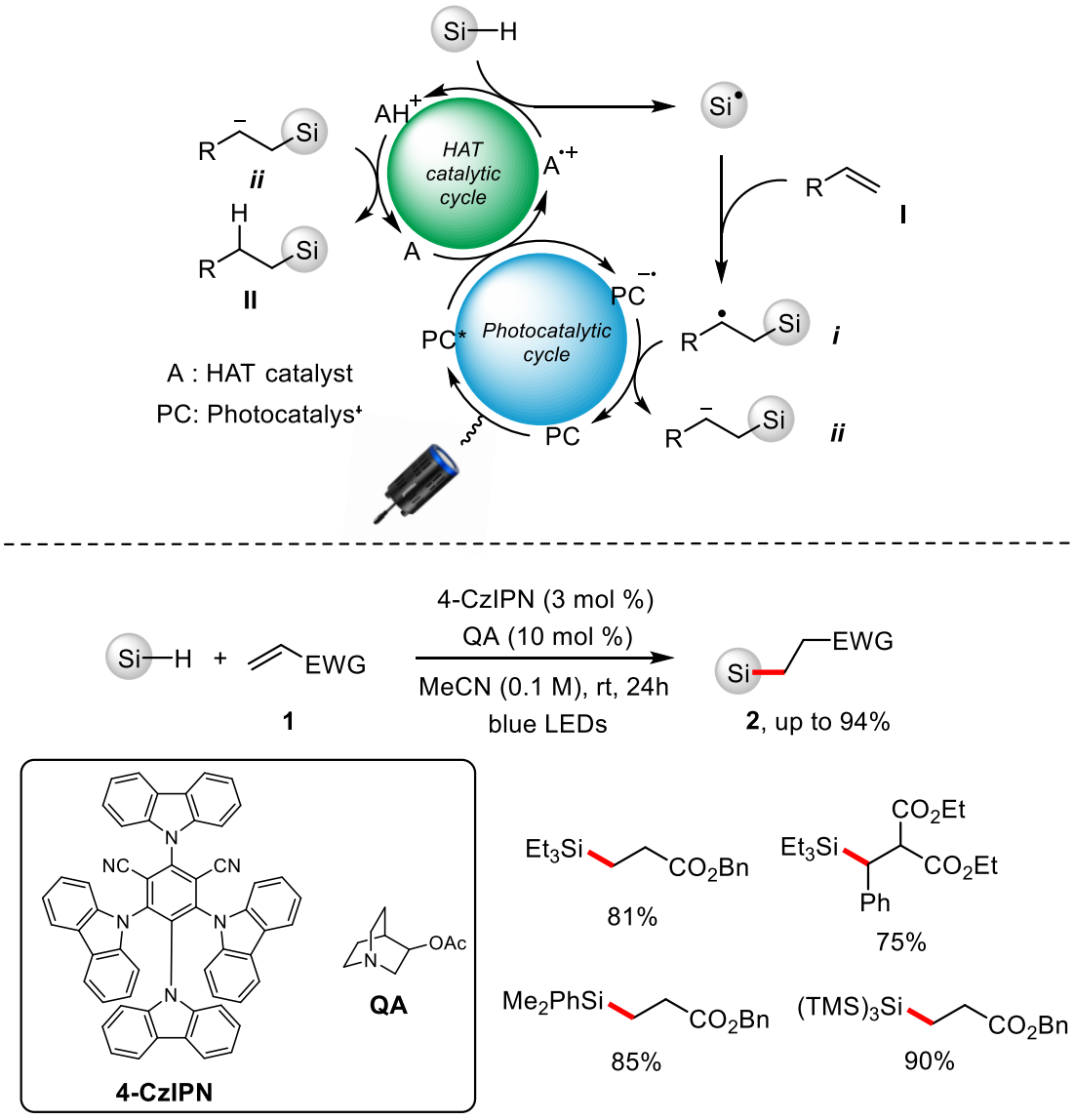


Figure 1. Catalyzed hydrosilylation of olefins.

A broad range of substituents is allowed both on the silicon center and on the olefinic partner. Hydrosilylation reactions are typically catalyzed by homogeneous and heterogeneous transition metal catalysts,[2,5] with some of the most common being platinum (particularly Speier[9] and Karstedt's[10] catalysts), rhodium, and ruthenium complexes. Less expensive earth abundant iron, nickel and cobalt catalysts have also been successfully employed to mediate hydrosilylations.[2,5] Finally, Lewis acids including boranes were recently found to catalyze this process.[11] The hydrosilylation reaction is efficient and regioselective for electron-rich olefins, but less with electro-withdrawing unsaturated systems.[12] Recent progress in this direction have however been made, relying on radical-mediated processes, using photocatalytic or electrochemical activation.[13,14,15] Hydrosilanes (Si-H)[16] are generally commonly used as silicon precursors, but sila-boranes (Si-B),[17,18] disilanes (Si-Si)[19] and silylcarboxylic acids (Si-CO_2H)[20] were also reported to be competent partners in radical hydrosilylation processes.

