Synthesis and characterization of alkyl bonded phases from a silica hydride via hydrosilation with free radical initiation

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Abstract

A new approach for the hydrosilation of silica hydride surfaces by free radical addition is evaluated. The method is successful using either AIBN or *tert.*-butyl peroxide as the free radical initiator. A variety of organic moieties such as 1-octene, 1-triacontene, 2-methyl-3-butenitrile, 7-octene-1,2-diol, 3-butene-1-ol and propiolic acid are bonded by using at least one of the free radical species. If the organic group is small then some polymerization is observed. If a large ratio of free radical to organic compound is used then the degree of polymerization increases for the shorter chain alkyl bonded materials. A few chromatographic tests on two of the bonded phases, C_{30} and 7-octene-1,2-diol, give results comparable to those obtained on identical materials made by metal complex catalysis and by conventional organosilanization.   © 1997 Elsevier Science B.V.

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1. Introduction

The silanization/hydrosilation approach has been developed in the last five years [1] for the synthesis of chemically bonded stationary phases in chromatography [2–9], the modification of capillary walls for high-performance capillary electrophoresis [10] and the production of chemically modified etched surfaces in capillary electrochromatography [11,12]. The first step in this process can be described as follows:
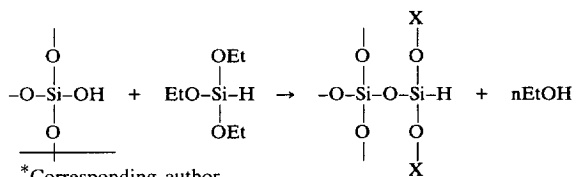
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Attachment of the organic moiety to the appropriate surface for the final product occurs when the hydride intermediate is reacted with a terminal olefin. The reaction is normally facilitated by the presence of a catalyst such as a transition metal complex (usually Speier's catalyst – 2-propanol solution of hexachloroplatinic acid) [13]:
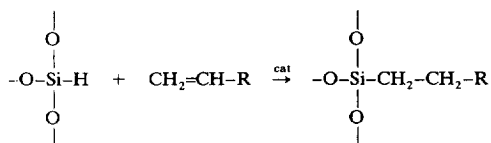
The reactions have proved to be successful for attaching a wide variety of organic ligands to silica surfaces. However, there are two problems which could affect the overall usefulness of this method.

First, the transition step in the attachment of the olefin to the hydride surface involves forming a complex with the catalyst. In the case of hexachloroplatinic acid or other transition metal complexes, the intermediate species can be of considerable size. This might result in a lower yield of organic species on the surface despite the inherently smaller size of the olefin in comparison to the comparable organosilane species which would be used in conventional bonding methods. The second is the possible reduction of the catalyst itself. A reaction between the hydride and the metal would result in the deposition of Pt(0) on the surface. Such an observation was made in the synthesis of diol bonded species when the concentration of the catalyst was too high [14]. In some cases, chromatographic performance can be affected by the presence of the metal on the surface. In one instance, steroids exhibited tailing peaks with certain eluent compositions in the normal-phase mode [14]. The presence of the reduced catalyst was detected both visually by a darkening of the support material as well as spectroscopically by ESCA (electron spectroscopy for chemical analysis).

One possible solution to both problems is the use of free radical initiation instead of a transition metal complex for catalysis [13]. As with metal complex catalysis, a number of different species could serve as a free radical initiator. The most common free radical initiators for hydrosilation have been peroxides [15–18] and azoisobutyronitrile AIBN) [19]. While hydrosilation via metal complex catalysis has been shown to be successful on silica hydride, no experiments have been done using free radical initiators. Since a different reaction mechanism is involved, there is no guaranty that free radical initiation will work on a surface as it does in homogeneous solution. In addition, results in solution studies show that silicon atoms substituted with halogens or phenyl groups are most successful in donating hydrogens to alkyl radicals [20]. For a silica hydride surface, the silicon atoms are surrounded by oxygens which would be intermediate between a halogen and an alkyl group with respect to donation of the hydrogen. Free radical initiation has been used previously in the preparation of bonded phases for high-performance liquid chromatography (HPLC) but the main focus of these efforts has been

