

Hydride Abstraction Initiated Hydrosilylation of Terminal Alkenes and Alkynes on Porous Silicon

J. M. Schmeltzer,[†] Lon A. Porter, Jr.,[†] Michael P. Stewart,^{†,‡} and Jillian M. Buriak*

Department of Chemistry, 1393 Brown Laboratories, Purdue University, West Lafayette, Indiana 47907-1393

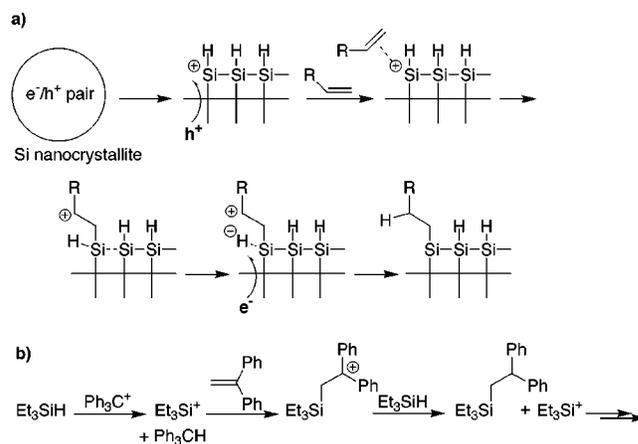
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Hydride abstraction by triphenylcarbenium cations in the presence of terminal alkynes and alkenes results in hydrosilylation at room temperature on hydride-terminated porous silicon surfaces, leading to alkenyl- and alkyl-terminated surfaces, respectively. A wide range of surface terminations are possible as the reaction conditions tolerate a variety of functional groups. Silicon–carbon bond formation is substantiated by Fourier transform infrared and ¹³C solid-state NMR spectroscopies, in addition to chemical and stability studies. Generation of an energetic surface silicon-based positive charge is thus a viable route to the formation of silicon–carbon bonds via hydrosilylation, a step previously postulated for the mechanism of exciton-mediated hydrosilylation on photoluminescent nanocrystalline silicon.

Introduction

The chemistry of silicon surfaces is a field of intense interest, not only for the prospect of exciting technological applications but also from a fundamental perspective.^{1,2} One of the most pervasive questions concerns the similarity of the organosilicon chemistry of surfaces compared to that of molecular compounds.³ While there are some analogies, silicon surfaces have shown some unique and fascinating reactivities which differentiate them from silicon-based molecules.^{4,5} For instance, an exciton-mediated hydrosilylation reaction unique to photoluminescent porous silicon was recently described in which electron/hole pairs forming in nanocrystalline silicon upon illumination appear to drive the silicon–carbon bond-forming event.^{6b} The proposed mechanism involves attack of a surface-localized positive charge (the hole) in a nucleophilic fashion by an alkene or alkyne, resulting in Si–C bond formation, as shown in Scheme 1a. To further substantiate this proposal, we sought to produce energetic surface-bound positive charges in the presence of alkenes and alkynes by chemical means. Recent work by Lambert and co-workers has shown that solution phase silylenium cations can react with 1,1-diphenylethene to form β -silyl carbocations that are stable at room temperature in solution, as outlined in Scheme 1b.⁷ The silylenium cation is formed through hydride abstraction with the triphenylcarbenium cation via Corey hydride transfer;^{8,9}

Scheme 1



nucleophilic attack by the alkene and subsequent hydride abstraction from an additional equivalent of silane results in the silylated alkane product. We sought to apply this reaction to hydride-terminated porous silicon in the presence of terminal alkenes and alkynes (i) to determine if Si–C bond formation via attack of a surface silicon-based positive charge by an alkene or alkyne is a viable mechanistic step on silicon surfaces, (ii) to determine if the known solution phase chemistry of carbocation-mediated hydrosilylation has parallels with silicon surface chemistry, and (iii) to evaluate the utility of this chemistry on porous silicon to allow access to a wide range of technologically interesting and stable surfaces.