Photocatalysis under visible light has seen a tremendous progress recently and it is not surprising that methods to carry out hydrosilylation under these mild conditions rapidly emerged.[13] General mechanism for the visible-light-induced hydrosilylation is shown in Scheme 1 below. Hydrogen-atom transfer agent **A** is oxidized by the photocatalyst in its excited state PC* to generate $PC^{\bullet-}$ and $A^{\bullet+}$. Subsequently, $A^{\bullet+}$ radical abstracts a hydrogen atom from the silane (HAT process), and the resulting silyl radical adds to the substrate **I** to form a radical adduct ***i*** (radical addition process), which is then reduced by the photocatalyst in its semi-reduced state ($PC^{\bullet-}$), leading to carbanion ***ii*** and the photoactive PC in its ground state. Finally, the carbanion intermediate ***ii*** undergoes a protonation, leading to product **II**, while the deprotonated HAT catalyst can re-enter into the catalytic cycle. An illustrative example of this photocatalytic process was provided by Wu and

co-workers, using 4-CzIPN as an organophotocatalyst and quinuclidin-3-yl acetate (AQ) as an HAT reagent.[21] The reaction was shown to proceed onto electron-deficient alkenes with excellent yields. For electron-rich alkenes, better yields were achieved using thiols ((*i*-Pr_3SiSH) as HAT and hydrogen donor reagent.[22] As mentioned above, the starting silyl radical may also be generated from the corresponding silaborane as reported in 2022 by Ohmiya[18] or through decarboxylation of the silacarboxylic acids under visible light mediated conditions, as shown by Uchiyama *et al.*[20]



Scheme 1. Photocatalyzed hydrosilylation of olefins.

Among hydrogen atom transfer agents, the chlorine radical holds a special place.[23] The formation of a strong H-Cl bond (102 kcal/mol) makes it possible to abstract hydrogen from strong apolar C-H bonds, with BDE ranging between 85-100 kcal/mol, such as those in alkanes. The $Cl^{\cdot}$ is generally easy to generate from Cl^-. Pioneering studies of Kochi have also shown that visible-light irradiation of metal chlorides including $CuCl_2$ generated $Cl^{\cdot}$ through a Ligand to Metal Charge Transfer process (LMCT).[24] 3d transition metal chloride complexes, such as those from Ni, Cu, Fe, Ce or Ti are suitable precursors of the chlorine radical.[25] Based on these premises, Rovis and co-workers recently reported on the $CuCl_2$-catalyzed alkylation of C(sp^3)-H bonds

through the coupling of unactivated C(sp^3)-H bonds with electron-deficient olefins.[26] They demonstrated that alkyl radicals could be formed through chlorine radical hydrogen abstraction from alkanes, and then add onto olefins through a Giese-type process. Si-H bond being weaker than the C-H bond,[16] it was also shown to be possible to generate silyl radicals through Cl· abstraction of hydrogens from hydrosilanes that could subsequently be used in olefin hydrosilylation processes (Figure 2). Such a strategy would allow an access to various carbosilanes using metal chloride salts under irradiation, using simpler reaction conditions than those described above (Scheme 1). We thus report here on our studies using this straightforward approach using $CuCl_2$ as a metal chloride catalyst and visible-light irradiation at 390 nm.

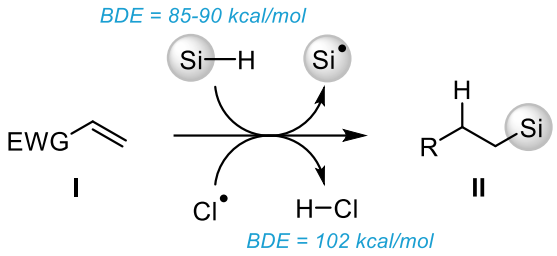
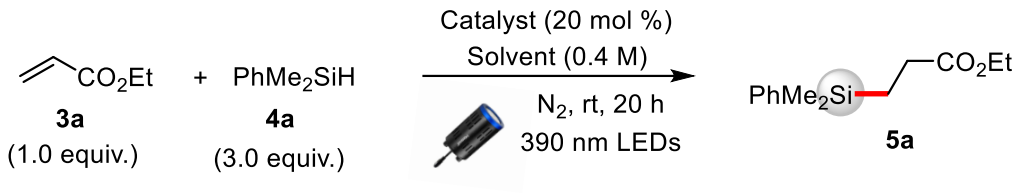


Figure 2. Hydrosilylation of olefins mediated by chlorine radical as HAT reagent.

Results and Discussion

Optimization of the process was first performed using ethyl acrylate **3a** as the model substrate, and dimethyl(phenyl)silane **4a** as the silicon source, with $CuCl_2$ as a catalyst (entry 1, Table 1). The reaction was initially conducted at room temperature in acetonitrile under irradiation at 390 nm using 34W LEDs. Pleasingly, under these conditions, product **5a** was obtained in 80% isolated yield. Various metal chloride salts were then screened (entries 2-5). While Ni, Ce and Co salts led to no reaction, $FeCl_3$ proved to be efficient (entry 2), albeit less than $CuCl_2$ under identical conditions.[27] A reduction of the amount of $CuCl_2$ resulted in a lower yield of **5a** (entries 1 vs 6-7). LiCl was then used as an additive (entry 8), but these conditions led to lower yield, showing that adding additional source of chloride was unnecessary. More importantly, the amount of silane proved to be crucial, as lowering the quantity of silane **4a** to 2 equivalents resulted in a significant drop in yield (entry 9). Various solvents such as DCM, THF and acetone were screened (entries 10-12), without success, showing that acetonitrile was the best solvent for this process, likely due to a better solubility of $CuCl_2$ under these conditions, resulting from the known ability of this solvent to coordinate to copper. Finally, the presence of the catalyst and light proved essential as no reaction occurred in their absence (entries 13-14).

