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Metal Mediated Reactions on Porous Silicon Surfaces

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Reactions that efficiently form Si–C bonds between silanes and unsaturated carbon–carbon bonds are widely known in molecular, solution phase chemistry. The possibility of covalent functionalization of porous silicon surfaces, which have similar chemical moieties to certain classes of molecular silanes, is intriguing. In this paper we describe approaches toward hydrosilylation of alkynes and alkenes and bis-silylation of alkynes utilizing known solution phase Lewis acid and late transition metal catalysts on silicon hydride terminated porous silicon surfaces. Both $EtAlCl_2$ and Wilkinson's catalyst, $RhCl(PPh_3)_3$, effectively induce hydrosilylation of alkynes and alkenes. Bis-silylation using palladium-based complexes, however, did not occur and thermally induced hydrosilylation took place in its stead. The Lewis acid mediated hydrosilylation is extremely efficient and yields highly stabilized surfaces. When Wilkinson's catalyst and palladium complexes are utilized, on the other hand, extensive oxidation upon exposure to air is observed. © 1999 Academic Press

Key Words: **porous silicon; surface; silicon–carbon bond; catalyst; catalysis; aluminum; rhodium; palladium; stabilization; covalent; hydrosilylation; bis-silylation; alkene; alkyne.**

INTRODUCTION

The anodic corrosion of crystalline silicon by fluoride-containing solutions creates a luminescent network of nanometer scale wire-like Si structures known as porous silicon. The porosity of this network can be as high as 95%, with surface areas on the order of hundreds of m^2/cm^3(1). It is widely believed that the luminescent properties (photo-, electro-, and chemo-) are due to quantum size effects (2) in sequestered "nanocrystallites" within the porous silicon network. The physical and material properties of porous silicon are highly accommodating for a variety of potential applications since the morphology and porosity of the material can be varied rationally with changes in etching conditions (e.g., fluoride concentration, etching duration, light exposure, doping concentration). The high surface area compares to that of porous silica materials such as aerogel or zeolite, but the semiconducting nanowire skeleton allows for electronic communication between the surface states and the underlying "bulk" silicon (3). Chemical surface states present on the nanocrystallites are known to dramatically influence the light emission characteristics and thus control of surface composition is critical (4). The native hydride passivated porous silicon is only metastable with respect to oxidation and the formation of nonradiative recombination traps at the surface under ambient conditions; appearance of surface oxide commences within tens of minutes, altering the luminescence and electronic properties of the nanocrystallites. Because recent studies on flat hydride terminated single crystal silicon have indicated that substitution of the hydrides with covalently bound organic passivating groups stabilize the surface (5), several workers have been pursuing related approaches on porous silicon (6). We have found that the surface metastability can, in fact, be used to its advantage: the porous silicon is stable enough to resist immediate destruction in air, but reactive enough to allow for "soft," wet chemical methods of modification.

In this work we demonstrate that analogs of Si–C bond-forming reactions in molecular chemistry are useful for chemistry on the silane-like porous silicon surface. As outlined in Scheme 1, hydrosilylation involves insertion of an alkyne or alkene into a surface silicon hydride group, yielding an alkenyl (vinyl) or alkyl functionality, respectively. Insertion of alkynes into Si–Si bonds has also been investigated here which would yield a bis-silylated, covalently attached olefin (Scheme 1). Previous results from our laboratory have shown that Lewis acids can mediate surface hydrosilylation to sufficiently protect porous silicon from ambient degradation through the formation of covalently bound protecting layers (6d). In order to further understand the chemistry of silicon–hydride terminated surfaces, and to access new and useful reactivity patterns, we have examined the Lewis acid hydrosilylation reaction in greater detail and have probed late transition metal mediated hydrosilylation and bis-silylation on porous silicon. Because certain metal complexes catalyze hydrosilylation and bis-silylation reactions involving molecular silanes in the solution phase, a number of known metal complexes were investigated here with the goal of accessing analogous chemistry on porous silicon surfaces. The exact ratio of catalyst to surface bound

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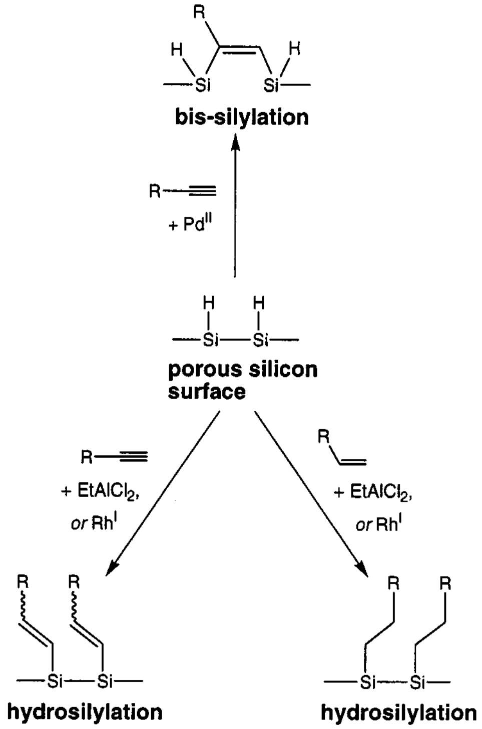


SCHEME 1. Hydrosilylation and bis-silylation reactions on the native hydride terminated porous silicon surface. Rh^I or EtAlCl$_2$ mediated hydrosilylation of alkynes and alkenes yields alkenyl and alkyl surfaces, respectively. Pd^{II} salts induce insertion of alkynes into silicon-silicon bonds, producing a bis-silylated olefin.

functional groups is not known and the reactions are thus defined as "metal complex mediated" and not catalyzed. The metal complexes investigated are shown in Fig. 1. The ability to gently create organic structures covalently attached to the semiconducting porous silicon network is crucial for progress toward Si-based nanoscale architectures and optoelectronic devices (7), as well as for a more fundamental understanding of porous silicon reactivity in general.