Porous silicon, produced by the anodic corrosion of crystalline silicon with hydrofluoric acid, is comprised of interconnected silicon nanocrystallites passivated by metastable hydride groups.¹ Due to its high surface area and mid-IR permittivity, porous silicon is an excellent “test substrate” for examining new chemistry since IR spectra can be accumulated rapidly (~16–64 scans) in transmission mode, a technique accessible to most researchers. Additionally, we have shown in previous work that the high surface area permits analysis by ¹³C solid-state NMR spectroscopy, a highly complementary technique for characterizing organic monolayers on silicon.^{10a} Porous silicon may also have important applications of its own which require tailoring of its interfacial character-

[†] Contributed equally to this work.

[‡] Current address: Department of Chemistry and Center for Nanoscale Science and Technology, Rice University, P.O. Box 1892, Houston, TX 77251-1892.

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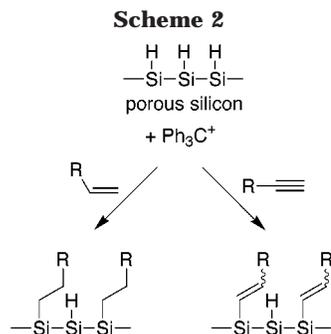
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istics, including chemical sensing,¹¹ physiological implantation,¹² bioanalysis,¹³ and optoelectronics.¹⁴ To modify, stabilize, and better understand the reactive hydride-terminated surface of porous silicon, there are a number of methods now developed for the formation of covalently bound organic monolayers on this material.^{4,5,15} In this letter, we describe a unique room-temperature approach toward silicon surface modification, involving hydride abstraction and subsequent Si-C bond formation by hydrosilylation of terminal alkenes and alkynes, as summarized in Scheme 2. The surfaces were characterized by Fourier transform infrared (FTIR) and ¹³C solid-state NMR spectroscopies, and their stabilities were probed through exposure to demanding chemical conditions.

Experimental Details

Sample Preparation. Hydride-terminated porous silicon substrates were prepared utilizing a standard electrochemical etching method.¹⁶ A polished monocrystalline silicon wafer (P-doped, (100) orientation, resistivity of 0.65–0.95 Ω cm, 1.1 cm² exposed area) was galvanostatically etched with a positive bias under white light illumination using a 300 W tungsten filament with 1:1 49% HF (aq)/EtOH in a homemade Teflon etching cell at a current density of 8.5 mA/cm² for 90 s, then increasing to 85 mA/cm² for 120 s. After etching, the wafer was rinsed with EtOH and pentane, drying gently with streaming dinitrogen. Functionalization of porous silicon was accomplished in an inert atmosphere glovebox by the addition of 0.01 M Ph₃CBF₄ in CH₂-Cl₂ (200–250 μL), followed by an equal volume of neat alkene or alkyne (filtered through anhydrous alumina to remove peroxides), to the freshly etched wafer. After standing at room temperature for 3 h, the wafer was rinsed copiously with

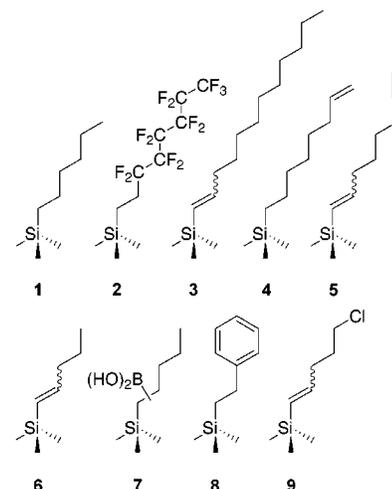


Figure 1. Examples of the surface terminations possible through hydride abstraction initiated hydrosilylation on porous silicon.

tetrahydrofuran (THF), EtOH, CH₂Cl₂, and pentane and was dried under a flow of dinitrogen. Hydroboration experiments were carried out by soaking the functionalized surface to 1.0 M BH₃·THF in THF for 12–16 h at room temperature in a glovebox.

FTIR Spectroscopy. FTIR spectra were collected using a Nicolet Nexus 670 spectrometer in transmission mode. The samples were maintained in the etching cell (which doubles as an IR cell) before and after functionalization to ensure that the same spot on the sample was being examined, thus permitting semi-quantitative analysis.