the encapsulation of the silica support by a polymer. Among the polymer-coated materials which have been prepared are those based on polybutadiene [21], polymethacrylate [22], polyethylene [23], poly(vinyl alcohol) [24] and phenylmethylpolysiloxane [25]. In contrast the experimental design described in this report is to bond the organic moiety directly to the surface by means of a silicon–carbon linkage which should also produce enhanced stability. This study is a preliminary investigation into determining whether free radical initiation is possible on a silica hydride surface and if this approach offers any advantages over metal complex catalysis.

2. Experimental

2.1. Materials

The silica gel used was Vydac 101 TP lot No. 900201 from The Separations Group (Hesperia, CA, USA) with a surface area of 106 $m^2 g^{-1}$ (BET), a particle diameter of 6.6 μm, and a pore size of 300 Å. The solvents were HPLC-grade from Fisher Scientific (Pittsburgh, PA, USA) and J.T. Baker (Phillipsburg, NJ, USA). De-ionized water was prepared on a Milli-Q system (Millipore, Bedford, MA) and then passed through a 0.45 μm filter before use. The 1-triacontene ($C_{30}H_{60}$) for one of the bonded phases was obtained from Chevron Research Labs. (Richmond, CA, USA). The 2-methyl-3-butenenitrile was a gift from DuPont Nylon (Wilmington, DE, USA). All of the other terminal olefins and free radical initiators used in the preparation of bonded phases were obtained from Aldrich (Milwaukee, WI, USA).

The solutes in this study were purchased from Aldrich, Sigma (St. Louis, MO, USA), Eastman Organic Chemicals (Rochester, NY, USA) and Matheson Coleman and Bell (Norwood, OH, USA). Solutes were diluted in the mobile phase such that less than 10 μg were injected for each 5 μl sample in order to avoid overloading of the column. The determination of t_0 was made by injecting KNO_3 for reversed-phased experiments and n-pentane in the normal-phase mode.

2.2. Instrumentation

Cross-polarization (CP), magic-angle spinning (MAS) solid-state NMR spectra were obtained on a Bruker (Billerica, MA, USA) MSL 300 spectrometer. The sample (200–300 mg) was placed in a double bearing ZrO_2 rotor. The spinning speed was typically 5 kHz. The ^{13}C CP-MAS spectra were acquired with a 3 ms contact time and a 5 s repetition rate. Chemical shifts were referenced to tetramethylsilane using external glycine as the standard. The ^{29}Si CP-MAS spectra were obtained with a 5 ms contact time and a 5 s repetition rate. Chemical shifts were referenced to external poly(hydrido)siloxane.

Diffuse reflectance infrared Fourier transform (DRIFT) spectra were acquired on a Perkin-Elmer (Norwalk, CT, USA) Model 1800 spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. Spectra were normally obtained over a spectral range of 4000–450 cm^{-1} at a resolution of 2 cm^{-1}. Spectra consisted of 200 sample scans against pure KBr as a reference. All spectra were normalized to 100% transmittance.

Carbon analysis by the conventional combustion method was carried out at Desert Analytics (Phoenix, AZ, USA). Columns were packed by the slurry method using a CCl_4–methanol (9:1, v/v) mixture. The bonded material was packed into a 15 cm×0.46 cm I.D. stainless-steel tube (Alltech, Deefield, IL, USA) using a Haskel (Burbank, CA, USA) pneumatic pump operating at 40 MP with methanol as the driving solvent. HPLC measurements were made with a Perkin-Elmer Model 200 liquid chromatography system.

2.3. Synthetic procedure

The procedure for making the silica hydride intermediate has been described previously [2,5,6]. The procedure described here for bonded phase synthesis involves the reaction of 5.0 g of the silica hydride with typical terminal olefins.