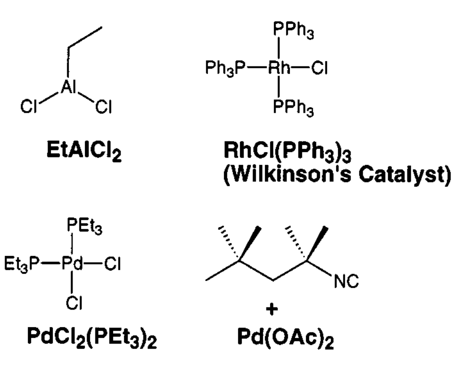


FIG. 1. Complexes tested for hydrosilylation and bis-silylation on porous silicon surfaces.

EXPERIMENTAL

General Procedures

All reactions were carried out under inert atmosphere, either in a nitrogen filled Vacuum Atmospheres glove box (< 1 ppm H_2O, O_2) or in Schlenk flasks on grease-free dual manifold argon–vacuum lines (ChemGlass). THF, CH_2Cl_2, hexanes, and toluene were purchased from Fisher (Optima or HPLC grade) and then purified using a variation of the Grubbs/Dow Chemical solvent purification system (8). All alkynes and alkenes were filtered over neutral, anhydrous alumina under inert atmosphere before use to eliminate water and peroxides and stored at − 35°C under nitrogen in absence of light. 1-Dodecyne, 1-dodecene, and phenylacetylene were further purified by distillation from molecular sieves (4 Å). $Pd(OAc)_2$ was a gift from Johnson Matthey/Alfa Aesar and was used without further purification 1,1,3,3-tetramethylbutyl isocyanide (Walborsky's reagent, 90 + %) was purchased from Aldrich, sparged with argon, and used with no further purification. The following chemicals were used as received: $RhCl_3$ hydrate (Next Chimica), triphenylphosphine (Acros), 1.0 M hexanes solution of $EtAlCl_2$ (Aldrich), hexamethyldisilane (packaged under nitrogen, Acros), 48% aqueous hydrofluoric acid (trace metals grade, Fisher), $PdCl_2(PEt_3)_2$ (Aldrich), and ethanol (200 proof, McCormick Distilling Company). ^1H NMR spectra were carried out on a 200 MHz Varian Gemini 200 instrument. Residual $CHCl_3$ in $CDCl_3$ (Cambridge Isotope Laboratories) was used as the internal reference (7.26 ppm).

Fourier Transform Infrared (FTIR) Spectroscopy

A Perkin Elmer 2000 FTIR spectrometer was used to collect the porous silicon spectra in transmission mode. Sixteen to 32 scans were accumulated with a usual spectral resolution of 4 cm^{-1}. The sample chamber was purged with dry air or nitrogen. Difference spectra involved reaction of the porous silicon within a homemade etching–reaction cell that also acted as the FTIR sample holder. This enables analysis by IR of the same spot on the sample surface each time in the same orientation, allowing for direct comparison of spectra before and after chemical functionalization. Because small experimental variations in electrolyte concentration, distance between surface and cathode, light intensity, temperature, slight doping changes from wafer to wafer, etching time (± seconds), precursor surface treatment and commercial source can have very substantial effects on the porous silicon % porosity, average pore size, surface area, sample thickness, and morphology, this procedure is necessary to directly compare a sample before and after functionalization. As a result, comparison of *absolute* intensities between different samples cannot be carried out due to difficulties in generating identical samples each time. *Relative* intensities are, however, identical within a spectrum for all the preparations and functionalizations described here, within experimental error.

Porous Silicon Preparation

Photoluminescent silicon samples were prepared according to previously published procedures through a galvanostatic etch (9). A 0.28 cm^2 exposed area of a polished, crystalline *n*-type silicon wafer (prime grade, P-doped, 100 orientation, 0.70 $\Omega \cdot$cm, Transition Technology International) was etched for 3 min in a Teflon cell at 75 $\mathrm{mA/cm}^2$ (positive bias) under 30 $\mathrm{mW/cm}^2$ white light illumination, derived from a 300 W tungsten filament ELH bulb using 1:1 49% HF (aq)/EtOH as the electrolyte/etchant. After etching, the porous silicon samples were rinsed copiously with ethanol, blown dry under a stream of nitrogen, and dried *in vacuo* for 1 h prior to use. Photoluminescence spectra were measured as previously described (6e).

