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Transition metal mediated surface modification of porous silicon

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Dedicated to Professor Barry M. Trost on the occasion of his 60th birthday

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Abstract—Porous silicon has received considerable attention lately due to its unique optical properties and use in sensor applications. The utility of this material can be further advanced with the aid of new surface chemical modification methods. Here we describe two transition metal mediated reactions that allow for the mild and chemoselective functionalization of porous silicon. The first method utilizes rhodium carbene chemistry to modify porous silicon surfaces with esters and amides. The second technique exploits a pt-based Karstedt's catalyst to affect the hydrosilylation of porous silicon with alkenes. The mildness and selectivity of the hydrosilylation is highlighted by modification of *n*-type porous silicon matrix with an 8-residue cyclic peptide. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Porous silicon, prepared from the electrochemical etching of single-crystals of *p*- or *n*-type silicon, is a versatile material with utility in optical, electronic, and sensor applications.[1–5] Recent advances in the design of porous silicon-based interferometric biosensors and desorption ionization (DIOS) mass spectrometry have highlighted the need for selective surface chemical modification methods that can meet the needs of a given application.[6,7] Here we describe two transition metal mediated surface functionalization schemes that are able to modify the porous silicon surface through mild and highly chemoselective processes.

Under certain conditions electrochemical etching of single-crystal *p*- or *n*- type silicon wafers produces a microporous material dubbed porous silicon (p-Si). The p-Si surface is a hydride-terminated material composed of three types of silicon hydride groups, Si–H_x (x=1, 2 or 3) as identified by characteristic IR absorbances (Fig. 1(a)).[8,9] Modification of the porous silicon surface with organic compounds can be monitored by changes in the IR spectrum due to the separation of the porous silicon spectrum from that of most common organic compounds. The chemistry used to introduce molecules onto the surface of porous silicon depends heavily on the class of molecules employed and can exploit the electrophilicity of Si–Si[9–11] centers as well as the reactivity of Si–H_x bonds.[5,12–14] Alcohols, Grignard, and alkyllithium reagents are the most commonly employed nucleophilic reagents for surface modification of porous silicon.[9–11] These reagents react through an Sn2 type mechanism by attacking a surface exposed silicon atom and breaking a Si–Si bond in the process. While effective in functionalizing the surface of porous silicon these methods do have some drawbacks. In reactions with alcohols, an alkylsilylether moiety is created which is moisture sensitive and not stable in aqueous environment. On the other hand, reactions of alkyllithiums and Grignard reagents with freshly etched p-Si yields alkylsilanes that are typically stable under a variety of conditions. However, these hard

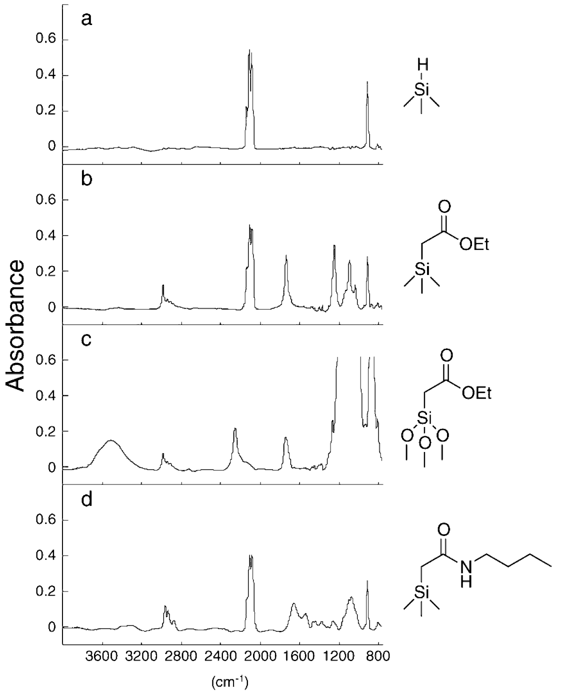

Figure 1.

Keywords: porous silicon; rhodium mediated carbene insertion; platinum hydrosilylation; surface modification.

