# Hydrolytically stable bonded chromatographic phases prepared through hydrosilation of olefins on a hydride-modified silica intermediate

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# Hydrolytically Stable Bonded Chromatographic Phases Prepared through Hydrosilation of Olefins on a Hydride-Modified Silica Intermediate

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A novel method for the preparation of bonded stationary phases is described in which a hydrocarbonaceous moiety is bound to silica surfaces through a direct silicon–carbon linkage. An established method involving the chlorination and reduction of silica was used to prepare an intermediate material containing fairly stable silicon hydride species. In the present report, such an intermediate was reacted with terminal vinyl organic functionalities in the presence of a platinum catalyst. IR and NMR spectroscopic evidence confirmed the attachment of hydrocarbonaceous ligands onto the silica surface. Typical alkyl surface densities were 4.4 and 2.5 $\mu mol/m^2$ for octyl and octadecyl groups, respectively. The extent of coverage was found to be strongly dependent on olefin concentration and reaction temperature. When compared to the corresponding organosilanization product, the bonded silica was shown to have improved hydrolytic stability toward aqueous solutions containing trifluoroacetic acid.

## INTRODUCTION

Organosilanization, a surface-modification procedure derived from "silane-coupling" methodology (*1*), may now be considered a well-established synthetic technique for the preparation of high-performance liquid chromatography (HPLC) column packings. Typically, porous, particulate silicas are reacted with organosilanes to yield an Si–R functionality attached to the support through an Si–O–Si (siloxane) linkage:

$$|Si-OH + R_{4-n}SiX_n \rightarrow |Si-OSiX_{n-1}R_{4-n} + HX \quad (1)$$
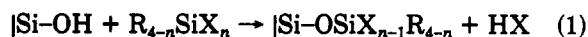
Where $n = 1-3$, R is an alkyl or substituted alkyl group, X is an easily hydrolyzable group such as halide, amine, alkoxy, or acyloxy, and the vertical line represents the support's surface. When di- or trifunctional silanes ($n = 2, 3$) are reacted with silica in the presence of a known amount of water, an organic layer is formed, the thickness of which may vary according to the reaction conditions. Traditionally, these so-called "polymeric" bonded phases have been considered disadvantageous with respect to their monomeric ($n = 1$) counterparts, presumably because of difficulties associated with control of the polymerization process which frequently results in irreproducible phase thickness and limited column efficiency (*2, 3*). Additionally, they show a tendency to contribute additional silanols to the bonded phase because, due to steric constrains, only a fraction of the silanol groups formed upon hydrolysis is eliminated via condensation. More recently, however, improved polymeric bonded phases have been prepared and shown to provide not only synthesis reproducibility comparable to that of monomeric bonded phases but also a better separation toward certain polyaromatic hydrocarbon mixtures (*4*).

When a monofunctional silane is used, only a single surface–silane linkage is possible and, consequently, an intrinsically reproducible monolayer is formed. A vast majority of

commercially available reversed phases are prepared using chlorodimethylalkylsilane reagents, according to the reaction

$$|Si-OH + Cl-Si(CH_3)_2-R \xrightarrow[\text{solvent}]{\text{base}}$$
$$|Si-O-Si(CH_3)_2-R + HCl \quad (2)$$
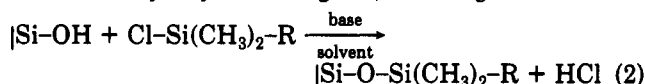
Monomeric bonded phases can also be prepared by reaction of silica under rigorously anhydrous conditions with polyfunctional silanes. They have the shortcoming, though, that residual X groups can be readily hydrolyzed when exposed to aqueous mobile phases, and therefore also contribute additional silanols to the phase.

Bonded silicas produced from monofunctional silanes have been the most thoroughly studied and have found wide use in a variety of analytical as well as preparative applications. The extensive usage of these bonded materials does not necessarily imply that they meet all requirements with respect to column stability and performance. On the contrary, monomeric bonded phases are subject to serious effects arising primarily from an unsatisfactory hydrolytic stability of the Si–O–Si–C linkage, particularly under moderately acidic or slightly alkaline elution conditions, and to a lesser extent from a relatively limited organic coverage. Poor hydrolytic stability and incomplete surface coverage both result in the exposure of a substantial number of surface silanols, groups which are thought to be primarily responsible for the residual adsorption phenomena that plague silica-based separation materials (*5*). One of the most striking cases of these "silanophilic" interactions occurs perhaps in the separation of certain compounds containing amino or other similar groups, particularly biomolecules. For instance, many proteins may interact very strongly with unreacted silanols leading to excessive band tailing or incomplete recovery of one or more solutes.

The problem of limited stability of the Si–O–Si–C linkage in current bonded phases has received a lot of attention in recent years (*6–10*). For instance, to achieve satisfactory reversed-phase separations of certain proteins, it is often desirable to incorporate in the mobile phase dilute aqueous solutions such as phosphate, at pH 2–3, or trifluoroacetic acid (*6, 7*). These mobile phases have been shown to be particularly aggressive toward the bonded ligand and, with virtually no exception, lead to the gradual loss of a significant fraction of the bonded material and a concomitant increase of silanol exposure. Poor long-term precision and potential fraction contamination are the two most evident deleterious effects arising from phase deterioration. Fraction contamination can be particularly disadvantageous in the case of preparative separations.

In an effort to overcome such problems, other organosilane reagents have been developed. Two related approaches have been proposed in which either the methyl groups of the organosilane reagent (eq 2) were replaced by bulkier groups or a "bidentate" silanizing reagent was used (*11–13*). In both cases the new groups serve to shield the unreacted silanols as well as the hydrolytically labile linkage that bonds the silane to the support. Although this steric protection has resulted in significantly improved bonded phases, the synthetic pro-

cedures still involve the formation of hydrolytically unstable Si-O-Si-C linkages.