Lewis Acid Mediated Hydrosilylation

Hydrosilylation reactions to produce surfaces 1–12 were carried out according to the following procedure in a glove box: A 1 cm^2 silicon wafer with the 0.28 cm^2 porous area was loaded into a 10 mL round bottom flask in air and sealed under inert atmosphere with a rubber septum. The 1.0 M $\mathrm{EtAlCl_2}$ hexanes solution (10 μl) was dropped onto the wafer surface with a microliter syringe through the rubber septum, followed by addition of the alkene (50 μl) or alkyne (3 μl), also via the rubber septum with a microliter syringe. The reaction was left to react for the desired length of time at room temperature, after which the sample was quenched under inert atmosphere with THF, followed by $\mathrm{CH_2Cl_2}$, then rinsed in air with EtOH, and dried under an $\mathrm{N_2}$ stream. Alkynes were allowed to react 1 h and alkenes at least 12 h. Longer times and larger quantities of alkenes are necessary due to their lower reactivity compared to alkynes. Control experiments for each alkyne and alkene were completed in an identical fashion but without addition of the 1.0 M hexanes solution of $\mathrm{EtAlCl_2}$. Stability studies in aqueous aerated solutions were carried out with $\mathrm{H_2SO_4}$ (pH 1) or either NaOH or KOH (pH 10) solutions. FTIR spectral information for surfaces 7, 8, 11, and 12 is listed below; FTIR spectra of surfaces 1–6, 9, and 10 have been published previously (6d).

Surface 7. Transmission FTIR: 3000–2974 cm^{-1} aromatic ν (C–H), 2105 cm^{-1} ν (Si–H), 1899 cm^{-1} aromatic overtone, 1595 cm^{-1} ν(C=C) aromatic and ν(C=C) vinyl group, 1488 and 1399 cm^{-1} ν(C=C) aromatic, 1040 cm^{-1} ν (Si–O), 903 cm^{-1} $\delta(\mathrm{SiH_2})$.

Surface 8. Transmission FTIR: 3040–2869 cm^{-1} aromatic ν(C–H) and $\nu(\mathrm{CH_3})$, 2107 cm^{-1} (Si–H), 1611 and 1562 cm^{-1} ν (C=C) aromatic, 1589 cm^{-1} ν(C=C) vinyl group, 1450 and 1379 cm^{-1} $\delta(\mathrm{CH_3})$, 1044 cm^{-1} ν(Si–O), 905 cm^{-1} $\delta(\mathrm{SiH_2})$.

Surface 11. Transmission FTIR: 3034 cm^{-1} ν(C–H) aromatic, 2930–2846 cm^{-1} $\nu(\mathrm{CH_2})$, 2112 cm^{1} ν(Si–H), 1604 cm^{-1}(C=C) skeletal in-plane vibration, 1492 and 1450 cm^{-1} $\delta(\mathrm{CH_2})$, 1064 cm^{-1} ν(Si–O), 906 cm^{-1} $\delta(\mathrm{SiH_2})$.

Surface 12. Transmission FTIR: 2961 cm^{-1} $\nu(\mathrm{CH_3})$, 2920 cm^{-1} $\nu(\mathrm{CH_2})$, 2112 cm^{-1} ν(Si–H), 1457 $\delta(\mathrm{CH_2})$, 1391 and 1364 cm^{-1} $\delta(\mathrm{CH_3})$, 905 cm^{-1} $\delta(\mathrm{SiH_2})$. The diastereomers formed were not determined.

1,7-Octadiyne polymerization and hydrosilylation. 1,7-octadiyne (3 μL, Aldrich) was reacted with the $\mathrm{EtAlCl_2}$ treated surface 1 min. Transmission FTIR: 3318 cm^{-1} ν(alkyne C–H), 2932 and 2856 cm^{-1} $\nu(\mathrm{CH_2})$, 2106 cm^{-1} ν(Si–H), 1641 cm^{-1} ν(RC=CR), 1595 cm^{-1} ν(RC=CSi), 1446 cm^{-1} $\delta(\mathrm{CH_2})$, 1050 cm^{-1} ν(Si–O), 904 cm^{-1} $\delta(\mathrm{SiH_2})$. If the reaction is allowed to proceed 2 h, the ν(C=C) at 1641 cm^{-1} broadens and relative integration increases, and the $\nu(\mathrm{CH_2})$ and δ $(\mathrm{CH_2})$ become more intense. The very dark surface turns pale yellow upon rinsing with EtOH.

1,7-Octadiene polymerization and hydrosilylation. 1,7-octadiene (3 μL, Aldrich) was reacted with the $\mathrm{EtAlCl_2}$ treated surface 1 h. Transmission FTIR: 2924 and 2856 cm^{-1} $\nu(\mathrm{CH_2})$, 2099 cm^{-1} ν(Si–H), 1643 cm^{-1} ν(C=C), 1458 cm^{-1} $\delta(\mathrm{CH_2})$, 1026 cm^{-1} ν(Si–O), 906 cm^{-1} δ $(\mathrm{SiH_2})$. The film formed is white and opaque.

5-Chloro-1-pentyne polymerization and hydrosilylation. 5-Chloro-1-pentyne (3 μL, GFS Chemicals) was reacted with the $\mathrm{EtAlCl_2}$ treated surface 15 min. Transmission FTIR: 2951, 2932, and 2869 cm^{-1} $\nu(\mathrm{CH_2})$, 2106 cm^{-1} ν(Si–H), 1644 cm^{-1} ν(RC=CR), 1596 cm^{-1} ν(RC=CSi), 1457 cm^{-1} $\delta(\mathrm{CH_2})$, 1065 cm^{-1} ν(Si–O), 899 cm^{-1} ν(Si–O), The film is dark purple.