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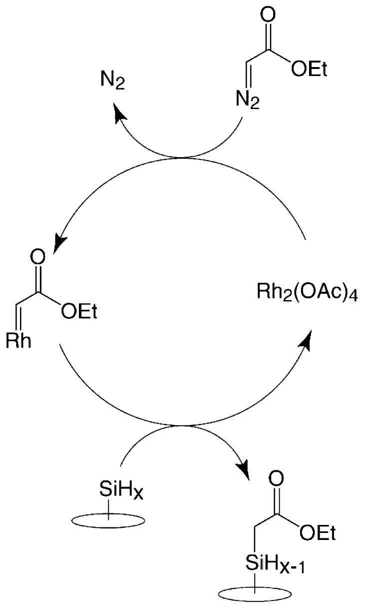


Scheme 1.

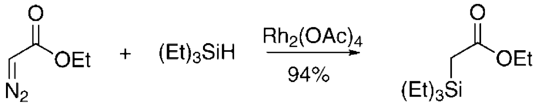
nucleophiles place a limit on the types of functionality that can be incorporated onto the p-Si surfaces. For example, functional groups such as esters and amides are not compatible with many of these reagents. The modification of porous silicon through the Si–H_x bonds provides an orthogonal method for surface modification. This strategy has been demonstrated in photo-induced hydrosilylation of alkenes to give patterned surfaces.[14] Other studies highlight the use of Si–H mediated reactions in providing stable surface modifications with many different classes of molecules.[5,12,13]

In this study we document the utility of two transition metal mediated processes for the chemical modification of hydride-terminated porous silicon matrices. The first reaction exploits rhodium catalyzed metallocarbene insertion reactions of diazo compounds into exposed silicon hydride bonds at the porous silicon surface. The second method employs a platinum based hydrosilylation reaction with alkenes. Both methods create stable carbon silicon bonds and are highly chemoselective. These mild chemical modification methods allow new functionality to easily be placed on the p-Si surface as highlighted by the incorporation of a peptide onto the silicon surface.

2. Results and discussion

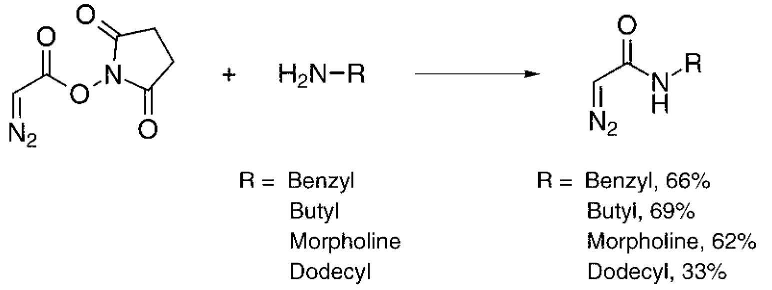
2.1. Rhodium mediated carbene insertions

In solution, carbene insertion reactions provide an efficient and selective method for modification of silanes. Exposure of a diazo compound to $Rh_2(OAc)_4$ produces rhodium carbene species that can insert into the Si–H bond to give a new silicon-carbon bond.[15] Doyle demonstrated that in the presence of $Rh_2(OAc)_4$ and triethylsilane, ethyldiazoacetate is converted cleanly into 2-(triethylsilyl)-ethylacetate in 94% yield.[16] This highly efficient reaction is also very selective with there being no side products stemming from reactions with the C–H, C–C, or Si–C bonds of the triethylsilane moiety. This favorable chemoselectivity makes this reaction an attractive candidate for developing a new method for surface modification of porous silicon.



A freshly etched *p*-type porous silicon wafer (Fig. 1(a)) placed in a benzene solution containing catalytic quantities of $Rh_2(OAc)_4$ was exposed to excess ethyldiazoacetate. Immediate evolution of N_2 ensued signifying formation of the metallocarbene intermediate (Scheme 1). The reaction mixture was then heated until gas evolution ceased (~10 min). The porous silicon chip was then removed from the reaction mixture, washed, and analyzed by FT-IR spectroscopy. The IR spectrum of the p-Si matrix showed appearance of new peaks characteristic of ethylester functionality (peaks at 2900 cm^{-1} belonging to the aliphatic CH stretching and a strong absorbance at 1760 cm^{-1} corresponding to the carbonyl stretch) (Fig. 1(b)). Reactions performed in the absence of catalyst or in the absence of the diazo compound displayed no surface modification. The modified wafer was then subjected to sonication in THF for 30 min with no change in the IR spectrum thus ruling out physisorbtion and supporting covalent modification of the p-Si surface.