In a different approach, bonded silicas bearing direct Si-C linkages have been developed (14-16). They involve the sequential reaction of the silica substrate with a chlorinating reagent (e.g., thionyl chloride) and a proper alkylating reagent (e.g., a Grignard or organolithium compound):

$$|Si-OH \xrightarrow{SOCl_2} |Si-Cl \xrightarrow{R-M} |Si-R \qquad (3)$$
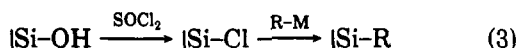
where -M = -Li or -MgBr. In principle, this method should provide not only a closer attachment and a denser coverage of organic functionalities but also a more hydrolytically stable bonded phase than that obtained by the corresponding Si-O-Si-C linkage. However, the wide usage of a chlorination/Grignard or chlorination/organolithium reaction scheme as a routine method to modify silica substrates has been hindered by several factors. One factor is that the two-step halogenation/alkylation sequence is significantly more difficult to carry out than the one-step organosilanization procedure. Difficulties associated with the removal of residual salts which may be occluded in the porous silica matrix during the alkylation process is also an important factor which has contributed to the limited usage of this synthetic approach. Finally, but no less important, the preparation of the alkylation reagent exhibits strong interferences with many reactive functionalities. As clearly pointed out by Morisson and Boyd (17), "the great reactivity which makes a Grignard reagent so useful in many synthetic approaches seriously limits its applicability". The organic group, R, in the Grignard reagent reacts with acidic groups to form the corresponding hydrocarbon species R-H. Additionally, it readily adds to carbon-oxygen or carbon-nitrogen multiple bonds. It seems clear therefore that only a very limited number of organic functionalities may be present in the halide compound from which a Grignard reagent can be prepared. Being even more reactive than the corresponding Grignard reagent, an organolithium reagent should exhibit the same limitations described above to a similar or greater extent. Such limitations, of course, greatly hinder the versatility of this approach. It is therefore desirable to address the shortcomings of existing bonded packings by applying an alternate silane chemistry which should combine the superior coverage and hydrolytic stability of direct Si-C linkages with the preparation simplicity of organosilanization.

Because of its minimal interferences with many reactive organic functionalities and the relative ease with which it is carried out, the catalytic hydrosilation (addition of silicon hydride, SiH) of terminal olefins represents a promising alternative to produce bonded chromatographic phases, provided that a suitable support containing surface silane species is available. In a previous work we prepared such an intermediate support by sequentially chlorinating and reducing silica with SOCl_2/toluene and LiAlH_4/ether, respectively. Treatment of the "reduced" silica with dilute HCl then follows to remove chemisorbed aluminum byproducts (18, 19).

Hydrosilation is normally carried out in the presence of a metal catalyst. A variety of inorganic and organic complexes of transition metals such as platinum, rhodium, palladium, ruthenium, iridium, and nickel (group VIII) appear to be very effective catalysts for the reaction. The catalyst often consists of a solution of a halide, olefin, carbonyl, or phosphine complex of the transition metal. A 2-propanol solution of hexachloroplatinic acid ("Speier's catalyst") is one of the most commonly used forms. Normally $10^{-7}$ to $10^{-4}$ mol of platinum/mol of silicon hydride is sufficient for an effective hydrosilation. An "induction period" is often required before the addition becomes manifest. Then, a highly exothermic reaction occurs, which, when relatively large amounts are

involved, may lead to hazardous situations if heat is not efficient and rapidly dissipated. For simple liquid olefins no additional solvent is normally required. For highly reactive olefins (particularly those with a strong tendency to polymerize, e.g., methacrylates, epoxides, etc.) a solvent such as toluene, benzene, saturated hydrocarbons, chloroform, etc. is normally used. In general, the reaction is conveniently carried out under dry conditions, at temperatures ranging from ambient to a full reflux. Typically, an excess of the olefin with respect to the available silicon hydride groups is used. The magnitude of such an excess depends on the nature of the substituents in the olefin. Highly reactive reagents (epoxy-containing olefins, for instance) require a 10-50% molar excess while simple (unsubstituted) olefins usually permit a 10-fold molar excess or more.

The most important goal of this work is to explore the feasibility of preparing bonded phases via hydrosilation of olefins on a hydrosilane-containing silica support:

$$|Si-H + CH_2=CH-R \xrightarrow{Pt \; cat.} |Si-CH_2CH_2-R \qquad (4)$$
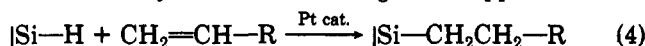
The heterogeneous reaction should result in the formation of an anti-Markovnikov adduct at the silica surface.

## EXPERIMENTAL SECTION

**Materials.** 1-Octene (Aldrich Chemical Co.) and 1-octadecene (Sigma Chemical Co.) were used as received. When required, toluene and other solvents (EM Industries Inc.) were dried with calcium hydride and distilled before use. Trifluoroacetic acid (TFA) was also used as received. A 100 mM hexachloroplatinic acid (37.5% as Pt, Aldrich Chemical Co.) solution in 2-propanol and a 50 mM dicyclopentadienylplatinum(II) chloride solution in chloroform were used as catalysts for hydrosilation. The diolefin-Pt(II) complex was prepared according to Apfel et al. (20). The method, based on procedures developed by Drew and Doyle (21), involved the reaction of hexachloroplatinic acid and dicyclopentadiene in aqueus acetic acid solution. Bonded phases were prepared from single batches of 40 μm particle diameter Partisil-40 (Whatman Inc., Clifton, NJ) and 5.6 μm Vydac 101TPB (Separations Group, Hesperia, CA). The specific surface area and mean pore diameter (Brunauer-Emmett-Teller (BET) nitrogen adsorption) were determined as 315.3 m²/g and 90.3 Å, respectively, for Partisil-40 and 88.8 m²/g and 334 Å for Vydac 101TPB.

**Instrumentation.** The spectrometric methods used have been previously described (18). The BET isotherms were obtained with a Micromeritics Model ASAP 2400 at Chevron Research and Technology (Richmond, CA). Carbon determinations were made at the Department of Chemistry, University of California (Berkeley, CA) by a conventional combustion method. Precision of the carbon determination was evaluated by repeated submission of the same sample over a period of about 6 months. A relative standard deviation of ±1.2% resulted for a total of 10 independent measurements.

**Silica Derivatization.** Hydride silica intermediates were prepared by a chlorination/reduction sequence on the native silica according to a procedure previously described (18, 19). Prior to hydrosilation, the hydride silica was dried at 110 °C for 6 h or more. In a typical preparation of an octyl-bonded silica, 75 mL of 1-octene (density 0.715 g/cm³, 97% purity) containing 255 μL of freshly prepared 100 mM hexachloroplatinic acid solution in 2-propanol was heated to about 60-70 °C while being agitated magnetically for about 1 h (a clear solution was obtained after about 15-20 min of mixing). A 5-g sample of hydride intermediate substrate was then slowly added to the olefin/catalyst solution, and the reaction was allowed to proceed for at least 24 h at 100 ± 2 °C. The mixture was then centrifuged and the solid washed with three 40-mL portions of toluene followed by similar washings with dichloromethane and diethyl ether. After the solvent was removed, the solid was dried under vacuum at 110 °C overnight. A similar procedure, this time with 1-octadecene (density 0.79 g/cm³, 99% purity) instead of 1-octene, was followed to prepare an octadecyl-bonded silica. Alternatively, an equivalent molar amount of 50 mM dicyclopentadienylplatinum(II) chloride in chloroform was used as catalyst. When required, conventional octyl- and octadecyl-dimethylsilyl silicas were prepared from

Partisil-40 according to the procedures described by Berendsen et al. (22, 23).