Table 1. Optimization of the metal chloride-mediated hydrosilylation of acrylate **3a** with silane **4a**

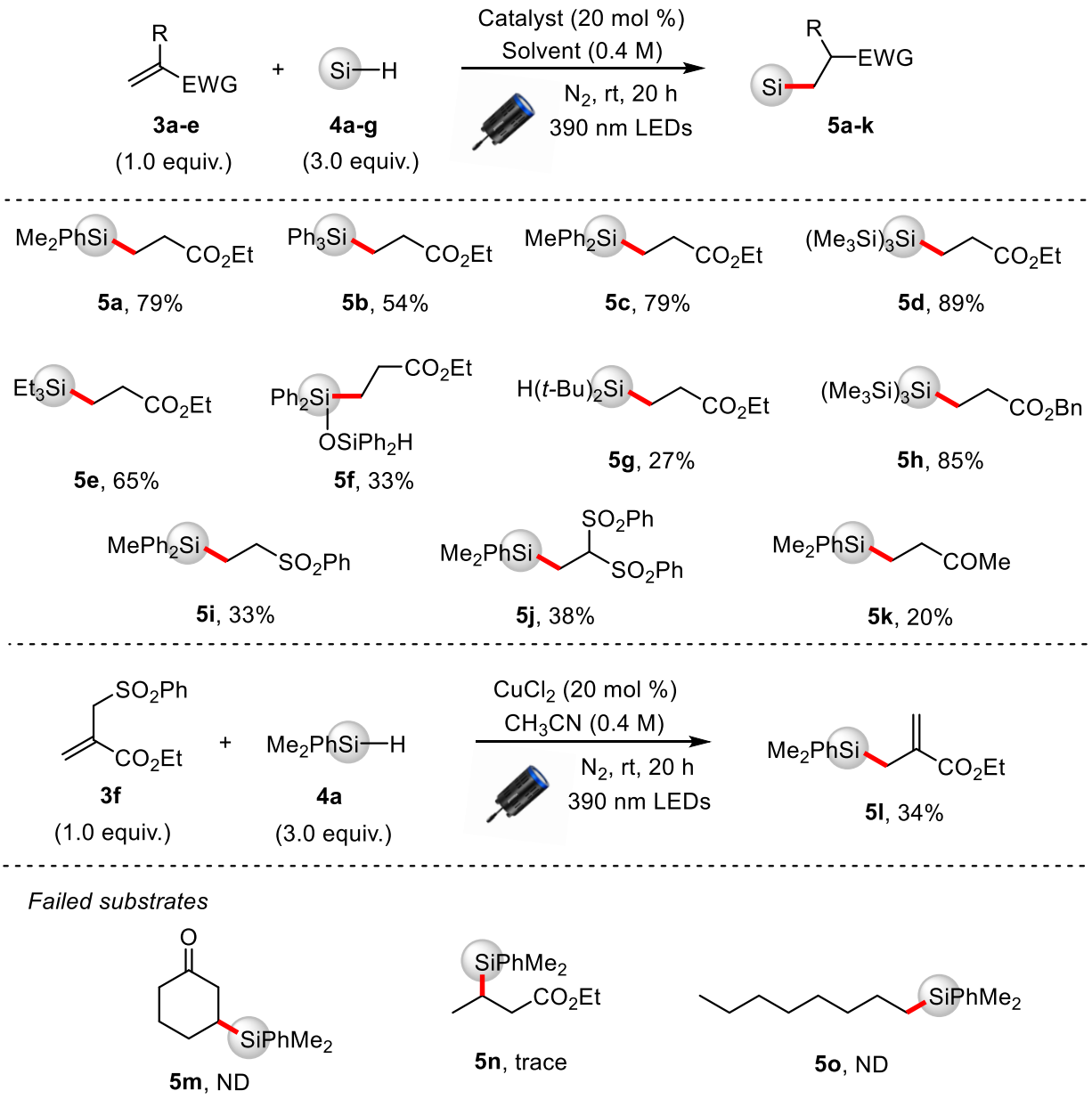


Entry[a]	Catalyst	Solvent	Additive	Yield(%)
1	$CuCl_2$ (20 mol %)	CH_3CN	-	79
2	$FeCl_3$ (20 mol %)	CH_3CN	-	51
3	$NiCl_2$ (20 mol %)	CH_3CN	-	0
4	$CeCl_3$ (20 mol %)	CH_3CN	-	0
5	$[Co(NH_3)_6]Cl_3$ (20 mol %)	CH_3CN	-	0
6	$CuCl_2$ (10 mol %)	CH_3CN	-	64
7	$CuCl_2$ (5 mol %)	CH_3CN	-	44
8	$CuCl_2$ (20 mol %)	CH_3CN	LiCl (50 mol %)	53
9[b]	$CuCl_2$ (20 mol %)	CH_3CN	-	57
10	$CuCl_2$ (20 mol %)	DCM	-	0
11	$CuCl_2$ (20 mol %)	THF	-	0
12	$CuCl_2$ (20 mol %)	Acetone	-	0
13	-	Acetone	-	0
14[c]	$CuCl_2$ (20 mol %)	CH_3CN	-	0

[a] Standard condition: $CuCl_2$ (20 mol %), **4a** (0.6 mmol, 3 equiv.), **3a** (0.2 mmol, 1 equiv.), CH_3CN (0.5 mL), Kessil (34W) 390 nm LEDs, rt, N_2, 20 h, isolated yields. [b] **4a** (0.4 mmol, 2 equiv.). [c] in the dark.