Although disappearance of Si–H_x bands in the IR spectrum of the reacted p-Si matrix is indicative of insertion into the silicon hydride bonds, a priori additional insertions into surface exposed Si–Si bonds can not be ruled out. The work of Hatanaka and coworkers, provides some important experimental precedent regarding the relative reaction rates of the C–H vs Si–Si bond insertion during a rhodium carbene insertion reactions.[17] In their study various silacycloalkanes were probed in $Rh_2(OAc)_4$ catalyzed reactions with ethyl- or *tert*-butyl diazoacetate. Two substrates used in their study are of particular interest because of the presence of a Si–Si bond within a five-member ring. When these disilacyclopentanes were reacted with a diazo compound in the presence of $Rh_2(OAc)_4$ the only product detected was that of C–H insertion. This suggests that insertion into a C–H bond is more favorable than insertion into a Si–Si bond.[17] On the other hand, Doyle has shown that insertion into the Si–H bond is kinetically more favorable than insertion into C–H bond.[16] Collectively these examples indicate that carbene insertion into the Si–H bond is much more favorable than reactions with Si–Si bond. Therefore, by analogy in the above rhodium-catalyzed p-Si modification reactions, Si–H_x insertions are expected to be the dominant reaction pathway. To further support this hypothesis an oxidized porous silicon surface lacking exposed Si–Si bonds was employed in a similar modification reaction. Surface oxidized p-Si wafer was produced by first exposing a freshly etched p-Si substrate to bromine gas followed by exposure to air. This method produces a thin layer of silicon oxide at the p-Si surface by reacting with and thus removing all surface exposed Si–Si bonds while still retaining silicon hydride bonds in the form of –OSi–H_x groups.[7] Exposure of the oxidized p-Si wafers to



Scheme 2.

the Rh-catalyzed carbene insertion reactions gave a product with characteristic IR bands at 2985 cm^{-1} corresponding to the alkyl group of the ester as well as the carbonyl stretch at 1743 cm^{-1} (Fig. 1(c)). Therefore, the similar reactivity of the oxidized substrates lacking surface exposed Si–Si bonds lends further support to the Si–H insertion as the only mechanism in surface derivatization.

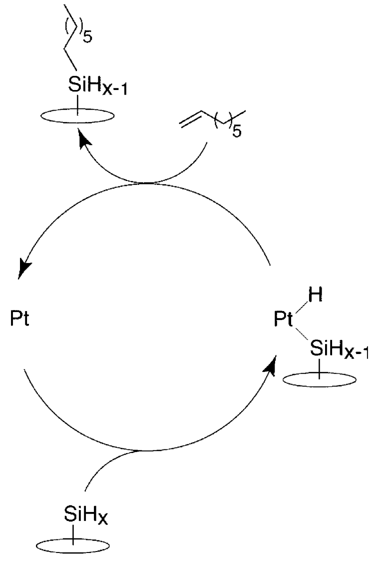
The scope and utility of the above method was demonstrated using different diazoacetamide starting reagents prepared according to the methods of Ouihia and coworkers (Scheme 2).[18] For example, the reaction between n-butyldiazoacetamide and p-Si provided the expected surface bound butyl amide moiety as evidenced by IR spectroscopy (appearance of new stretching frequencies at 2964 cm^{-1} belonging to the butyl group, as well as amide I and II stretches at 1659 and 1539 cm^{-1}) (Fig. 1(d)). Therefore, transition metal-mediated carbene insertion provides a facile route to modify p-Si matrices with amide and ester functionality that is largely inaccessible using most of the previously available methods.