Norbornadiene (NBD) polymerization and hydrosilylation. NBD (3 μL, Aldrich) was reacted with the $\mathrm{EtAlCl_2}$ treated surface 16 h. Transmission FTIR: 3060 cm^{-1} olefinic ν(C–H), very broad and intense 2943 $\nu(\mathrm{CH_2})$, 2098 cm^{-1} ν(Si–H), 1542 cm^{-1} ν(C=C), 1463 cm^{-1} δ $(\mathrm{CH_2})$, 1304 cm^{-1} δ(C–H). The surface coating is glassy and pale brown.

Cyclooctatetraene polymerization and hydrosilylation. Cyclooctatetraene (50 μL, Lancaster) was reacted with the $\mathrm{EtAlCl_2}$ treated surface 16 h. Transmission FTIR: 3000 cm^{-1} olefinic ν(C–H), broad 2924 $\nu(\mathrm{CH_2})$, 2104 cm^{-1} ν(Si–H), 1636 cm^{-1} ν(C=C), other vibrations observed at 1493 cm^{-1}, 1449 cm^{-1}, 1106 cm^{-1} ν(Si–O), 903 cm^{-1} $\delta(\mathrm{SiH_2})$. The film formed is red and turns pale yellow upon rinsing with EtOH.

Attempted (COD) polymerization and hydrosilylation. COD (3 μL, Aldrich) was reacted with the $\mathrm{EtAlCl_2}$ treated surface 16 h. Use of 200 μL gives an identical IR spectrum and in either case, only weak incorporation is noted by comparison of incorporated COD vibrations with the intensity of the residual ν(Si–H). Transmission FTIR: 2940 and 2864 cm^{-1} $\nu(CH_2)$, 2104 cm^{-1} ν(Si–H), 1451 cm^{-1} $\delta(CH_2)$, 1106 cm^{-1} ν(Si–O), 903 cm^{-1} $\delta(SiH_2)$. No noticeable film was formed.

Late Transition Metal Mediated Reactions on Porous Silicon

Attempts to produce surfaces 1, 6, and 9 through late transition metal mediated reactions are described here. Stock solutions of the following late transition metal complexes were prepared: a 10 mM CH_2Cl_2 solution of $RhCl(PPh_3)_3$, a 5.0 mM toluene solution of $PdCl_2(PEt_3)_2$, and a 5.0 mM toluene solution of $Pd(OAc)_2$. All reactions were carried out under inert atmosphere. After completion of the reaction, the samples were rinsed with dichloromethane and EtOH and dried under an N_2 stream. Control experiments were carried out in a consistent fashion with omission of metal complex. Bis(trimethylsilyl)phenethene was prepared according to a literature procedure through a $Pd(OAc)_2$/1,1,3,3-tetramethylbutyl isocyanide catalyzed bis-silylation of phenylacetylene (22). Wilkinson's catalyst, $RhCl(PPh_3)_3$, was prepared according to published procedures (10).

$RhCl(PPh_3)_3$ mediated hydrosilylation of 1-dodecyne (surface 1). The $RhCl(PPh_3)_3$ stock solution (10 µL, 10^{-7} n) was added to 1.0 ml of toluene, followed by 1-dodecyne (10 µL, 4.7×10^{-5} n) and stirred at room temperature for 24 h. Transmission FTIR: 2951 cm^{-1} $\nu(CH_3)$, 2924 and 2855 cm^{-1} $\nu(CH_2)$, 2103 cm^{-1} ν(Si–H), 1607 cm^{-1} ν(C=C), 1462 cm^{-1} $\nu(CH_2)$, 1060 cm^{-1} ν(Si–O), 903 cm^{-1} $\delta(SiH_2)$.

$RhCl(PPh_3)_3$ mediated hydrosilylation of phenylacetylene (surface 6). The $RhCl(PPh_3)_3$ stock solution (10 µL, 1×10^{-7} n) was added to 1.0 ml of toluene, followed by 10 µl of phenylacetylene (9.1×10^{-5} n) and stirred at room temperature for 24 h. Transmission FTIR: 3060 cm^{-1} aromatic ν(C–H), 2103 cm^{-1} ν(Si–H), 1597 cm^{-1} overlapping ν(C = C) aromatic and ν(C=C) vinyl group, 1570, 1494, and 1442 cm^{-1} ν(C=C) aromatic, 1029 cm^{-1} ν(Si–O), 902 cm^{-1} $\delta(SiH_2)$.

$RhCl(PPh_3)_3$ mediated hydrosilylation of 1-dodecene (surface 9). The $RhCl(PPh_3)_3$ stock solution (10 µL, 10^{-7} n) was added to 1.0 ml of toluene, followed by 1-dodecene (10 µl, 4.5×10^{-5}n) and stirred at room temperature for 24 h. Transmission FTIR: 2951 cm^{-1} $\nu(CH_3)$, 2926 and 2856 cm^{-1} $\nu(CH_2)$, 2253 cm^{-1} ν(oxygen back-bonded Si–H), 2103 cm^{-1} ν(Si–H), 1468 cm^{-1} $\nu(CH_2)$, 1072 cm^{-1} ν(Si–O), 903 cm^{-1}. In contrast to the alkyne hydrosilylation reactions with Wilkinson's catalyst, vibrations observed at 1484 and 1438 cm^{-1} corresponding to triphenylphosphine ring modes suggest contamination by $RhCl(PPh_3)_3$ adduct(s) and/or decomposition products. Identical vibrations were observed in the control experiment involving $RhCl(PPh_3)_3$ addition to porous silicon, in absence of alkyne or alkene.