**Long-Term Hydrolytic Stability Test.** A 0.75-g amount of bonded phase material was suspended in 1 mL of dioxane by magnetically stirring for 5 min. Then, 40 mL of an aqueous 0.1% v/v TFA solution containing 20% v/v dioxane was carefully added. The mixture was magnetically agitated at room temperature for 12 h. After this period, a 2-mL aliquot of the well-agitated suspension was taken and the liquid of the remaining mother suspension was removed by centrifugation. A fresh treating solution was added and the hydrolysis continued for a new 12-h period. After each sampling, the volume of the treating solution was decreased so as to maintain a constant liquid-to-solid ratio during the entire process. The procedure was repeated over a total time of about 100 h. The silica from each 2-mL aliquot sample was washed consecutively with 3-mL portions of 1:1 v/v THF/water, THF, and finally diethyl ether. The solid was dried at 110 °C under vacuum for several hours and its remaining carbon content determined. The decrease in carbon content (percent by weight), or its corresponding molar surface coverage ($\mu$mol/m$^2$), is a direct measure of the loss of bonded material from the support. The test was performed on an octyl-bonded silica prepared using (hydrided) Vydac 101TPB as the support. For comparison purposes, a parallel test was also performed on a commercially prepared (via a conventional silanization procedure) non-end-capped octyldimethylsilyl–silica. The starting silica support was the same for both the commercial batch and the hydrosilation product.

**Surface Coverage.** The concentration, $\alpha_R$, of surface-bonded groups was obtained from the carbon content of the bonded material along with the BET specific surface area of the substrate before bonding (i.e., the hydride intermediate). Since the hydride–silica intermediate is a surface-modified substrate, a *monolayer* of organic groups should result from surface hydrosilation and, therefore, the equation proposed by Berendsen and de Galan (22) can be used:

$$\alpha_R \ (\mu mol/m^2) = 10^6 p_c/(10^2 M_c n_c - p_c M_R)S_{BET} \qquad (5)$$

where $p_c$ is the carbon percentage by weight of the bonded material (after correction from any carbon present before bonding), $n_c$ is the number of carbon atoms in the bonded organic group (in this case, the olefin), $S_{BET}$ is the specific surface area (m$^2$/g) of the hydride substrate, $M_R$ is the molecular weight of the olefin, and $M_c$ is the atomic weight of carbon. Notice that since the bonding reaction is an *addition*, the atomic weight of hydrogen ($M_H$) does not need to be subtracted from the molecular weight of the bonded molecule as in the case of conventional organosilanization in which one hydrogen atom is lost during the surface (substitution) reaction (22). Additionally, the $S_{BET}$ value does not refer to the original (native) silica but rather to the hydride intermediate.

## RESULTS AND DISCUSSION

**Spectroscopy.** The substantial structural changes taking place on the silica surface (namely, formation of Si–C linkages at the expense of Si–H species) permit unequivocal characterization of the addition product by spectroscopic as well as chemical methods. Figure 1 shows the DRIFT spectral changes that take place upon silica derivatization, from a native substrate (curve A), through the hydride intermediate (curve B), to an octyl (curve C) or octadecyl (curve D) bonded phase. The appearance of strong stretching bands in the 3000–2800-cm$^{-1}$ region concomitant with a substantial decline of the Si–H stretching band at 2260 cm$^{-1}$ clearly indicates chemical bonding to the silica surface.

Another way of proving that the olefins indeed undergo Si–H addition at the silica surface is by means of solid-state NMR spectroscopy. Figures 2 and 3 show the $^{13}$C cross polarization-magnetic angle spinning (CP-MAS) NMR spectra of the octyl- and octadecyl-bonded phases. On the basis of previous reports of studies involving conventional bonded silicas (24, 25), resonance positions can be readily assigned. The peak positions are virtually the same for both bonded silicas, as expected, with only changes in intensity due to the difference in chain length. The peak near 12 ppm can be
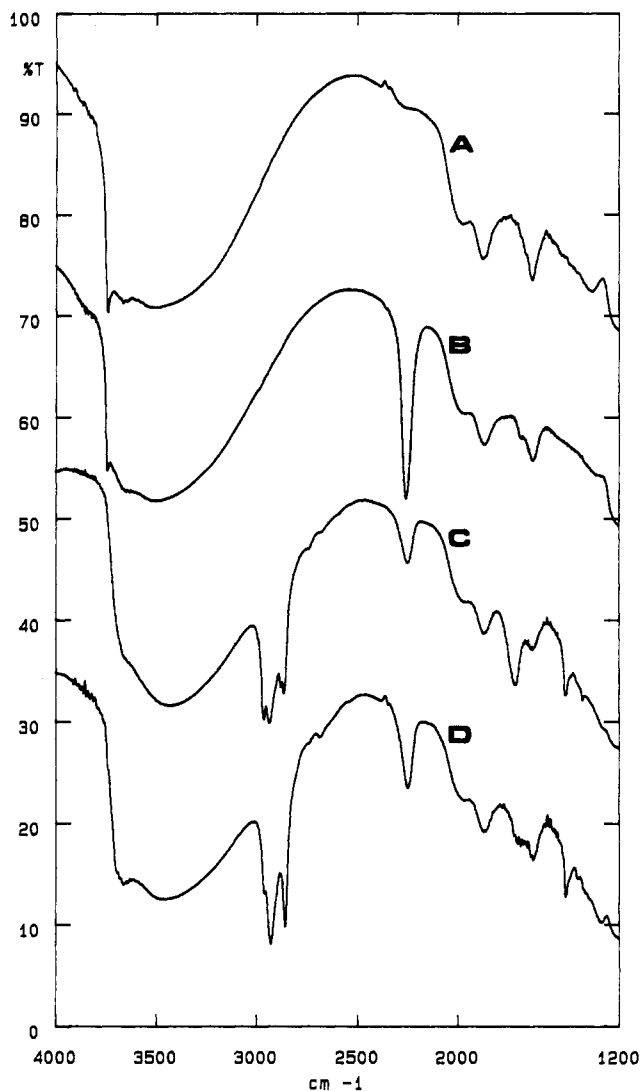