2.2. Platinum mediated hydrosilylation

The second method developed for the modification of *n*-type p-Si utilized Pt-mediated hydrosilylation reaction using alkenes as starting reagents. Out of a number of different catalysts known to promote hydrosilylation reactions in solution, only Karstedt's catalyst gave the desired reactivity pattern for surface modification of p-Si (Scheme 3).[19,20] Karstedt's catalyst is a highly active colloidal Pt-based species that is commonly used in mild and chemoselective hydrosilylation reactions. The utility of this method in modification of freshly etched porous silicon was studied using a 3.5% Pt solution of Karstedt's catalyst in the presence of 1-octene. The IR spectra of porous silicon surfaces, after the reaction in benzene at 45°C for 20 h clearly indicated incorporation of octyl moieties. New peaks corresponding to the C–H stretching frequencies for octyl methylenes and methyl group now appeared at 2850–2960 cm^{-1} as well as alkane bending modes at 1466 and 1387 cm^{-1} (Fig. 2(a)). The olefinic stretch of 1-octene, which appears at 1670 cm^{-1}, is not present, indicating that the alkene is not simply physisorbed on the surface. Control experiments demonstrated that the surface remains essentially unchanged in absence of added catalyst.

Concomitant with hydrosilylation was a substantial amount of oxidation as evidenced by the increase in intensity of the broad Si–O absorption centered at 1070 cm^{-1} (Fig. 2(a)). Interestingly, if hydrosilylation was carried out in strict absence of air under an N_2 atmosphere, the porous silicon surface remained unchanged as neither oxidation nor octyl incorporation was noted, indicating that molecular oxygen was essential for the reaction to proceed. The rate of surface oxidation was dramatically accelerated in the presence of the Pt catalyst as has also been noted for copper salts.[21] Oxidation of the surface silicon atoms to form OSi–H species, increases the reaction rate because hydrosilylation of the oxygen backbonded silicon hydrides occurs preferentially over nonoxygen bound Si–H functionalities. This trend is consistent with what has been seen with homogeneous silanes where oxygen back bonded silanes (i.e. $HSi(OEt)_3$) are much more reactive than C- or Si-bound silanes (i.e. $HSiMe_3$).[20]

The high reactivity of oxygen back-bonded SiH functionalities was verified upon thermal oxidation of the porous silicon surface. Surface oxidation for 5 days at a 100°C in air results in the quantitative transformation of silicon bound SiH groups to OSiH surface species as determined by IR. When this surface was submitted to Pt catalyzed hydrosilylation conditions using 1-octene in benzene with Karstedt's catalyst solution, either in the presence or absence of air (N_2



Scheme 3.

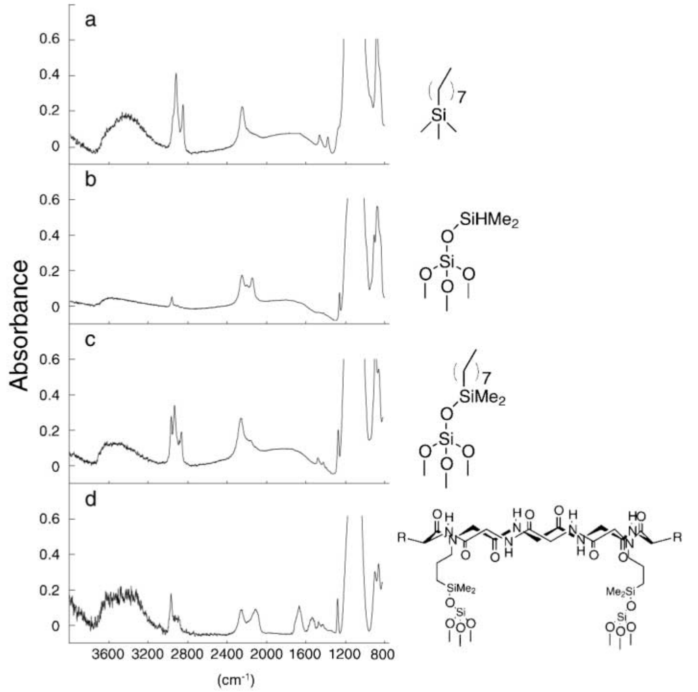


Figure 2.