After having established the optimal conditions for the hydrosilylation of activated olefins, these were applied to a range of substrates. Various substitutions are allowed on the silane partner, including hydrogen, aryl, TMS and alkyl groups. Steric hindrance is not a limiting factor as shown by comparable yields obtained for hydrosilylation products **5a**, **5c** and **5d**. Ph_3SiH provides lower yields upon addition to ethyl acrylate. Di-hydrosilane *t*-Bu_2SiH_2 and $(HPh_2Si)_2O$ also afforded the desired products **5f-g**, albeit in low yield. In these reactions, several minor by-products (possibly including bis-addition products) were observed on TLC but none of them could be isolated. Dihydrosilanes are therefore not optimal silanes for these conditions. The Si-Si bond proved to be resistant to the reaction conditions as shown by the efficient formation of TTMS product **5d** and **5h**. Furthermore, the reaction was tested with a wide range of electron-deficient alkenes to establish the scope and limitation of the process. Alkyl acrylates, such as ethyl or benzyl acrylates **3a-b**, are viable alkene partners (*i.e.* **5d** and **5h**). Reaction with (vinylsulfonyl)benzene **3c** and (ethene-1,1-diyldisulfonyl)dibenzene **3d** led respectively to the addition products **5i** and **5j** in moderate yields. The but-3-en-2-one **3e** led to the addition product **5k** in modest yield as compared with the ester equivalent (*i.e.* **5a**). Finally, allylsilane **5l** was obtained in useful yields from the corresponding acrylate **3f** bearing an allylsulfone moiety. The reaction was also extended to β-substituted ketones **3m** and ester **3n**, which unfortunately led to no product (*i.e.* **5m**) or only trace amounts of the desired hydrosilylation adduct **5n**. This suggests that steric hindrance may hinder the approach of the bulky silyl radical onto the β-carbon center, thus preventing the 1,4-addition from

occurring. Electron-rich alkenes, such as 1-octene were also tested, but did not afford the desired addition product (*i.e.* **5o**), thus limiting this $CuCl_2$-mediated hydrosilylation process to olefins activated by electron-withdrawing functional groups.



Scheme 2. Photocatalyzed $CuCl_2$-mediated hydrosilylation of olefins.

The scope and limitation established above and previous literature reports[26] led us to propose a plausible mechanism for the $CuCl_2$-mediated hydrosilylation of activated olefins (Figure 3). First, upon irradiation with the 390 nm LED, $CuCl_2$ reaches the excited state noted [$CuCl_2$*], which then undergoes a Ligand-to-Metal Charge Transfer (LMCT) process,[25] generating a chlorine atom radical. The latter then reacts with the silane forming HCl along with the required silyl radical. The latter then adds onto the activated olefin to afford a stabilized radical ***i*** α to the electron-withdrawing group. ***i*** may also be written as its enoyl radical ***ii*** having the spin density on the oxygen atom. Recombination of the latter with CuCl then provides a Cu(II)-enolate ***iii*** that is protonated by HCl, affording the hydrosilylation product **II**, regenerating the photoactive $CuCl_2$. The limited

scope of this hydrosilylation, restricted to activated olefins, may be tentatively explained by the inappropriate redox potential of the Cu(I) /Cu(II) couple, which does not allow the reduction of radical ***i/ii*** in the case of electron-rich olefins.

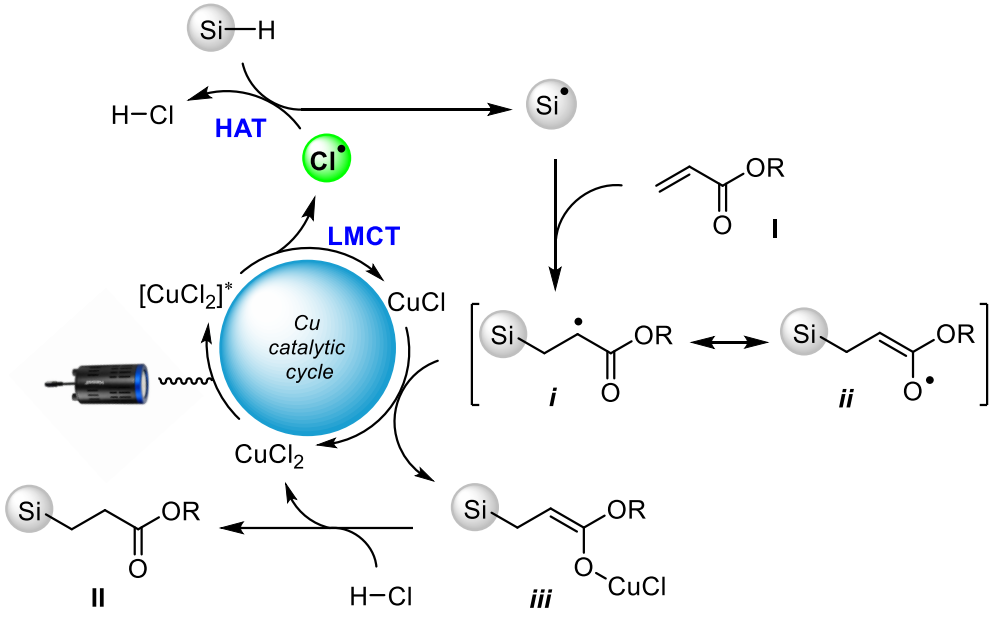


Figure 3. Tentative mechanism of the photocatalyzed $CuCl_2$-mediated hydrosilylation of olefins.