Attempted $PdCl_2(PEt_3)_2$ mediated bis-silylation of 1-dodecyne. The $PdCl_2(PEt_3)_2$ stock solution (10 µL, 5×10^{-8} n) was added to 1.0 ml of toluene, followed by 10 µl of 1-dodecyne (4.7×10^{-5} n) and refluxed for 2 h. Transmission FTIR: 2951 cm^{-1} $\nu(CH_3)$, 2925 and 2855 cm^{-1} $\nu(CH_2)$, 2108 cm^{-1} ν(Si–H), 1602 cm^{-1} ν(C=C), 1464 cm^{-1} $\nu(CH_2)$, 1050 cm^{-1} ν(Si–O), 906 cm^{-1} $\delta(SiH_2)$.

Attempted $PdCl_2(PEt_3)_2$ mediated bis-silylation of phenylacetylene. The $PdCl_2(PEt_3)_2$ stock solution (10 µL, 5×10^{-8} n) was added to 1.0 ml of toluene, followed by 10 µl of phenylacetylene (9.1×10^{-5} n) and refluxed for 2 h. Transmission FTIR: 3065 cm^{-1} aromatic ν(C–H), 2111 cm^{-1} ν(Si–H), 1597 cm^{-1} overlapping ν(C=C) aromatic and ν(C=C) vinyl group, 1570, 1494, and 1442 cm^{-1} ν(C=C) aromatic, 1061 cm^{-1} ν(Si–O), 907 cm^{-1} $\delta(SiH_2)$.

Attempted bis-silylation of phenylacetylene with $Pd(OAc)_2$/1,1,3,3-tetramethylbutyl isocyanide. The $Pd(OAc)_2$ stock solution (10 µl, 5×10^{-8} n) was reduced *in situ* with 1 µl neat hexamethyldisilane (4.9×10^{-6} n) in 1 mL toluene, in the presence of 0.14 ml 1, 1, 3, 3-tetramethylbutyl isocyanide (8.0×10^{-4} n) and 0.11 mL phenylacetylene (3.2×10^{-4} n). This mixture was refluxed 30 min and then transferred via cannula into a Schlenk flask containing the porous silicon wafer and refluxed 6 h. The $Pd(OAc)_2$ salt was reduced *in situ* with the hexamethyldisilane (a sacrificial reducing agent) before contact with porous silicon to prevent formation of surface bound acetates (Si–OAc, 20). While Si–OAc groups were never observed directly, the overall amount of spurious oxidation was reduced if the palladium salt was prereduced. Transmission FTIR: 3065 cm^{-1} aromatic ν(C–H), 2111 cm^{-1} ν(Si–H), 1599 cm^{-1} overlapping ν(C=C) aromatic and ν(C=C) vinyl group, 1492, and 1443 cm^{-1} ν(C=C) aromatic, 1073 cm^{-1} ν(Si–O).

RESULTS AND DISCUSSION

Lewis Acid Mediated Hydrosilylation on Porous Silicon Surfaces

Because the native surface of anodically etched porous silicon is silicon–hydride terminated, the possibility exists for hydrosilylation, that is, insertion of unsaturated carbon–carbon bonds (alkene or alkyne) into Si–H bonds, as demonstrated in Scheme 1. The surface hydrides, SiH_x, can be observed clearly in the transmission FTIR spectrum of freshly etched porous silicon (Fig. 3a) as a complex group of overlapping vibrations centered around 2100 cm^{-1} (11).

Lewis acid mediated hydrosilylation reactions seemed ideal for functionalization of porous silicon because of the mild reaction conditions involved and high selectivity and specificity of the corresponding solution phase reaction (12). $AlCl_3$ is known to be an effective catalyst in solution phase for alkenes as well which suggested that Lewis acid mediated surface chemistry would not be limited to alkynes (12b, c).

As we have shown previously, hydrosilylation of alkynes and alkenes on porous silicon mediated by the hydrocarbon-soluble Lewis acid $EtAlCl_2$ (Fig. 1) can be performed cleanly and efficiently at room temperature under inert atmosphere, some examples of which are shown in Fig. 2 (6d). Reactions involving alkynes are complete within 1 h and alkenes within 12 h. As demonstrated by Fig. 3b, little incorporation of dodecenyl groups is noted in absence of added Lewis acid. The Lewis acid is tolerant of a wide range of substituents, including Lewis bases such as hydroxy, nitrile, and ester groups, and can successfully induce hydrosilylation of trisubstituted olefins. α-Pinene [(1R)-(+)], a trisubstituted chiral olefin, yields a myristyl terminated surface which may be interesting for enantioselective