atmosphere) at 45°C, octyl incorporation occurred and selective disappearance of one of the oxygen back-bonded OSi–H absorption at 2202 cm^{-1} was observed over a 3 day period. The oxygen back-bonded OSi–H absorption at 2254 cm^{-1} remains essentially unchanged. The band at 2254 cm^{-1} has been assigned to O_3Si–H (silicon hydride back-bonded to three oxygen atoms) while the absorption at 2202 cm^{-1} has been assigned to O_2SiSi–H in which the silicon hydride is back-bonded to one silicon and two oxygen atoms.[22,23] It may be that the O_2SiSi–H groups are in a less sterically hindered position on the porous surface than O_3Si–H, allowing convergence of alkene, Pt-colloid and Si–H. Molecular O_2 has been shown to be important in stabilizing Pt colloids[20] but in these reactions on porous silicon, it is not essential if the surface is previously oxidized.

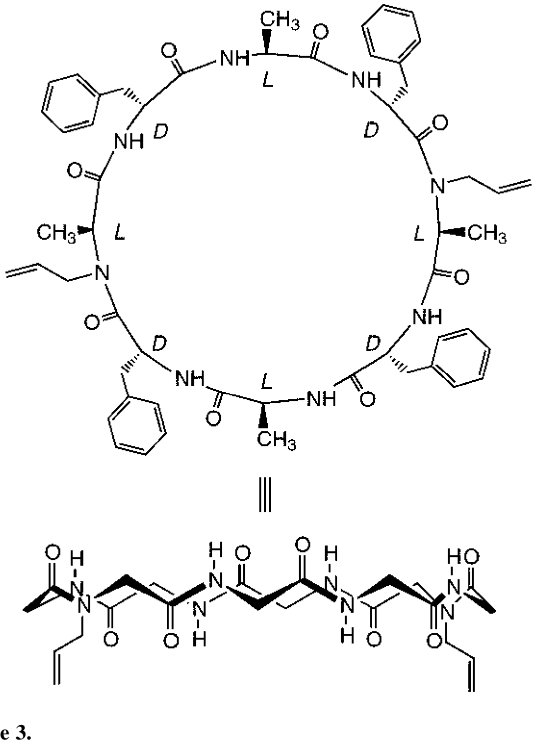
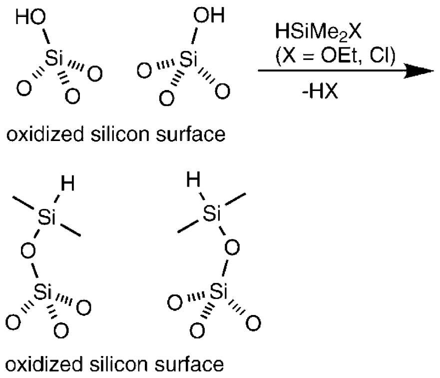


Figure 3.

Similar to its molecular equivalent, hydrosilylation of surface bound OSi–H species should involve formation of silicon-carbon bonds. Unfortunately, the Si–C vibrational mode could not be seen in the IR due to an intense Si–O band which buried all other stretching frequencies in that area. Since the proposed silicon-carbon bond could not be identified spectroscopically, the chemical stability of the surface-bound species was examined. Si–C bonds should be highly stable to hydrolysis and alcoholysis, as compared with SiO–C bonds that undergo rapid exchange. Indeed, the octyl monolayers on porous silicon are stable indefinitely in air and the octyl-decorated surface remains unchanged for at least 72 h in neat MeOH at room temperature. In contrast, a porous silicon surface coated with $SiO(CH_2)_7CH_3$ groups resulted in total exchange of octyl groups for methyl groups in 10 min of soaking in methanol. While the silicon–carbon bond was not observed through direct methods, only groups covalently attached to silicon or oxidized silicon surfaces through Si–C bonds have been shown to have such stability.[24]

In an attempt to improve the reaction we postulated that precoating the oxidized surface with more accessible silicon hydrides should allow the catalyst to function more efficiently. This process began by preparing thermally oxidized wafers by heating wafers at 100°C for 5 days and then soaking them for 16 h in neat dimethylethoxysilane, which coated the surface with a layer of H–$SiMe_2OSi$ groups.