Conclusions

In summary, we reported an efficient and practically simple hydrosilylation of olefins activated by electron-withdrawing groups, using $CuCl_2$ as a HAT catalyst under visible-light irradiation. The interaction between copper(II) chloride and acetonitrile likely produces a photoactive species, which generates a reactive chlorine radical through ligand-to-metal charge transfer under light irradiation. This radical abstracts the hydrogen atom from the silane to form HCl along with a silyl radical, which can then undergo a 1,4-addition onto the activated olefin. This HAT process from the silane (BDE ~ 90 kcal/mol)[16] is thermodynamically driven by the formation of the stronger H-Cl bond (BDE 106 kcal/mol). This strategy is practical and easier to operate than the previously reported methodology, using cheap copper salts and readily available reagents and proceeds under mild conditions. Finally, while this work was in progress, a similar approach was reported by Wang and co-workers using $FeCl_3$ as HAT reagent.[27]

Experimental Section

General. All reactions were carried out under an argon atmosphere. Solvents were dried over activated alumina columns on a M-BRAUN Solvent Purification System (SPS-800) unless otherwise noted. The calculated experimental yields refer to chromatographically and spectroscopically (^{1}H-NMR) homogeneous materials unless otherwise stated. All reagent-grade chemicals were obtained from commercial suppliers and were used as received unless otherwise stated. ^{1}H NMR and ^{13}C NMR were recorded at room temperature on various

spectrometers: a Bruker Avance 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz, ^{19}F: 282 MHz) and a Bruker Avance 600 (^{1}H: 600 MHz, ^{13}C: 150 MHz) using $CDCl_3$ as internal reference unless otherwise indicated. The chemical shifts (δ) and coupling constants (*J*) are expressed in ppm and Hz respectively. The following abbreviations were used to explain the multiplicities: br broad, s singlet, d doublet, t triplet, q quartet, dd doublet of doublets, m multiplet, quint quintet, hex hex(sex)tet, hept hep(sep)tet. FTIR spectra were recorded on a Perkin-Elmer Spectrum 100 using a KBr pellet. High-resolution mass spectra (HRMS) were recorded with a Waters Q-TOF 2 spectrometer in the electrospray ionization (ESI) or Field Ionization mode (FI). Melting points were not corrected and determined by using a Stuart Scientific SMP3 apparatus. Analytical thin layer chromatography was performed using silica gel 60 F254 pre-coated plates (Merck) with visualization by ultraviolet light. Flash chromatography was performed on silica gel (0.043-0.063 mm) with ethyl acetate (EA) and Petroleum ether (PE) as eluents unless otherwise indicated. Kessil lamp (LED Photoreaction Lighting) PR160L at 390 nm (34 W) were used for the photocatalyzed process. The lamp was generally located at a distance of ~4 cm from the reaction vessel. No filter was used. Hydrosilanes **4a**, **4b**, **4d**, **4e**, **4f** and **4g** are commercially available.

General procedure for $CuCl_2$-mediated hydrosilylation of olefins 3. In a glovebox under an argon atmosphere, $CuCl_2$ (5.4 mg, 0.04 mmol, 20 mol %), alkene **3** (0.2 mmol, 1 equiv.), and silane **4** (0.6 mmol, 3 equiv.) in anhydrous MeCN (0.5 mL) were placed in a dried sealed tube. The tube was placed ~4 cm away from a (34W) 390 nm LED and stirred for 20 h with a cooling setup using a fan (T° ~ 30°C). The mixture was then concentrated in vacuo. The resulting residue was purified by chromatography through silica gel using petroleum ether and EtOAc as eluent to afford the hydrosilylation product **5**.

Ethyl 3-(dimethyl(phenyl)silyl)propanoate (5a).[28] Based on the general procedure above, starting from dimethyl(phenyl)silane **4a** (82 mg, 0.6 mmol) and ethyl acrylate **3a** (20 mg, 0.2 mmol), carbosilane **5a** was obtained as an oil (37.4 mg, 0.158 mmol, 79% yield). Rf 0.5 (PE: EA 10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 2H), 7.41 – 7.37 (m, 3H), 4.12 (q, *J* 7.1 Hz, 2H), 2.37 – 2.25 (m, 2H), 1.26 (t, *J* 7.2 Hz, 3H), 1.20 – 1.06 (m, 2H), 0.33 (s, 6H). Spectroscopic data in agreement with those in the literature.[28]