**Figure 1.** Partial DRIFT spectra of a silica (Partisil-40) after derivatization: (A) native silica; (B) hydride intermediate prepared via a chlorination/reduction sequence; (C) octyl-bonded phase; (D) octadecyl-bonded phase. For better illustration, the ordinates were contracted by a common factor and the curves were moved downward. Ordinate units are therefore arbitrary.
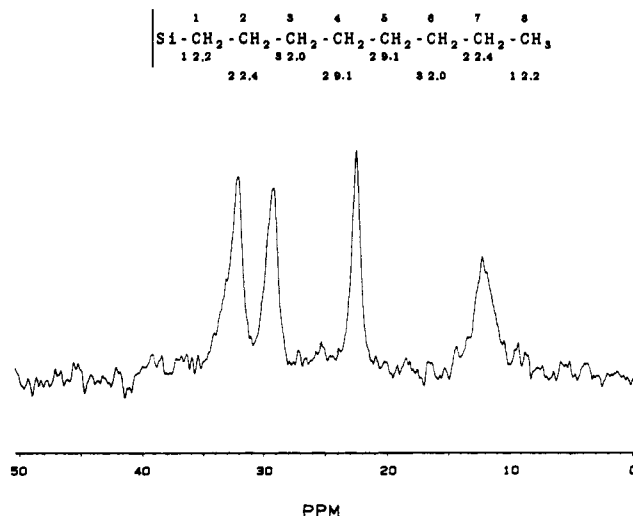
$$\begin{array}{cccccccc} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 \\ Si-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3 \end{array}$$

12.2   32.0   29.1   22.4
22.4   29.1   32.0   12.2



**Figure 2.** $^{13}$C CP-MAS NMR spectrum of an octyl-bonded phase.

assigned to the combined contributions from the terminal methyl group of the alkyl chain (C$_8$ and C$_{18}$ for octyl– and octadecyl–silica, respectively) and the methylene group which

Figure 3. $^{13}$C CP-MAS NMR spectrum of an octadecyl-bonded phase.

is directly attached to the surface silicon atom ($C_1$ for both silicas), i.e. the carbon involved in the direct bonding of the terminal olefin to the hydride in the hydrosilation reaction. The peak at 22.4 ppm can be assigned to $C_2 + C_7$ (octyl–silica), and $C_2 + C_{17}$ (octadecyl–silica) composites, while the resonance at 32.0 ppm can be assigned to $C_3 + C_6$ (octyl) and $C_3 + C_{16}$ (octadecyl) composites. The peak near 29 ppm is a composite which represents the remainder of the alkyl chain, i.e., carbon atoms $C_4 + C_5$ (octyl), and $C_4$ through $C_{15}$ (octadecyl). The last peak, of course, is the dominant absorption in the octadecyl–silica spectrum. It is not surprising that the $^{13}$C CP-MAS NMR spectra of our bonded materials closely resemble those of the corresponding polymeric bonded silicas (24), since both contain a single type of alkyl group attached to silicon.

With $^{29}$Si CP-MAS NMR spectrometry it is possible to obtain further insight into the structure of the hydride intermediate as well as the $C_8$ and $C_{18}$ product phases. Curve A of Figure 4 is the spectrum of the hydride intermediate showing five distinct peaks. Three of them have been observed in several previous studies (26, 27). These are the peaks at −110.4 ppm, which represents framework Si*(OSi≡)$_4$ structures, −100.9 ppm, which represents surface single silanols, HOSi*(OSi≡)$_3$, and −89.3 ppm, which represents surface geminal silanols, (HO)$_2$Si*(OSi≡)$_2$. The new peak at −85.3 ppm in the spectrum can be assigned to the hydride H—Si*(OSi≡)$_3$ species, in agreement with the resonance at −85.5 ppm observed by Engelhardt et al. on an oligomeric hydrosiloxane material, (HSiO$_{3/2}$)$_8$ (28). The other new resonance at about −74.8 ppm can be tentatively assigned to the H—Si*(OH)(OSi≡)$_2$ group. Curve B of Figure 4 shows the $^{29}$Si CP-MAS NMR spectrum for the $C_8$ product. The three peaks
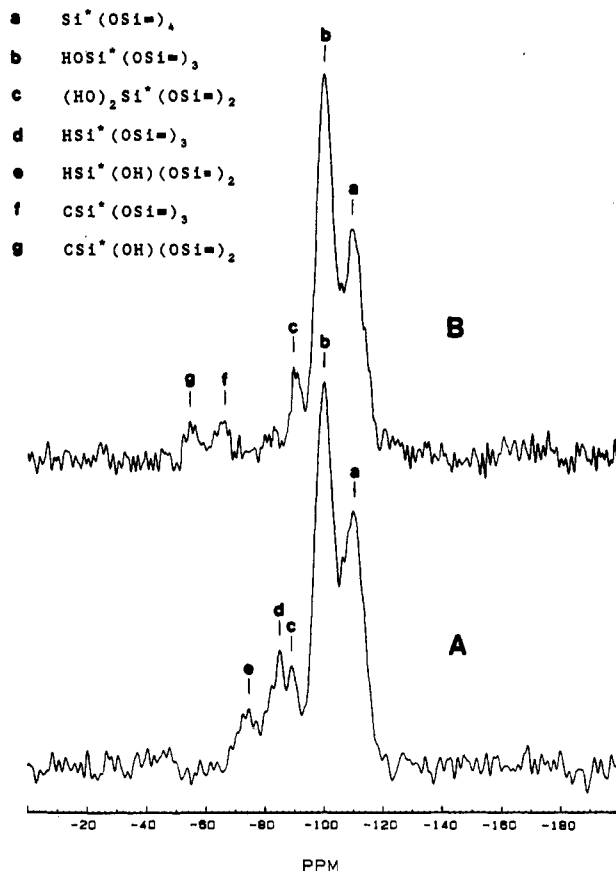


Figure 4. $^{29}$Si CP-MAS NMR spectra of (A) hydride intermediate and (B) octyl-bonded silica.

at −110.2, −100.2, −100.8, and −89.9 ppm are as described above. The peaks near −85 and −75 ppm have virtually disappeared due to the bonding reaction. Two new peaks at −66.2 and −54.6 ppm have now appeared in the spectrum. These have been previously assigned to CSi*(OSi≡)$_3$ and C(HO)-Si*(OSi≡)$_2$, respectively (27). The spectrum of the $C_{18}$ phase (not shown) exhibits the same characteristics as the spectrum of the $C_8$ product described above. In all cases for $^{29}$Si CP-MAS NMR spectra, the relative intensities of the peaks vary considerably depending on the contact time used (26).