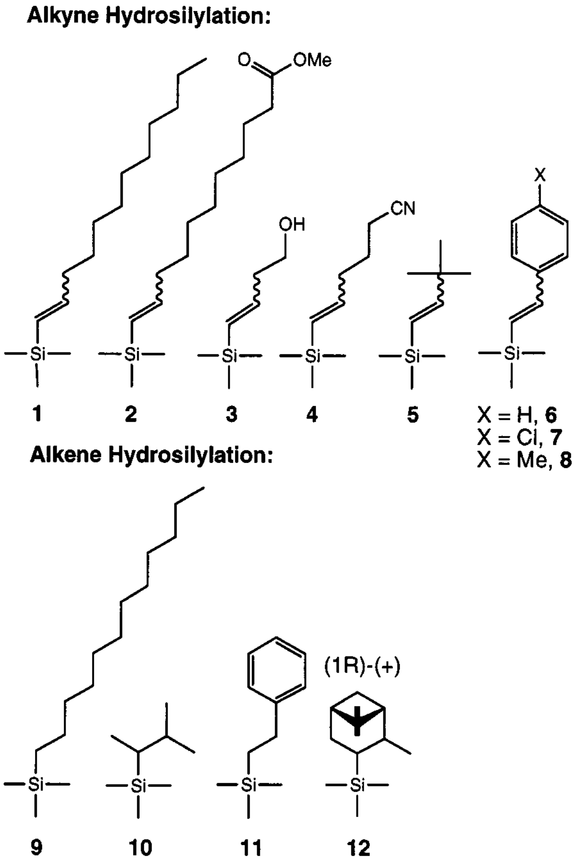


FIG. 2. Porous silicon surface terminations produced through hydrosilylation of alkynes and alkenes.

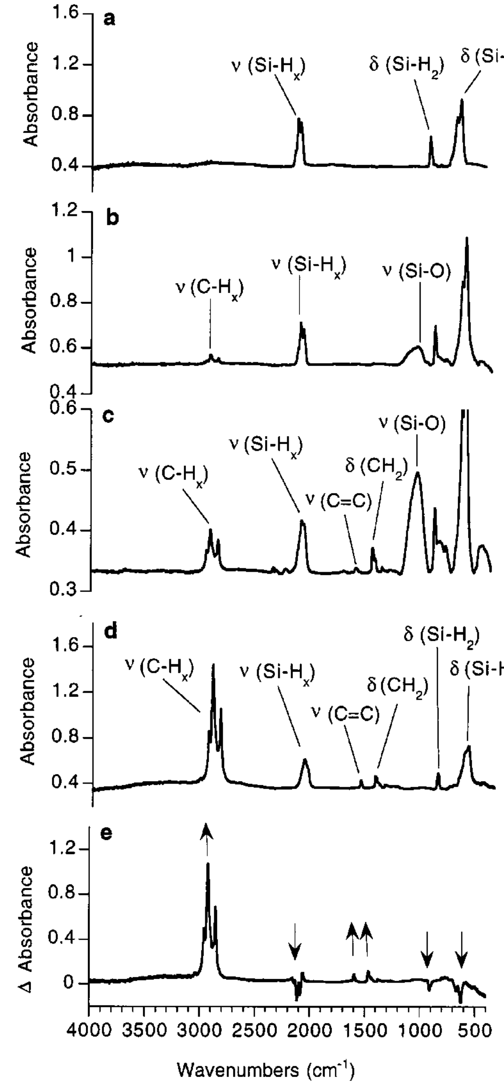


FIG. 3. Transmission FTIR spectra of porous silicon samples. (a) A typical native Si–H terminated surface. (b) Control reaction of 1-dodecyne with the Si–H terminated porous silicon surface in absence of added metal complex. Little incorporation of dodecenyl groups is noted. (c) Surface hydrosilylation of 1-dodecyne with $RhCl(PPh_3)_3$. (d) Surface hydrosilylation of 1-dodecyne with $EtAlCl_2$. (e) Difference spectra for spectra 3e and 3a which indicates consumption of Si–H groups and appearance of the dodecenyl associated vibrations. Because of the heterogeneous nature of the porous silicon samples utilizing the simple etching procedure described here, the absolute intensities as observed by FTIR are expected to vary from sample to sample. The chemistry, however, leads to an identical IR profile for a given sample, although the absolute intensities may vary; the relative intensities in a spectrum are the same, within the window of experimental error. In order to carry out the difference spectrum of (e), IR spectra of the same sample before (Fig. 3a) and after functionalization (Fig. 3d) are utilized and the measurements taken of the same spot on the sample surface. An etching–reaction cell which doubles as an IR cell holder is used to ensure an accurate measurement of Si–H consumption and incorporation of alkyl–alkenyl moieties to allow for direct comparison of spectra 3a, 3d, and 3e. As would be expected, samples for spectra 3b and 3c are different samples and thus are to be used for relative comparisons of incorporated functional groups and residual Si–H only.