Ethyl 3-(triphenylsilyl)propanoate (5b)[26] Based on the general procedure above, starting from ethyl acrylate **3a** (20 mg, 0.2 mmol) and triphenylsilane **4b** (156 mg, 0.6 mmol), carbosilane **5b** was obtained as a white solid (39 mg, 0.108 mmol, 54% yield). Rf 0.5 (PE: EA 10:1). Mp 66 – 67ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.49 (m, 6H), 7.47 – 7.33 (m, 9H), 4.07 (q, *J* 7.1 Hz, 2H), 2.51 – 2.37 (m, 2H), 1.81 – 1.68 (m, 2H), 1.22 (t, *J* 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.8, 135.7, 134.3, 129.8, 128.1, 60.6, 29.1, 14.3, 8.4. ^{29}Si NMR (60 MHz, $CDCl_3$) δ -10.64. Spectroscopic data in agreement with those in the literature.[26]

Ethyl 3-(methyldiphenylsilyl)propanoate (5c).[29] Based on the general procedure above, starting from ethyl acrylate **3a** (20 mg, 0.2 mmol) and methyldiphenylsilane **4c** (119 mg, 0.6 mmol), product **5c** was obtained as an oil (47 mg, 0.158 mmol, 79% yield). Rf 0.5 (PE: EA 10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.47 (m, 4H), 7.45 – 7.30 (m, 6H), 4.08 (q, *J* 7.1 Hz, 2H), 2.40 – 2.30 (m, 2H), 1.49 – 1.38 (m, 2H), 1.23 (t, *J* 7.2 Hz, 3H), 0.59 (s, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 174.8, 136.3, 134.6, 129.5, 128.1, 60.5, 29.0, 14.3, 9.5, -4.5. ^{29}Si NMR (60 MHz, $CDCl_3$) δ -6.77. Spectroscopic data in agreement with those in the literature.[29]

Ethyl 3-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)propanoate (5d).[30] Based on the general procedure above, starting from ethyl acrylate **3a** (20 mg, 0.2 mmol) and 1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane **4d** (149 mg, 0.6 mmol), product **5d** was obtained as an oil (62 mg, 0.178 mmol, 89% yield). Rf 0.65 (PE: EA 15:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.12 (q, *J* 7.1 Hz, 2H), 2.41 – 2.25 (m, 2H), 1.25 (t, *J* 7.1 Hz, 3H), 1.14 – 1.05 (m, 2H), 0.17 (s, 27H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 174.8, 60.5, 33.4, 14.4, 2.9, 1.2. ^{29}Si NMR (60 MHz, $CDCl_3$) δ -12.85, -80.79. Spectroscopic data in agreement with those in the literature.[30]

Ethyl 3-(triethylsilyl)propanoate (5e).[31] Based on general procedure above, starting from ethyl acrylate **3a** (20 mg, 0.2 mmol) and triethylsilane **4e** (70 mg, 0.60 mmol), product **5e** was obtained as an oil (28 mg, 0.13 mmol, 65% yield). Rf 0.6 (PE: EA 10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.12 (q, *J* 7.1 Hz, 2H), 2.42 – 2.08 (m, 2H), 1.74 – 1.58 (m, 1H), 1.47 – 1.34 (m, 1H), 1.25 (td, *J* 7.2, 2.0 Hz, 3H), 0.94 (td, *J* 7.7, 3.1 Hz, 9H), 0.60 – 0.50 (m, 6H). Spectroscopic data in agreement with those in the literature.[31]

Ethyl 3-(1,1,3,3-tetraphenyldisiloxaneyl)propanoate (5f). Based on the general procedure above, starting from ethyl acrylate **3a** (20 mg, 0.2 mmol) and diphenylsilane **4f** (111 mg, 0.6 mmol), product **5f** was obtained as an oil (31 mg, 0.066 mmol, 33% yield). Rf 0.5 (PE: EA 10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.48 (m, 8H), 7.47 – 7.28 (m, 12H), 5.63 (s, 1H), 4.02 (q, *J* 7.1 Hz, 2H), 2.35 – 2.23 (m, 2H), 1.50 – 1.39 (m, 2H), 1.19 (t, *J* 7.1 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 174.6, 135.3, 134.5, 134.4, 130.4, 130.1, 128.1, 128.0, 60.5, 28.1, 14.3, 10.7. ^{29}Si NMR (60 MHz, $CDCl_3$) δ -9.14, -20.30. HRMS (ESI): calcd for $C_{29}H_{30}O_3NaSi_2$ $[M+Na]^+$: 505.16257, found 505.1631.

Ethyl 3-(di-tert-butylsilyl)propanoate (5g). Based on general procedure **B**, starting from ethyl acrylate **3a** (20 mg, 0.2 mmol) and of di-*tert*-butylsilane **4g** (87 mg, 0.6 mmol), product **5g** was obtained as an oil (13 mg, 0.054 mmol, 27% yield). Rf 0.4 (PE: EA 30:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.12 (q, *J* 7.1 Hz, 2H), 3.44 (s, 1H), 2.31 – 2.23 (m, 2H), 1.65 – 1.59 (m, 1H), 1.41 – 1.36 (m, 1H), 1.25 (t, *J* 6 Hz, 3H), 1.04 (s, 9H), 0.97 (s, 9H).