**Surface Coverage.** A typical plot of alkyl surface coverage as a function of reaction time at 100 ± 2 °C is shown in Figure 5. Similarly with other surface modification processes, a major fraction of the total surface coverage occurs during the early stages of the reaction, while at longer times, increases in surface coverage are progressively less pronounced. Figure 5 also suggests a decrease in alkyl coverage with increasing carbon chain length (curve A vs B). This observation should, however, be interpreted with caution. Both olefins, 1-octene and 1-octadecene, were used as neat liquids. Their molar concentrations are about 6.18 and 3.10 M, respectively, being in a ratio of 1.99 at room temperature (assuming a similar thermal expansion coefficient for both olefins, this ratio should not be significantly different at the reaction temperature). The corresponding ratio of surface coverages, $\alpha_{octyl}/\alpha_{octadecyl}$, is approximately constant (as suggested by the close parallelism of the two curves) averaging 1.89 ± 0.14 (nine data points), a value which approaches that of the molarity ratio. This finding suggests independence of hydrosilation yield from carbon chain length, a behavior which appears to oppose that of conventional silanization (29, 30). Additional experimental evidence should be obtained to further substantiate this point. Equality of coverage and concentration ratios also suggests first-order kinetics with respect to the olefin. Indeed, a roughly linear relationship was found between surface coverage and

**Table I. Surface Coverages of Bonded Silica Phases[a]**

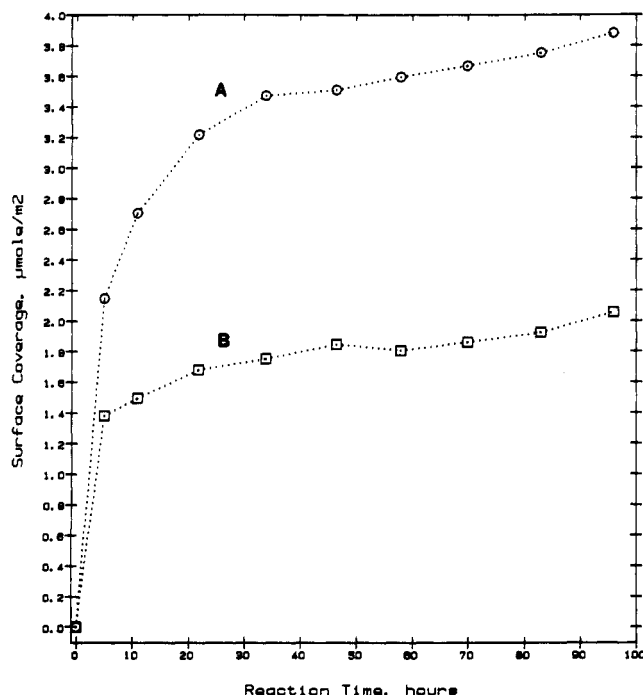| silica support | $S_{BET}$, m$^2$/g | anchored group | $n$ | $M_R$ | % C | $\alpha_R$, $\mu$mol/m$^2$ |
|---|---|---|---|---|---|---|
| Partisil-40 | 296.7 | $-C_8H_{17}$ | 8 | 112.22 | 11.00 | 4.43 |
| Partisil-40 | 315.3 | $-OSi(CH_3)_2C_8H_{17}$ | 10 | 170.37 | 12.85 | 4.15 |
| Partisil-40 | 296.7 | $-C_{18}H_{37}$ | 18 | 252.49 | 13.40 | 2.48 |
| Partisil-40 | 315.3 | $-OSi(CH_3)_2C_{18}H_{37}$ | 20 | 310.64 | 20.45 | 3.67 |
| Vydac 101TPB | 89.1 | $-C_8H_{17}$ | 8 | 112.22 | 2.10 | 2.51 |
| Vydac 101TPB | 88.8 | $-OSi(CH_3)_2C_8H_{17}$ | 10 | 170.37 | 1.78 | 1.71 |

[a] As defined for eq 5.



**Figure 5.** Effect of reaction time on alkyl surface coverage for the hydrosilation of (A) 1-octene and (B) 1-octadecene on a hydride-modified silica (Partisil-40).



**Figure 6.** Surface coverage as a function of reaction temperature of the hydrosilation of (A) 1-octene and (B) 1-octadecene on a hydride-modified silica (Partisil-40) with a 20-h reaction time.

olefin concentration (linear fitting results for 1-octadecene were intercept = 0.04 ± 0.08, slope = 0.45 ± 0.04, $R^2$ = 0.9791).

Surface coverage is also strongly dependent on the temperature of reaction, as illustrated by Figure 6. The data advocate the use of high reaction temperatures to obtain maximum surface coverage. The highest allowed temperature is, however, limited by the boiling point of the liquid olefin and the thermal stabilities of the olefin, the product, and particularly, the catalyst. It was observed that for a 24-h hydrosilation darkening of the product was appreciable at about 110 °C, being more pronounced on the $C_{18}$ phase at higher temperatures and with longer reaction times. It has been known that hydrosilation may be accompanied by some darkening of the reaction mixture, concomitant with a decline of catalyst activity (31–33). The observation has been attributed to irreversible reduction of the metal catalyst by the hydrosilane. The extent of catalyst reduction depends on the reaction temperature and the nature of the transition metal and complexing ligands, as well as the structure of the hydrosilane and the olefin. Presumably, the metal precipitates in the form of extremely fine particles which, in the case of the hydride-modified silica, may remain trapped inside the porous support. Although extensive darkening of the bonded silica product was observed, Figure 6 also suggests that, even at the higher temperatures used, the catalyst was still active. When electron spectrometry for chemical analysis (ESCA) was used to examine the bonded products, only one of the octadecyl–silicas (datum for 140 °C) exhibited traces of platinum (the detection limit of the instrument used was about 0.2 atom
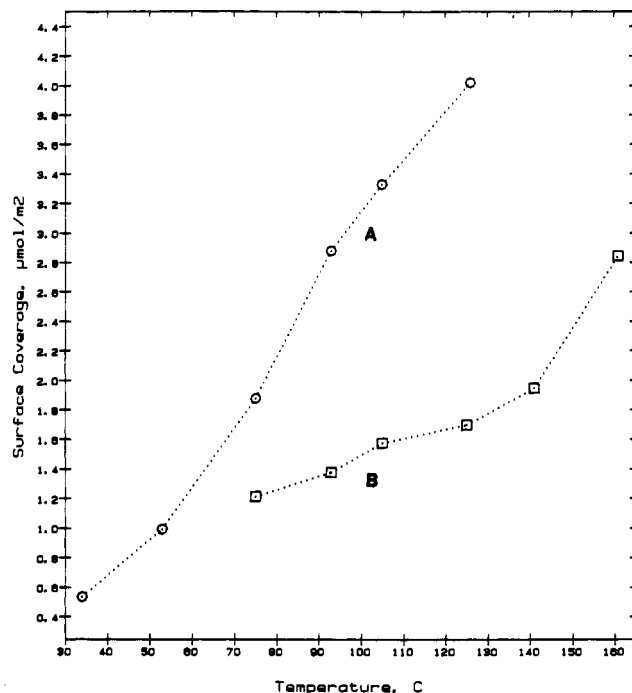
%). Whether the presence of minute amounts of platinum adversely affects the chromatographic performance of the bonded silicas has not been yet determined. The eventual lack of such a deletereous effect would not be without precedent: when investigating the in situ bonding of alkyldimethylchlorosilanes (prepared via olefin hydrosilation with dimethylchlorosilane) on silica, Shih-Hsien et al. (34) found that the presence of adsorbed platinum did not have any observable effect on the bonded phase's performance.