recognition or separations. Dialkynes and dialkenes like 1,7-octadiyne and 1,7-octadiene and 5-chloro-1-pentyne were observed, however, to undergo both hydrosilylation and polymerization reactions on the surface as indicated by transmission FTIR, yielding a solid, durable overlayer in the presence of the Lewis acid, presumably through carbocation mediated polymerization (13). For 1,7-octadiyne, the carbon–carbon double bond $\nu(C{=}C)$ stretch corresponding to the polymer alkene is observed at $1641\ cm^{-1}$ while the $\nu(C{=}CSi)$ stretch, the hydrosilylation product, can be seen at $1595\ cm^{-1}$. Because porous silicon is fragile and mechanically unstable, formation of polymer coatings on the surface and within the pores could potentially be important for commercial technological applications. *In situ* polymerization–hydrosilylation can be carried out with a variety of other dienes and polyenes including 2,5-norbornadiene (NBD), cylooctatetraene, and 1,5-cyclooctadiene (COD). 2,5-Norbornadiene hydrosilylation–polymerization results in a clear, resin-like hard coating (14) while cylooctatetraene forms a red-brown film, suggestive of conjugation. In all cases, the films are resistant to THF, dichloromethane, hexane, or a 1 : 1 49% HF (aq)/EtOH solution. 1,5-Cyclooctadiene, however, polymerized poorly both on the surface and in solution (in absence of porous silicon) under these conditions.

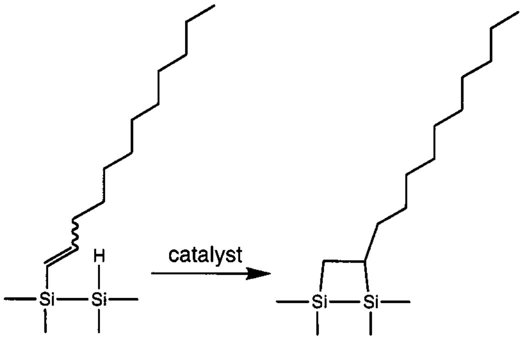
Hydrosilylation reactions of carbon–carbon unsaturated bonds are clearly occurring on the porous silicon surface as indicated by the dodecyne example shown in Figs. 3a, 3d, and 3e. When 1-dodecyne is hydrosilylated on porous silicon in the presence of $EtAlCl_2$, the resulting surface bound vinyl $\nu(C{=}C)$ group appears clearly at $1595\ cm^{-1}$ in the transmission FTIR spectrum. The $\nu(C{=}C)$ stretch of carbon–carbon double bonds monosubstituted with a silicon atom regularly appears between 1585 and $1605\ cm^{-1}$ (12a) whereas *cis* disubstitution with silicon leads to an even lower energy $\nu(C{=}C)$ stretch at $\sim 1540\ cm^{-1}$ (15). Simple hydrogen or carbon substituted C=C bonds typically appear at $\sim 1640\ cm^{-1}$ (16). Thus the ν (C = C) stretch on the porous silicon surface is entirely consistent with a vinyl functionality bound to the surface of porous silicon through one silicon–carbon bond. We have shown previously that the vinyl group can be quantitatively hydroborated, demonstrating clearly that this stretch is indeed that of an olefin. The difference spectrum for the dodecyne reaction (Fig. 3e) indicates consumption of Si–H groups which supports hydrosilylation of the alkyne with surface bound silicon–hydride functionalities. A vibration observed at $3040\ cm^{-1}$ may correspond with the vinyl $\nu(C{-}H)$ of the surface bound dodecenyl group. This vibration is absent in dodecyl terminated surfaces. The lack of a strong stretch centered around $1100\ cm^{-1}$ indicates that Si–OC bonds are not formed under these conditions (17).

Surfaces 1, 5, and 6–9, functionalized with bulky aryl and alkyl groups, demonstrate excellent chemical stability to boiling aqueous, aerated solutions of pH 1–10 for several hours as determined by FTIR spectroscopy (6d) and extensive aqueous HF rinsing. Under basic reflux conditions, native silicon–hydride porous silicon surfaces dissolve within seconds; at acidic and neutral pH under reflux, extensive degradation of unfunctionalized porous silicon is observed after 15 min. This remarkable and unique stabilization procedure for porous silicon indicates adequate coverage to prevent attack by both water and hydroxide ion and also eliminates the possibility of Si–O–C bond formation which would not be expected to demonstrate such stability (5b). The porous silicon surfaces 1 and 9, substituted with long alkyl chains, also protect the surface from ambient oxidation (laboratory atmosphere, absence of light); long term investigations are continuing. These surfaces retain some photoluminescence which is crucial for various technological applications of porous silicon (18).

Late Transition Metal Mediated Hydrosilylation/Bis-Silylation

Late transition metal complexes based upon platinum, palladium, and rhodium are known to be highly effective solution phase hydrosilylation catalysts (19). Because of the potential for activation of the weaker Si–Si bonds (20) on the surface (bond strengths: Si–Si = 53 kcal/mol, Si–H = 76 kcal/mol) (21), palladium-based complexes capable of mediating bis-silylation reactions were also examined to investigate the possibility of alkyne insertion between silicon–silicon bonds (22). Complexes with phosphine or isonitrile ligands which may stabilize low valent homogeneous mononuclear species were used exclusively in this study to avoid colloid formation which could result in steric interference with the porous surface (23). The reactions were carried out in rigorously air and water free environments since surface oxidation can be induced by the rhodium and palladium complexes, as has been observed for platinum metal salts on hydride terminated silicon single crystal surfaces (5d).