Solid-State NMR. ¹³C cross-polarization/magic angle spinning (CP/MAS) NMR experiments were conducted on a Varian Infinity 400 MHz solid-state instrument. Approximately 150 mg of porous silicon, prepared as previously described,^{10a} was loaded into a 5 mm pencil rotor and spun at frequencies of 5–6 kHz during acquisition. The ¹³C spectra were obtained using ¹H–¹³C cross polarization with a ¹H t₉₀ of 3.00 ms and contact pulse widths of 2–8 ms. The ¹³C T₁'s were relatively short (1–3 s), allowing recycle delays of 3–8 s. Due to the diminutive concentration of organic adsorbate, approximately 10 000–20 000 scans were accumulated for each solid-state spectrum. The ¹³C resonances are reported relative to tetramethylsilane (TMS) by use of an external reference to glycine, assigning the carbonyl peak to δ 174.3 ppm.

Results and Discussion

This hydride abstraction hydrosilylation method is sufficiently gentle to allow access to a wide variety of functionalized surfaces, as summarized in Figure 1. Transmission mode FTIR spectroscopy of functionalized porous silicon samples indicates that hydrosilylation of terminal alkenes and alkynes leads to alkyl- and alkenyl-terminated surfaces, respectively, shown in Figure 2. The FTIR spectrum of freshly prepared hydride-terminated porous silicon exhibits a tripartite band centered at 2100 cm⁻¹ characteristic of Si–H_x (x = 1–3) stretches. Reaction with 1-dodecyne in the presence of the carbocation salt results in the appearance of sharp aliphatic ν(C–H) stretching bands in the region of 2850–2960 cm⁻¹, accompanied by broadened ν(Si–H_x) stretching modes of diminished intensity (vide infra). The expected ν(SiC=C) vibration is observed at 1600 cm⁻¹, substantiating formation of the dodeceny-substituted surface.^{10,17} An accompanying band at 979 cm⁻¹ is attributed to extraplanar C–H bending of a trans-disubstituted alkene, γ(=CH),

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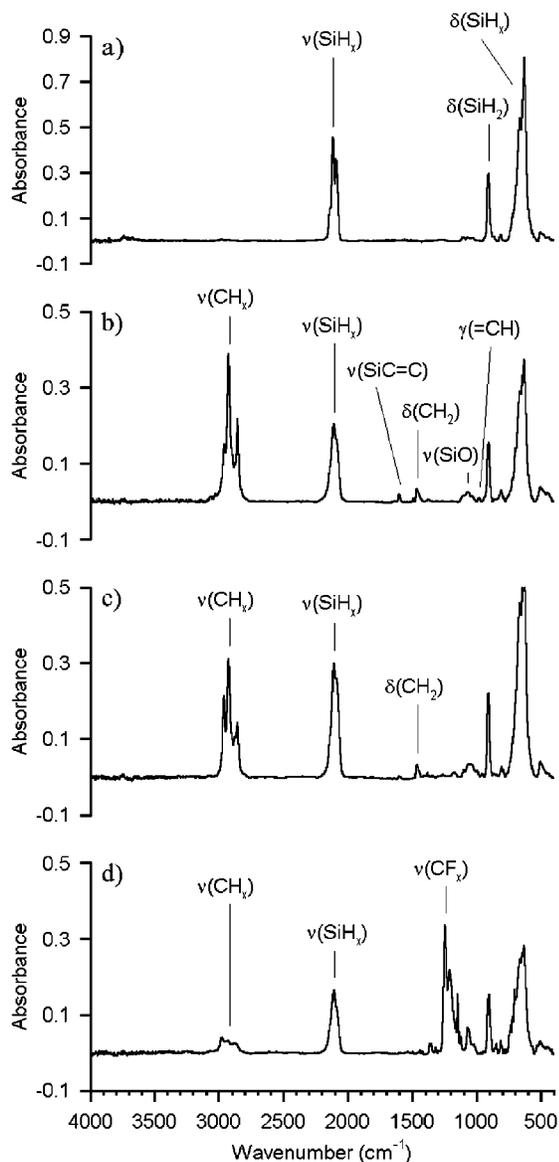