A reaction temperature of about 100 °C along with 60 h of reaction time were routinely used during this preliminary work. Table I shows typical alkyl surface coverages obtained from hydrosilation on two different silicas. For comparison purposes, coverages obtained from conventional silanization on the same batches of silica are also shown. It can be seen that, for a given silica substrate, somewhat improved surface group density was obtained from hydrosilation in the case of $C_8$ bonded materials. On the other hand, conventional organosilanization appears to perform better in the case of $C_{18}$ phases. Note, however, that the coverage values obtained through conventional organosilanization appear to be near the upper end of the range normally found in the literature (roughly, 3.0–4.0 and 2.5–3.5 $\mu$mol/m$^2$ for $C_8$ and $C_{18}$ packings, respectively) (23, 30). Additionally, it should be recalled that uncertainties for calculated $\alpha_{alkyl}$ values are normally around 5% and in some cases as high as 10%.

Surprisingly enough, Table I also suggests that, for hydrosilation as well as organosilanization, a narrower pore silica resulted in greater octyl coverages. In the case of hydrosilation,
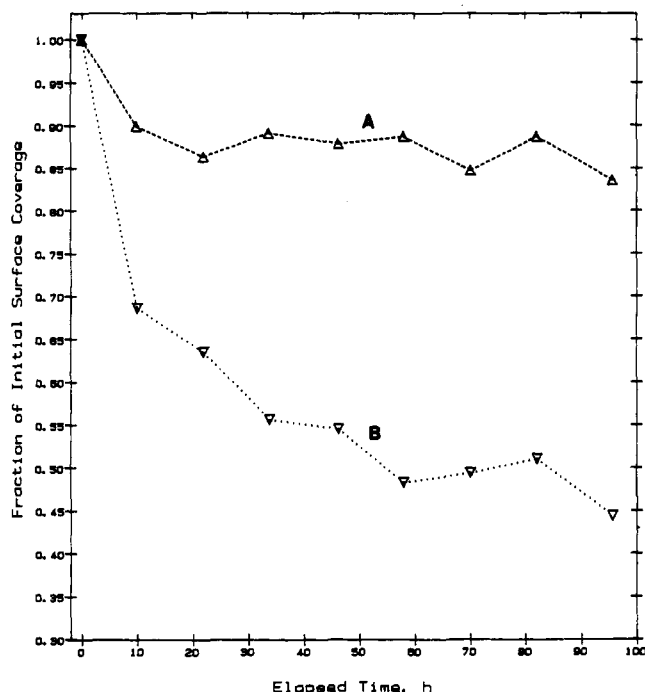
**Figure 7.** Relative surface coverage of octyl-bonded Vydac 101TPB silicas as a function of hydrolysis time. Prolonged treatment was at room temperature in 0.1% v/v TFA aqueous solution containing 20% v/v dioxane: (A) octyl-silica prepared by hydrosilation; (B) octyl-dimethylsilyl silica by silanization from a commercial procedure.

a cursory examination of the DRIFT spectrum of the $C_8$-bonded wide-pore support (not shown) reveals that no remaining Si–H stretching band was present; i.e., virtually all the silicon hydride groups were consumed by the reaction with the olefin. A $C_{18}$ product from the same substrate showed the same spectral characteristic. Therefore, the low availability of hydride sites rather than a lack of efficiency in hydrosilation appears to be the factor limiting alkyl coverage on wide-pore Vydac TPB silicas. If one assumes that, compared to their isolated counterparts, associated silanols exhibit a lower reactivity toward chlorination *and* organosilanization, then the unusually low yields on wide-pore Vydacs can be readily rationalized in terms of the predominantly associated silanol population on these silicas (35, 36).

The use of equivalent amounts of dicyclopentadienylplatinum(II) chloride instead of Speier's catalyst resulted essentially in the same level of surface coverage, provided that other reaction conditions remained the same.

**Hydrolytic Stability.** Assuming that good column-handling practices are observed by the chromatographer, hydrolytic stability of a reversed-phase packing is perhaps the most important factor determining the frequency with which columns are discharged after use. Due to the superior hydrolytic stability of the Si–C bond as compared to that of Si–O–Si–C linkages, we anticipated improved stability for the hydrosilation product over that of the organosilanization analogue. In order to estimate the extent of bonded-phase deterioration, selected bonded materials were subjected to prolonged exposure to a water/dioxane solution containing 0.1% v/v TFA. The amount of remaining bonded ligand was obtained from elemental carbon determinations on sample aliquots periodically taken from the reaction vessel. The plot in Figure 7 clearly shows that the rate of degradation of the silica modified via hydrosilation (present work) is significantly lower than that of the same substrate modified via organosilanization. At the end of the test, the commercial product had lost about 50% of its initial coverage while, under identical conditions, the hydrosilation product lost only about 15% of its starting alkyl load. It should also be noticed in Figure 7
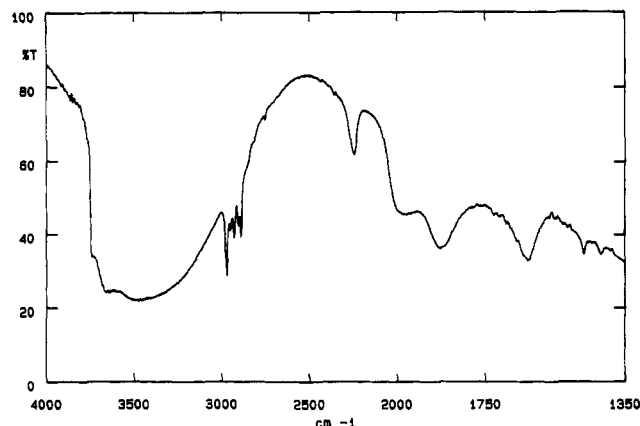