Benzyl 3-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)propanoate (5h).[21] Based on the general procedure above, starting from benzyl acrylate **3b** (32.4 mg, 0.2 mmol) and 1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane **4d** (149 mg, 0.6 mmol), product **5h** was obtained as an oil (70 mg, 0.17 mmol, 85% yield). Rf 0.65 (PE: EA 20:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.31 (m, 5H), 5.13 (s, 2H), 2.45 – 2.34 (m, 2H), 1.20 – 1.10 (m, 2H), 0.19 (s, 27H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.6, 136.3, 128.7, 128.4, 128.3, 66.4, 33.3, 3.0, 1.2. ^{29}Si NMR (60 MHz, $CDCl_3$) δ -12.83, -80.73. Spectroscopic data in agreement with those in the literature.[21]

Methyldiphenyl(2-(phenylsulfonyl)ethyl)silane (5i).[32] Based on the general procedure above, starting from (vinylsulfonyl)benzene **3c** (33.6 mg, 0.2 mmol) and methyldiphenylsilane **4c** (119 mg, 0.6 mmol), product **5i** was obtained as an oil (24 mg, 0.066 mmol, 33% yield). Rf 0.3 (PE: EA 5:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 – 7.84 (m, 2H), 7.70 – 7.61 (m, 1H), 7.59 – 7.53 (m, 2H), 7.46 – 7.29 (m, 10H), 3.08 – 2.97 (m, 2H), 1.54 – 1.43 (m, 2H), 0.55 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 134.8, 134.4, 133.7, 130.0, 129.4, 128.4, 128.3, 52.4, 7.3, -4.5. ^{29}Si NMR (60 MHz, $CDCl_3$) δ -7.04. Spectroscopic data in agreement with those in the literature.[32]

(2,2-Bis(phenylsulfonyl)ethyl)dimethyl(phenyl)silane (5j). Based on the general procedure above, starting from (ethene-1,1-diyldisulfonyl)dibenzene **3d** (62 mg, 0.2 mmol) and dimethyl(phenyl)silane **4a** (82 mg, 0.6 mmol), product **5j** was obtained as an oil (34 mg, 0.076 mmol, 38% yield). Rf 0.3 (PE: EA 3:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 – 7.60 (m, 6H), 7.53 – 7.39 (m, 9H), 4.39 (t, *J* 6.6 Hz, 1H), 1.61 (d, *J* 6.6 Hz, 2H), 0.45 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.6, 136.6, 134.4, 134.3, 129.8, 129.7, 129.0, 128.3, 81.9, 11.4, -1.9. ^{29}Si NMR (60 MHz, $CDCl_3$) δ -0.14. HRMS (ESI): calcd for $C_{22}H_{24}O_4NaSiS_2$ $[M+Na]^+$: 467.07775, found 467.0781.

4-(Dimethyl(phenyl)silyl)butan-2-one (5k).[21] Based on the general procedure above, starting from but-3-en-2-one **3e** (14 mg, 0.2 mmol) and dimethyl(phenyl)silane **4a** (82 mg, 0.6 mmol), product **5k** was obtained as an oil (8 mg, 0.04 mmol, 20% yield). Rf 0.5 (PE: EA 10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 – 7.45 (m, 2H), 7.42 – 7.31 (m, 3H), 2.42 – 2.32 (m, 2H), 2.09 (d, *J* 0.6 Hz, 3H), 1.05 – 0.96 (m, 2H), 0.28 (s, 6H). Spectroscopic data in agreement with those in the literature.[21]

Ethyl 2-((dimethyl(phenyl)silyl)methyl)acrylate (5l). Based on the general procedure above, starting from ethyl 2-((phenylsulfonyl)methyl)acrylate **3f** (51 mg, 0.2 mmol) and dimethyl(phenyl)silane **4a** (82 mg, 0.6 mmol), product **5l** has been obtained as an oil (17 mg, 0.068 mmol, 34% yield). Rf 0.6 (PE: EA 10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.37 – 7.34 (m, 3H), 5.98 (d, *J* 1.6 Hz, 1H), 5.24 (q, *J* 1.3 Hz, 1H), 4.10 (q, *J* 7.1 Hz, 2H), 2.07 (d, *J* 1.1 Hz, 2H), 1.24 (t, *J* 7.1 Hz, 3H), 0.29 (s, 6H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 167.7, 138.2,

133.8, 133.1, 129.2, 127.8, 122.3, 60.8, 21.5, 14.3, -3.2. ^{29}Si NMR (60 MHz, $CDCl_3$) δ -3.57. HRMS (ESI): calcd for $C_{14}H_{20}O_2NaSi$ $[M+Na]^+$: 217.11248, found 217.1128.

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Supplementary Material

Copies of ^{1}H, ^{13}C and ^{29}Si NMR spectra of products have been submitted along with the manuscript.