Figure 2. Transmission FTIR spectra of porous silicon samples. (a) Freshly etched hydride-terminated porous silicon. (b) Sample functionalized through the hydride abstraction chemistry with 1-dodecyne, leading to dodecyl-terminated material. (c) Sample functionalized with 1-hexene, yielding a hexyl-terminated surface. (d) Sample functionalized with 1*H*,1*H*,2*H*-tridecafluoro-1-octene, yielding a perfluorooctyl-derivatized surface.

suggesting that at least a fraction of the derivatized surface has trans stereochemistry.^{6,18} Exposure of this surface to BH₃·THF results in disappearance of both the ν(SiC=C) and γ(=CH) modes due to hydroboration of the olefin, thus providing chemical proof for dodecyl termination (see Supporting Information).¹⁰ Functionalization of porous silicon with 1-hexene yields an alkyl-terminated substrate **1**, supported by the appearance of aliphatic C–H features and complete consumption of the olefinic group. We previously defined the term “efficiency of hydrosilylation”, which refers to the estimation of percent consumption of Si–H_x groups, by comparing the integration of the ν(Si–H_x) before and after hydrosilylation by FTIR.^{10a,19} For hydride abstraction initiated hydrosily-

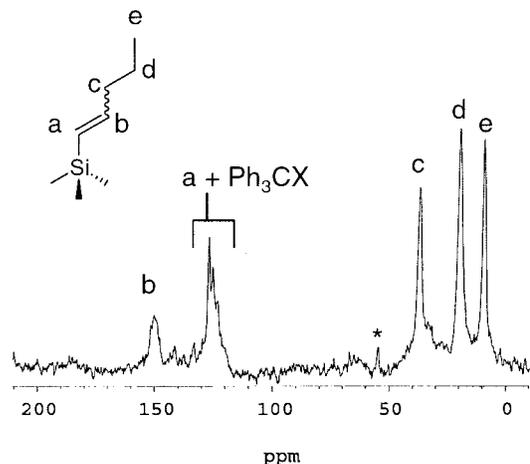


Figure 3. Solid-state ¹³C CP/MAS NMR spectrum of pentenyl-functionalized free-standing porous silicon prepared by hydride abstraction initiated hydrosilylation. Peak b, the carbon α to the silicon surface, is obscured by the residual non-*ipso* carbons (15 total) of the triphenylcarbenium cation. The peak marked with an asterisk corresponds to residual dichloromethane.

ation, the efficiency or percent conversion of Si–H bonds to Si–C bonds is calculated to average ~27% and 19% for the alkenes and alkynes studied, respectively, comparable to that afforded by Lewis acid mediated hydrosilylation.¹⁰ Weak bands ascribed to the ν(Ar–H) stretches at ~3100 cm⁻¹, one of the ν(C=C) aryl ring modes at 1600 cm⁻¹, and a γ(Ar–H) deformation at 698 cm⁻¹ of residual triphenylcarbenium cation and potential degradation products (triphenylmethane and/or triphenylmethanol) persist even after determined rinsing and sonication for 15 min in CHCl₃. Physisorption of free alkenes (1650 cm⁻¹, ν(C=C)) or alkynes (3315 cm⁻¹, ν(≡CH)) is not evident; the FTIR spectra suggest that hydrosilylation of alkenes and alkynes at the porous silicon surface proceeds to the formation of covalent silicon–carbon bonds. A sample of porous silicon exposed to the carbocation solution in the absence of alkene/alkyne exhibits substantial oxidation, along with the background incorporation of triphenylcarbenium cation and possible degradation products.

In addition to standard FTIR analysis, solid-state ¹³C NMR spectroscopy has recently been shown to be a very useful characterization tool for elucidating the chemical composition of organic monolayers on porous silicon.^{10a} Large masses (~150 mg) of free-standing disks of porous silicon that have been detached from the silicon wafers were used for this purpose and functionalized with pentenyl groups via carbocation-mediated hydrosilylation of 1-pentyne (surface **6**). The resonance frequencies for the five carbons of the pentenyl monolayer measured by solid-state ¹³C CP/MAS NMR spectroscopy (Figure 3) correlate well to those observed for the Lewis acid mediated hydrosilylation of 1-pentyne on porous silicon.^{10a} The peak corresponding to the vinylic carbon located α to the surface silicon atom is obscured by the non-*ipso* phenyl resonances (15 carbons total) of the triphenylcarbenium cation or those of its degradation products.²⁰ As indicated earlier,^{10a} ¹³C NMR cannot provide insight into the ratio of *cis/trans* products due to the very similar chemical shifts (within ~1 ppm) of the vinylic carbons in both species.²⁰