The infrared spectrum showed new silicon hydride absorption bands at 2151 cm^{-1} stemming from the H–$SiMe_2OSi$ group (Fig. 2(b)). Submission of this hydride-coated porous silicon surface to hydrosilylation conditions in the presence of 1-octene for 3 days resulted in octyl incorporation and disappearance the H–$SiMe_2OSi$ groups as evidenced by IR spectroscopy. Additionally, the hydride absorption at 2202 cm^{-1}, from the O_2SiSi–H species, is also consumed during the reaction (Fig. 2(c)). Thus, higher level of octyl group incorporation can be achieved on surfaces that have silicon hydride groups added subsequent to the HF etch. Additionally, a second porous silicon surface devoid of any native Si–H bonds was prepared by heating at 600°C for 24 h in air. This treatment eliminates all native silicon hydrides and leaves a fairly thick oxide layer. Deposition of H–$SiMe_2OEt$ onto this porous silicon wafer results in only one Si–H absorption at 2163 cm^{-1} and a corresponding Si–H bending mode at 910 cm^{-1} in the IR spectrum. Hydrosilylation of this surface with 1-octene was more efficient with the reaction being essentially complete in less than 24 h as indicated by the disappearance of the Si–H absorption and the appearance of peaks corresponding to the C–H stretching and C–H bending vibrations of the octyl group.

With the reaction conditions optimized with 1-octene we looked to test the chemoselectivity of the hydrosilylation. Hydrosilylation of the cyclic peptide *cyclo*[(-N^{allyl}-L-Ala-D-Phe->L-Ala-D-Phe$)_2$-][25] (Fig. 3) which contains 2 allyl functionalities proceeds rapidly and is essentially complete in 24 h in air. The amide I and II stretching vibrations are observed at 1661 and 1518 cm^{-1} respectively along with the NH absorption at 3317 cm^{-1} (Fig. 2(d)). The surface coverage of the peptide is approximately 15–20% based on the absorbance of the amide I and II stretching vibrations. The peptide cannot be washed off with excess volumes of any solvents in which the peptide is soluble such as DMF, CH_2Cl_2, EtOH or MeOH. Only 24% HF in EtOH wipes the surface clean since the surface oxide is unstable to HF. This substrate shows that the chemoselectivity of this reaction allows the modification of the surface with completely new classes of molecules. Furthermore, this modification of the surface with this cyclic peptide opens up the possibility of self-assembling peptide nanotubes onto the silicon surface for ion sensing applications.[26–29]

In summary, we have described two transition metal mediated reactions that take advantage of the reactivity of the silicon hydride bonds present on the surface of porous silicon. The silicon carbon bonds created through these reactions render the functionalized surface highly stable. Furthermore, the mild conditions applied permit the use of entirely new classes of functional groups. Together these two attributes are expected to allow the newly functionalized porous silicon surfaces to be used in novel ways opening up the door for its applications in analytical and materials settings.

3. Experimental

3.1. General

FT-IR spectra were collected on a Nicolet Mangna Series 550 spectrometer in transmission mode. A 4 cm^{-1} resolution was used with 128 scans collected for each spectrum. All reagents were purchased from Aldrich and used without further purification. For the carbene insertion porous silicon was made from the electrochemical etch of *p*-type silicon wafers (3 Ω-cm) under a current of 33 mA/cm^2 for 20 min in a solution of HF/H_2O/Ethanol (1/1/2) yielding a surface area of about 50 cm^2. For hydrosilylation reactions *n*-type silicon wafers (0.5 Ω-cm) were etched under a current of 88 mA/cm^2 for 3 min in a solution of HF/H_2O/Ethanol (1/1/2) while being illuminated by a 30 mW/cm^2 white light to afford a surface area of about 50 cm^2. These processes yielded a 1.2 cm^2 circular area of etched porous silicon. Karstedt's catalyst was purchased as a 3–3.5% solution in xylenes (Petrarch).