References

1. Marciniec, B. *Hydrosilylation: A Comprehensive Review on Recent Advances*, Springer, Berlin, 2009.
2. Duarte de Almeida, L.; Wang, H.; Junge, K.; Cui, X.; Beller, M. *Angew. Chem., Int. Ed.* **2020**, *60*, 550-565. https://doi.org/10.1002/anie.202008729
3. Marciniec, B. *Coord. Chem. Rev.* **2005**, *249*, 2374-2390. https://doi.org/10.1016/j.ccr.2005.02.025
4. Troegel, D.; Stohrer, J. *Coord. Chem. Rev.* **2011**, *255*, 1440-1459. https://doi.org/10.1016/j.ccr.2010.12.025
5. Nakajima, Y.; Shimada, S. *RSC Adv.* **2015**, *5*, 20603-20616. https://doi.org/10.1039/C4RA17281G
6. Roy, A. K. *Adv. Organomet. Chem.* **2008**, *55*, 1-59. https://doi.org/10.1016/S0065-3055(07)55001-X
7. Ramesh, R.; Reddy, D. S. *J. Med. Chem.* **2018**, *61*, 3779-3798. https://doi.org/10.1021/acs.jmedchem.7b00718
8. Langner, A.; Panarello, A.; Rivillon, S.; Vassylyev, O.; Khinast, G.; Chabal, Y. J. *J. Am. Chem. Soc.* **2005**, *127*, 12798-12799. https://doi.org/10.1021/ja054634n
9. Speier, L.; Webster, J. A.; Barnes, G. H. *J. Am. Chem. Soc.* **1957**, *79*, 974-979. https://doi.org/10.1021/ja01561a054
10. Karstedt, B. D. General Electric Company, US3775452A, 1973.
11. Oestreich, M.; Hermeke, J.; Mohr, J. *Chem. Soc. Rev.* **2015**, *44*, 2202-2220. https://doi.org/10.1039/C4CS00451E
12. Steiman, T. J.; Uyeda, C. *J. Am. Chem. Soc.* **2015**, *137*, 6104-6110. https://doi.org/10.1021/jacs.5b03092
13. Li, J.-S.; Wu, J. *ChemPhotoChem.* **2018**, *2*, 839-846. https://doi.org/10.1002/cptc.201800110
14. Zhou, H.-Y.; Fei, L.-Q.; Zhang, J.-L.; Pan, Y.-M.; Tang, H.-T. *Adv. Synth. Cat.* **2023**, *365*, 1591-1595. https://doi.org/10.1002/adsc.202300343

15. Ghosh, S.; Lai, D.; Hajra, A. *Org. Biomol. Chem.* **2021**, *19*, 2399-2415. https://doi.org/10.1039/D1OB00082A
16. Chatgilialoglu, C.; Ferreri, C.; Landais, Y.; Timokhin, V. *Chem. Rev.* **2018**, *118*, 6516-6572. https://doi.org/10.1021/acs.chemrev.8b00109
17. Matsumoto, A.; Ito, Y. *J. Org. Chem.* **2000**, *65*, 5707-5711. https://doi.org/10.1021/jo000547w
18. Takemura, N.; Sumida, Y.; Ohmiya, H. *ACS Catal.* **2022**, *12*, 7804-7810. https://doi.org/10.1021/acscatal.2c01964
19. Yu, X.; Lübbesmeyer, M.; Studer, A. *Angew. Chem. Int. Ed.* **2021**, *60*, 675-679. https://doi.org/10.1002/anie.202011738
20. Xu, N.; Li, B.; Wang, C.; Uchiyama, M. *Angew. Chem. Int. Ed.* **2020**, *59*, 10639-10644. https://doi.org/10.1002/anie.202003070
21. Zhou, R.; Goh, Y. Y.; Liu, H.; Tao, H.; Li, L.; Wu, J. *Angew. Chem., Int. Ed.* **2017**, *56*, 16621-16625. https://doi.org/10.1002/anie.201711250
22. Zhu, J.; Cui, W.-C.; Wang, S.; Yao, Z.-J. *J. Org. Chem.* **2018**, *83*, 14600-14609. https://doi.org/10.1021/acs.joc.8b02409
23. Velasco-Rubio, A.; Martinez-Balart, P.; Alvarez-Constantino, A. M.; Fananas-Mastral, M. *ChemComm.* **2023**, *59*, 9424-9444. https://doi.org/10.1039/D3CC02790B
24. Kochi, J. K. *J. Am. Chem. Soc.* **1962**, *84*, 2121-2127. https://doi.org/10.1021/ja00870a025
25. Julia, F. *ChemCatChem*, **2022**, *14*, e202200916. https://doi.org/10.1002/cctc.202200916
26. Treacy, S. M.; Rovis, T. *J. Am. Chem. Soc.* **2021**, *143*, 2729-2735. https://doi.org/10.1021/jacs.1c00687
27. Ding, L.; Niu, K.; Liu, Y.; Wang, Q. *ChemSusChem* **2022**, *15*, e202200367. https://doi.org/10.1002/cssc.202200367
28. Ibrahim, A. D.; Entsminger, S. W.; Zhu, L.; Fout, A. R. *ACS Catal.* **2016**, *6*, 3589-3593. https://doi.org/10.1021/acscatal.6b01091
29. Takeuchi, R.; Ishii, N.; Sugiura, M.; Sato, N. *J. Org. Chem.* **1992**, *57*, 4189-4194. https://doi.org/10.1021/jo00041a025
30. Cheng, S.; Ouyang, J.; Li, M.; Diao, Y.; Yao, J.; Li, F.; Lee, Y.; Sung, H.; Williams, I.; Xu, Z.; Quan, Y. *Angew. Chem.Int. Ed.* **2023**, *62*, e2023009. https://doi.org/10.1002/anie.202300993
31. Seyferth, D.; Mammarella, R. E.; Klein, H. A. *J. Organomet. Chem.* **1980**, *194*, 1-7. https://doi.org/10.1016/S0022-328X(00)90330-9
32. Iannazzo, L.; Molander, G. A. *Eur. J. Org. Chem.* **2012**, 4923-4926. https://doi.org/10.1002/ejoc.201200767