Carbocation-mediated functionalization of porous silicon yields surfaces that exhibit increased stability to oxidation under both ambient and extreme conditions. Surface **3**, immersed in aerated boiling water and ethanolic solutions,

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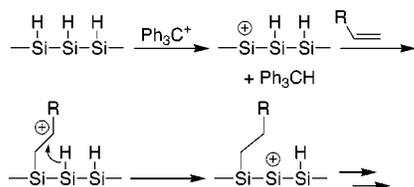


Figure 4. Proposed mechanism for hydride abstraction initiated hydrosilylation on porous silicon. The triphenylcarbenium cation removes H^- from the surface, producing a surface silicon-based positive charge. Nucleophilic attack of this positive charge by an alkene results in $\text{Si}-\text{C}$ bond formation and a β -silyl-substituted carbocation fragment. This Lewis acidic group can then abstract a neighboring hydride from a $\text{Si}-\text{H}$ group, forming a new silicon-based positive charge.

shows little appreciable oxidation after 30 min. Such surfaces boiled in basic (pH 10) ethanolic solutions exhibit stability comparable to that afforded to porous silicon terminated with monolayers via $\text{Si}-\text{C}$ bonds.^{10,15} Hydride-terminated porous silicon dissolves rapidly under these conditions. It is believed that the hydrophobicity of the functionalized porous silicon surface retards reaction of water and nucleophiles with the underlying material, imparting resistance to degradation.

A proposed mechanism for this method of hydrosilylation closely resembles the chemistry reported by Lambert and co-workers for solution phase organosilanes, involving the formation of a silylenium cation (Figure 4).⁷ The triphenylcarbenium cation is proposed to abstract a hydride from porous silicon,^{8,9} leading to a positively charged silicon-based surface cation which then reacts with an alkene or alkyne to yield a β -silyl carbocation. Although the stability of such species in the gas phase²¹ and in low-temperature, superacidic condensed phases²² is well established, only recently have stable species been prepared under ambient conditions.^{7,23} Propagation may occur through abstraction of an adjacent hydride, leading to a new silicon-based positive charge; experiments in which the surface is exposed to triphenylcarbenium salt, washed, and then treated with alkene, however, did not

lead to high levels of incorporation.²⁴ As a result, the reaction has not been shown to be catalytic, as is the case in solution. Carbocation-mediated hydrosilylation of 1-hexene and 1-octyne with porous silicon in the presence of 2,4,6-tri-*tert*-butylphenol, a radical inhibitor, proceeds without interference, suggesting little or no contribution from a parallel radical-based chain reaction.²⁵ Hole injection to bulk silicon through exposure of $\text{Si}(111)-\text{H}$ to the ferrocenium ion has also been shown to lead to surface chemistry; in this case, 2 equiv of methanol reacts to produce a methoxy-terminated surface.²⁶ More detailed mechanistic studies of this reaction are currently being undertaken, including analysis of anion effects.

In conclusion, the hydrosilylation of a variety of alkenes and alkynes on hydride-terminated porous silicon is achieved under mild conditions through the use of a hydride abstracting agent. Hydrosilylation driven by a highly reactive silicon-based positive charge on the surface draws parallels between silicon surface chemistry and that of molecular silanes in the solution phase. In addition, this work helps to substantiate the proposed mechanism of exciton-mediated hydrosilylation, which depends on the initiation of a surface-localized positive charge, in a related manner. Unlike the exciton chemistry, this reaction should not be limited to nanocrystalline silicon, and work is progressing in the extension of this chemistry to a range of other surface morphologies.

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Supporting Information Available: FTIR data for all surfaces mentioned here (1–9), FTIR spectra of dodecenyli-terminated surfaces after exposure to boiling ethanolic base and before and after hydroboration treatment with $\text{BH}_3\cdot\text{THF}$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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