**Figure 8.** Partial DRIFT spectrum of a hydride-modified silica (Partisil-40) reacted with ethylene gas. C–H stretching bands are at 2971 $cm^{-1}$ ($CH_3$, antisymmetric), 2950 $cm^{-1}$ ($CH_2$, antisymmetric), 2929 and 2904 $cm^{-1}$ ($CH_3$, symmetric), and 2890 $cm^{-1}$ ($CH_2$ symmetric). C–H bending bands are at 1467 and 1418 $cm^{-1}$.
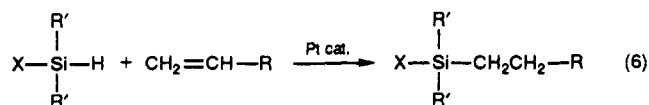
that a major fraction of the total losses occurs during the early stages of the long-term hydrolysis. This is in good agreement with the observations of Kirkland and co-workers (7, 13) when monitoring the loss of chromatographic retention for a number of bonded silicas.

**Hydrosilane "End-Capping".** Similarly with any surface modification procedure, the sites of the bonding reaction will eventually become sterically hindered at some point and, consequently, not all of the Si–H sites will be converted to Si–C. In some instances, it may be desirable to remove as many of the remaining hydrides as possible by means of a "hydride end-capping" procedure which follows the primary bonding reaction. Ethylene gas can be conveniently used for this purpose since it offers the smallest possible steric hindrance in olefin addition. Once the main bonding reaction is considered complete, the ethylene gas can be introduced into the reactor and maintained at high pressure. The reaction can then be continued for an additional period of time. The need for hydride end-capping might be particularly critical when aqueous alkaline solutions are used. Under these conditions and the assumption that efficient shielding is not provided by the bonded alkyl groups, hydride groups can be rapidly hydrolyzed, generating hydrogen gas, with deleterious effects occurring during the course of a separation. Under acidic conditions, on the other hand, silicon hydride groups are virtually indefinitely stable and, therefore, hydride end-capping may not be necessary.

In order to explore the feasibility of hydrosilane end-capping with ethylene, a $C_2$-bonded silica was prepared by merely bubbling the gas through a hydrided silica/toluene suspension containing dicyclopentadienylplatinum(II) chloride catalyst, at 60 °C for 18 h. Addition of the hydride silica was preceded by an induction period of about 1 h at the same temperature. The resultant product had an ethyl coverage of about 2.3 $\mu mol/m^2$, an acceptable value, given the mild reaction conditions (pressure and temperature) used. Its DRIFT spectrum (see Figure 8) depicts a number of C–H stretching and bending bands in good agreement with previously reported data for silicon–ethyl linkages (37).

**Versatility of Hydrosilation.** In general, the hydrosilation reaction has a great deal of versatility. This is due to the fact that relatively few reactive functionalities interfere with the olefinic addition. Thus, catalytic hydrosilation can be used to attach to silicon organic moieties containing a wide variety of functional groups such as alkyl, nitrile, amine, epoxy, etc. (38, 39). Although the ester group does not seem to interfere with the hydrosilation reaction, addition to the carbonyl group of aldehydes and ketones frequently takes

place. This seems to be particularly true for $\alpha,\beta$-unsaturated carbonyls. A similar behavior is exhibited by unsaturated nitriles as well as epoxides of 1,3-dienes. By using olefins whose C=C bond is separated from the heteroatom unsaturation by at least a methylene (-CH$_2$-) group, normal 1,2-addition can be readily achieved. It should be pointed out that, in fact, the great versatility of the existing organosilanization methodology (eq 1) is largely due to the freedom from interference of the hydrosilation reaction. Such a reaction is the most commonly used method to prepare a great variety of organosilanization reagents:

$$X\!-\!\overset{\underset{\displaystyle R'}{|}}{\underset{\underset{\displaystyle R'}{|}}{Si}}\!-\!H \;+\; CH_2\!=\!CH\!-\!R \;\xrightarrow{\text{Pt cat.}}\; X\!-\!\overset{\underset{\displaystyle R'}{|}}{\underset{\underset{\displaystyle R'}{|}}{Si}}\!-\!CH_2CH_2\!-\!R \qquad (6)$$

where R' = CH$_3$- or X and R and X are as defined for eq 1. In some cases, olefin hydrosilation provides the only pathway on which an organosilanization reagent can be made. A coupling reagent such as [(methacryloxy)propyl]trimethoxysilane (useful in gel capillary electrophoresis) or a surface modifier such as (glycidoxypropyl)trimethoxysilane (useful, among other things, in the preparation of affinity chromatography supports) cannot be prepared by means of a Grignard reagent, due to the reasons discussed above.

**Mechanism of Hydrosilation.** The mechanistic aspects of hydrosilation in the homogeneous phase have been described elsewhere (31–33, 38). If one assumes that the same mechanism scheme is applicable to the reaction in the heterogeneous phase, the surface hydrosilation of olefins catalyzed by platinum(II) complexes should proceed as shown in Figure 9. During the induction period a catalytically active (olefin)·Pt$^{II}$ complex (i) is formed. Oxidative addition of the silicon hydride to the metal generates an (olefin)·Pt$^{IV}$H(-Si≡) intermediate (ii). Hydride addition to the olefin then gives an (alkyl)·Pt$^{IV}$(-Si≡) complex (iii), presumably stabilized by coordination of more olefin. Finally, reductive elimination of alkylsilane occurs, regenerating the starting (olefin)·Pt$^{II}$ complex. It should be noted that the whole process takes place around the coordination sphere of the transition-metal catalyst. When Pt(0) complexes are used, the oxidation state of the metal in species i–iii should be lowered by 2 units (32, 33).

Most experimental facts related to olefin hydrosilation (predominance of the terminal adduct, olefin isomerization, stereochemistry at the silicon atom, reductive catalyst deactivation, etc.) have been explained in terms of the proposed mechanism. The well-known effect of oxygen as a cocatalyst has, however, yet to be elucidated. It appears that areation of the reaction mixture is often required for the reaction to start and/or to be sustained. It has been suggested that an oxygen-containing ligand constitutes the active catalytic species. (40).