3.2. Rhodium carbene insertion reactions

A freshly etched wafer was placed into a round bottom flask with benzene (10 mL) and $Rh_2(OAc)_4$ (0.4 mg). The reaction was initiated by addition of the diazo compound {ethyl diazoacetate (1 mL, 9.5 mM)} to the solution. The reaction was detected by the evolution of nitrogen. The reaction mixture was then heated for about 10 min or until gas evolution ceases. The wafer was then immediately removed washed with ethanol and methylene chloride and dried under a gentle stream of nitrogen prior to analysis by IR.

3.3. Oxidation of the porous silicon substrate

A freshly etched wafer was placed under an inert atmosphere of Argon. Bromine (100 μL) was added into the flask and the flask sealed. After 1 h, the wafer was removed and exposed to ambient air.

3.3.1. Preparation of diazoacetamides. Succinimidyl diazoacetate (92 mg, 0.5 mmol, 1 equiv.) was dissolved in THF (5 mL). Neat butyl amine (98 μL, 1 mmol, 2 equiv.) was added to the solution via syringe in one portion. After 1 h, the solution was concentrated in vacuo. The crude material was purified by flash chromatography (EtOAc) to yield 49 mg (69%) of a pale yellow solid. IR ($CDCl_3$): 3305, 3099, 2962, 2933, 2875, 2104, 1726, 1618, 1552, 1524, 1383, 916 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 0.847 (3H, t, J=5.736 Hz), 1.31 (m, 4H), 3.19 (2H, m), 6.34 (1H, s). ^{13}C NMR (95 MHz, $CDCl_3$) δ: 13.60, 19.89, 25.41, 31.83, 39.60, 46.72, 165.93. Mass calcd for $C_6H_{11}ON_3$: 142.0980; Found: 142.0986, 4.2 ppm.

3.3.2. *n*-Dodecyldiazoacetamide. IR ($CDCl_3$): 3300, 3093, 2954, 2920, 2850, 2104, 1709, 1612, 1549, 1396 cm^{-1}. ^1H NMR(200 MHz, $CDCl_3$) δ: 0.838 (3H, t, J=5.16 Hz), 1.21 (18H, m), 1.46 (2H, m), 3.21 (1H, d, 4.37 Hz), 4.77 (1H, s), 5.61 (1H, s). ^{13}C NMR (95 MHz, $CDCl_3$) δ: 13.98, 22.57, 26.83, 29.24, 29.51, 29.80, 31.80, 39.95, 46.71, 165.83. Mass calcd for $C_{14}H_{27}ON_3$: 254.2232; Found: 254.2223, 3.5 ppm.

3.3.3. *n*-Benzyldiazoacetamide. IR ($CDCl_3$): 3294, 3099, 2927, 2110, 1610, 1558, 1389, 1358 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 4.35 (2H, d, J=4.61 Hz), 4.71 (1H, s), 5.70 (1H, m), 7.22 (5H, m). ^{13}C NMR (95 MHz, $CDCl_3$) δ: 43.73, 47.06, 126.25, 127.37, 127.45, 128.59, 166.04. Mass calcd for $C_9H_9ON_3$: 176.0824; Found: 176.0831, 4 ppm.

3.3.4. *n*-Morpholinediazoacetamide. IR ($CDCl_3$): 3481, 3082, 2970, 2900, 2860, 2110, 1603, 1432, 1240, 1117, 1039 cm^{-1}. ^1H NMR(200 MHz, $CDCl_3$) δ: 3.43 (4H, m), 3.59 (4H, m), 4.96 (1H, s). ^{13}C NMR (95 MHz, $CDCl_3$) δ: 44.00, 46.37, 66.51, 164.99. Mass calcd for $C_6H_9O_2N_3$: 156.0773; Found: 156.0766, 4.5 ppm.

3.4. Platinum catalyzed hydrosilylation reactions

A freshly etched porous silicon wafer was washed thoroughly with EtOH, CH_2Cl_2 and dried under a stream of N_2. To this wafer was added 1 mL of benzene, 20 mL of 1-octene and 1 mL of Karstedt's catalyst solution (3–3.5% solution in xylenes). This mixture was then heated at 45°C until the reaction was complete as determined by IR spectroscopy.

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