Wilkinson's catalyst, $RhCl(PPh_3)_3$, effectively catalyzes the solution phase hydrosilylation of alkenes and alkynes (24). Hydrosilylation 1-dodecyne and phenylacetylene proceeded smoothly in the presence of the Rh^I complex with respect to surface Si–H functionalities on porous silicon at room temperature in toluene under inert atmosphere after 24 h. The carbon–carbon double bond of the surface silicon-bound vinyl group appears at $1607\ cm^{-1}$ for the dodecenyl termination (surface 1, Fig. 3c). The relative intensity of the $\nu(C{=}C)$ bond is substantially lower with respect to the $\nu(CH_2)$ stretches centered around $2920\ cm^{-1}$ than that observed when the 1-dodecyne reaction is mediated by the Lewis acid, $EtAlCl_2$, as can be observed by comparing Fig. 3c and 3d. In the Lewis acid case, the reaction most likely gives the *cis* product, as occurs with soluble molecular silanes (12a) although the stereochemistry here has not been definitively determined on porous silicon. Because the IR absorption of a *trans* olefin is much weaker as compared to a *cis* olefin (16), the low intensity $\nu(C{=}C)$ stretch may be due to a greater proportion of *trans* olefins formed through the hydrosilylation reaction. Indeed, alkyne hydrosilylation with $RhCl(PPh_3)_3$ yields a mixture of *cis* and *trans* olefin products in molecular reactions (25). The weak $\nu(C{=}C)$ stretch may also be due to subsequent hydrosilylation of the surface bound vinyl group by a neighboring silicon hydride functionality.



The vinyl group $\nu(C{=}C)$ in the styrenyl terminated surface (surface 6) overlaps with the C=C skeletal in-plane vibration of the aromatic ring at $1600\ cm^{-1}$ which makes intensity comparisons difficult. In both cases, the golden yellow surfaces turned dark brown, as was observed in the control experiments with $RhCl(PPh_3)_3$ and total quenching of the photoluminescence was observed. The hydrosilylation reaction with 1-dodecene resulted in minor incorporation of dodecyl moieties on the surface (surface 9). Hydrosilylation did not occur for either alkynes or alkenes in absence of $RhCl(PPh_3)_3$ under these conditions.

Palladium catalysts have been shown to be effective for insertion of alkynes into molecular silicon–silicon bond containing compounds, forming a bis-silyl substituted olefin. Addition of a disilane to acetylene to give the bis-silylated olefin is exothermic by about 40 kcal/mole (26). $PdCl_2(PEt_3)_2$ has been shown to carry out bis-silylation of alkynes with tetramethyldisilane ($Me_2HSi{-}SiHMe_2$), inserting into the silicon–silicon bond and not the silicon–hydride bond (27). Because the surface of porous silicon is terminated with silicon hydrides and silicon–silicon bonds, it was hypothesized that bis-silylation would occur under similar conditions, resulting in a new class of reactions possible on silicon surfaces. Attempted bis-silylation of either 1-dodecyne or phenylacetylene with surface Si–Si groups, mediated by $PdCl_2(PEt_3)_2$, in refluxing toluene for 2 h resulted exclusively in hydrosilylation as indicated by appearance of a $\nu(C{=}C)$ in both cases at 1602 and $1597\ cm^{-1}$, respectively. If bis-silylation had occurred, the $\nu(C{=}C)$ would appear at $\sim 1540\ cm^{-1}$ (vide supra, 15). Because it has been demonstrated that $Pd(OAc)_2$/1,1,3,3-tetramethylbutyl isocyanide smoothly bis-silylates alkynes with molecular disilanes such as hexamethyldisilane in refluxing toluene, this catalyst was also examined for bis-silylation on porous silicon (28). FTIR indicated, again, that hydrosilylation had occurred under these conditions. In these and all reactions involving palladium complexes, the porous silicon surfaces became dark brown and the photoluminescence completely quenched. Because it has been observed previously that metal deposition through simple immersion plating readily occurs on porous silicon (29) with photoluminescence quenching (30), presumably a similar reaction may have occurred. Control experiments indicated that hydrosilylation took place in the absence of palladium, suggesting that the reaction involved thermal induction (31). The lack of bis-silylation may be due to steric hindrance of the Si–Si bonds on the surface, rendering these bonds inaccessible to the palladium complex and the reactant alkyne.

CONCLUSIONS

Both the Lewis acid $EtAlCl_2$ and $RhCl(PPh_3)_3$ mediate insertion of alkynes and alkenes into silicon–hydride groups on porous silicon surfaces. The $EtAlCl_2$ reactions are considerably cleaner and when functionalized with hydrophobic substituents, stabilize the surface effectively against chemical attack with boiling basic solutions, and under ambient laboratory conditions. Palladium induced bis-silylation of alkynes on porous silicon did not occur; thermal hydrosilylation was instead observed. Oxidation of the surfaces is a consistent problem with the late transition metal complexes as evidenced by the appearance of oxygen back bonded $\nu(Si{-}H)$ groups at $\sim 2250\ cm^{-1}$ and a broad $\nu(Si{-}O)$ centered around $1100\ cm^{-1}$. Quantitative photoluminescence quenching was also a problem uniformly observed in all these attempts using either Wilkinson's catalyst or palladium salts to mediate surface reactions, thus limiting the usefulness of this approach. Because the $EtAlCl_2$ approach results in a highly stable surface and does not quantitatively quench the photoluminescence, it is clearly the ideal reagent with which surface hydrosilylation reactions can be mediated.

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