The similar coverages obtained with the Speier's catalyst (hexachloroplatinic acid in 2-propanol) and cyclopentadienylplatinum(II) chloride can be easily interpreted if one considers that the active species in the Speier's catalyst corresponds to a (propene)·Pt$^{II}$ complex, as demonstrated by Benkeser and Kang (41). Like (cyclopentadienyl)·Pt$^{II}$, the propene complex readily exchanges ligands with the bonding olefin (eq 4) and produces the starting species (i) of Figure 9.

When olefin hydrosilation occurs on a hydrided silica surface, other factors in addition to those found in the homogeneous counterpart, play a fundamental role in determining the reaction's yield. The maximum surface density of alkyl groups is ultimately limited by the mean pore size of the silica substrate, the cross-sectional area of the anchored groups, and perhaps more importantly, the additional size exclusion requirement imposed by the reaction's intermedi-
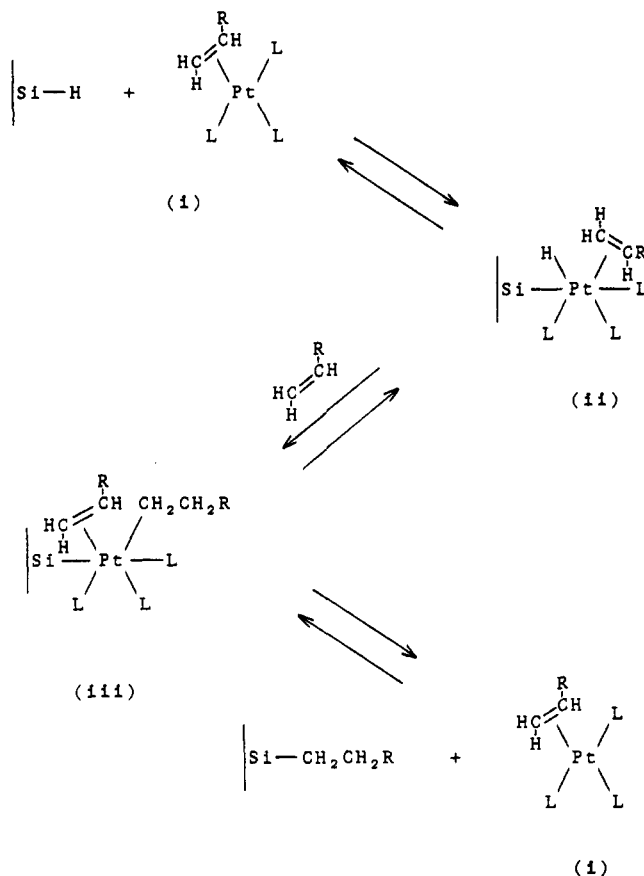


**Figure 9.** Reaction mechanism scheme for surface olefin hydrosilation catalyzed by platinum(II) complexes. L = halide, olefin, carbonyl, phosphine, etc.

ates. In other words, the accessibility of the surface active sites (SiH) is largely governed by the physical size of the "olefin carrier" (i) and subsequent species (ii and iii) derived from it. The subject of size exlusion has been discussed by Cheng and McCown (30) with regard to conventional organosilanization, while mechanistic aspects have been discussed by Kinkel and Unger (42). The size-exclusion requirement of organosilanization can thus be considered in the light of the pentacoordinated intermediate typical of bimolecular nucleophilic substitution reactions (S$_N$2):
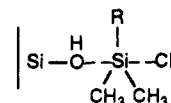


Presumably, the base used (see eq 2) is likely to assist in removal of hydronium and/or weakening of the Si–Cl bond (42) and, therefore, increases somewhat the size-exclusion value. Without going over molecular size calculations, it is apparent that the steric requirement for surface organosilanization is less stringent than that for surface hydrosilation. The lower-than-expected coverages obtained from hydrosilation in comparison to those for organosilanization can now be explained, at least partially, from the larger size-exclusion value associated with olefin hydrosilation. Interestingly enough, formation of Si–C linkages by alkylation of a chlorinated surface (eq 3) involves the formation of another S$_N$2 intermediate. Here, the alkylating group is the nucleophile while the pentacoordinate species occurs around the surface's silicon atom:
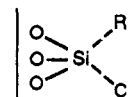
Given the immobility of the surface silicon, the penta-coordinate intermediate is likely to be formed through a flank-side attack of the nucleophile (43). In contrast, in organosilanization the surface silanol is the nucleophile and the pentacoordinate intermediate occurs around the reagent's silicon atom which is slightly removed from the surface. Again, the relatively high coverages obtained from alkylation of chlorinated silicas (14, 15) can be rationalized in the light of the less stringent size exclusion requirement associated with Grignard and organolithium reagents. These observations, however, have to be substantiated by appropriate experiments.

The chemical nature of the catalyst is, obviously, another important factor which requires further examination, as it relates to olefin hydrosilation on hydrided silica supports. Fortunately, there seems to be a plethora of group VIII transition-metal complexes from which to choose.

## CONCLUSIONS

Olefin hydrosilation provides a suitable method for the preparation of silica-based bonded stationary phases for chromatography. The method allows good alkyl coverages as well as improved hydrolytic stability toward aggressive mobile phases such as those containing aqueous TFA. The hydrolytic advantage of direct Si–C linkages can be achieved without the difficulties that occur when such a linkage is obtained by the known sequential reaction with a chlorinating reagent and an alkylating reagent such as Grignard or organolithium. Additionally, the intrinsic freedom from interference makes hydrosilation a particularly convenient approach to attach virtually any organic functionality to a hydride-modified support, resulting in a remarkably versatile separation material. In principle, virtually all currently available silica-based bonded phases are amenable to being prepared by olefin hydrosilation on the hydrided substrate. This might result in a new generation of bonded silicas with improved hydrolytic stability. Thus, surface hydrosilation of olefins not only combines the superior hydrolytic stability of direct Si–C linkages with a simplicity approaching that of currently available silanization procedures but also provides a versatile separation support suitable for virtually any application. For instance, these features may prove valuable for the chemical modification of the inner wall of fused-silica capillaries used in high-performance capillary electrophoresis.

Future developments are expected to improve the whole synthetic process by applying a simpler and more efficient method to prepare the hydride intermediate, thus avoiding the drudgeries associated with the chlorination/reduction sequence. In addition, for optimal bonding, evaluation of a number of group VIII transition-metal catalysts is required. Work is currently underway in our laboratory along these lines.

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