The reaction is carried out in a 250 ml three-necked flask fitted with a thermometer in one neck and a condenser equipped with a drying tube in a second neck. The third neck is closed with a glass stopper. The following materials are placed in the flask at the start of the synthesis: approximately 100 ml of dry toluene, 10 ml of the olefin and between 0.50 and 0.60 g of AIBN or 300 to 400 μl of tert.-butyl peroxide. This mixture is heated to 60–70°C and stirred for 1 h. Then the silica hydride is slowly added to the flask through the open neck after removal of the glass stopper. The flask is then closed and the temperature of the solution with the solid silica is raised to 100°C with continuous stirring. This mixture is then maintained at 100°C with stirring for 100 h. After this period, the solvent is removed and the solid is washed 4 times with 30 ml of toluene, 2 times with 30 ml of methylene chloride and 2 times with 30 ml of diethyl ether. The product is first dried for several hours at room temperature and then at least overnight at 110°C under vacuum.

3. Results and discussion

There are a number of variables which need to be tested and optimized for free radical hydrosilation in a manner similar to the one developed for metal complex catalysis using a compound such as hexachloroplatinic acid [2]. Before this is possible, the viability of free radical catalysis in a heterogeneous phase hydrosilation must first be established. There are two basic synthetic approaches which might be utilized in the reaction process. First, the free radical initiator and the silica hydride could be placed in the reaction flask followed by addition of the olefin. The second approach would be to place the free radical initiator and olefin in the reaction flask followed by addition of the silica hydride. When the first procedure was tried little if any of the olefin was bonded to the silica hydride surface as determined from carbon analysis, DRIFT spectra and ^{13}C CP-MAS NMR spectra.

In contrast to the first method, addition of the silica hydride to a solution of olefin and free radical initiator resulted in bonding of the organic moiety to the support surface. This can be proven by a number of different determinations. First the DRIFT spectrum of the product from the reaction of 1-octene with silica hydride in the presence of tert.-butyl peroxide is shown in Fig. 1. Two features of the spectrum which indicate successful bonding are strong absorbances in the aliphatic C–H stretching
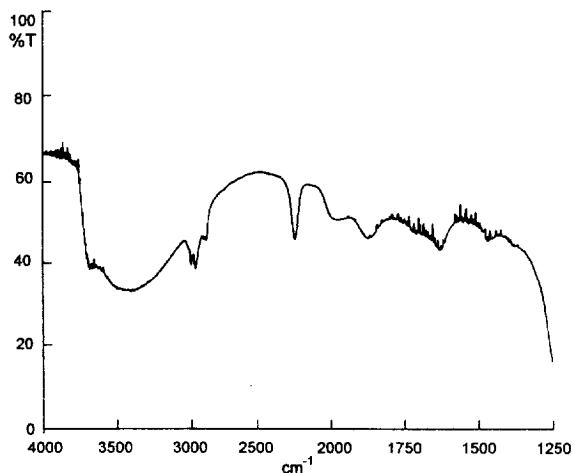
Fig. 1. DRIFT spectrum for the product of the reaction between silica hydride and 1-octene using free radical initiation by *tert.*-butyl peroxide.

region between 3000 and 2800 cm^{-1} and the Si–H stretching band at 2250 cm^{-1} is considerably diminished in comparison to the spectrum of the silica

hydride. When bonding of an olefin to a silica hydride surface occurs, the surface Si–H groups are replaced by the bonded organic moiety (Si–R) leading to a decrease in the intensity of the 2250 cm^{-1} band while C–H stretching bands appear in the region near 3000 cm^{-1} [1,2]. The ^{13}C CP-MAS NMR spectrum of the same material is shown in Fig. 2 and is very similar to the result obtained when hexachloroplatinic acid is used as the catalyst instead of the free radical initiator [2]. The carbon atoms for the bonded moiety are labeled in Fig. 2 as well as the two peaks from the residual ethoxy groups found on Vydac silica hydride [6]. Finally, carbon analysis allows quantitation of the amount of bonded phase on the surface after subtraction of the residual ethoxy groups ($\cong 0.7\%$ C). For the sample described above, the surface coverage is calculated to be 4.72 μmol m^{-2}. This is clearly a high value and its implications will be discussed later but the principle of bonding by free radical addition has been definitely established.

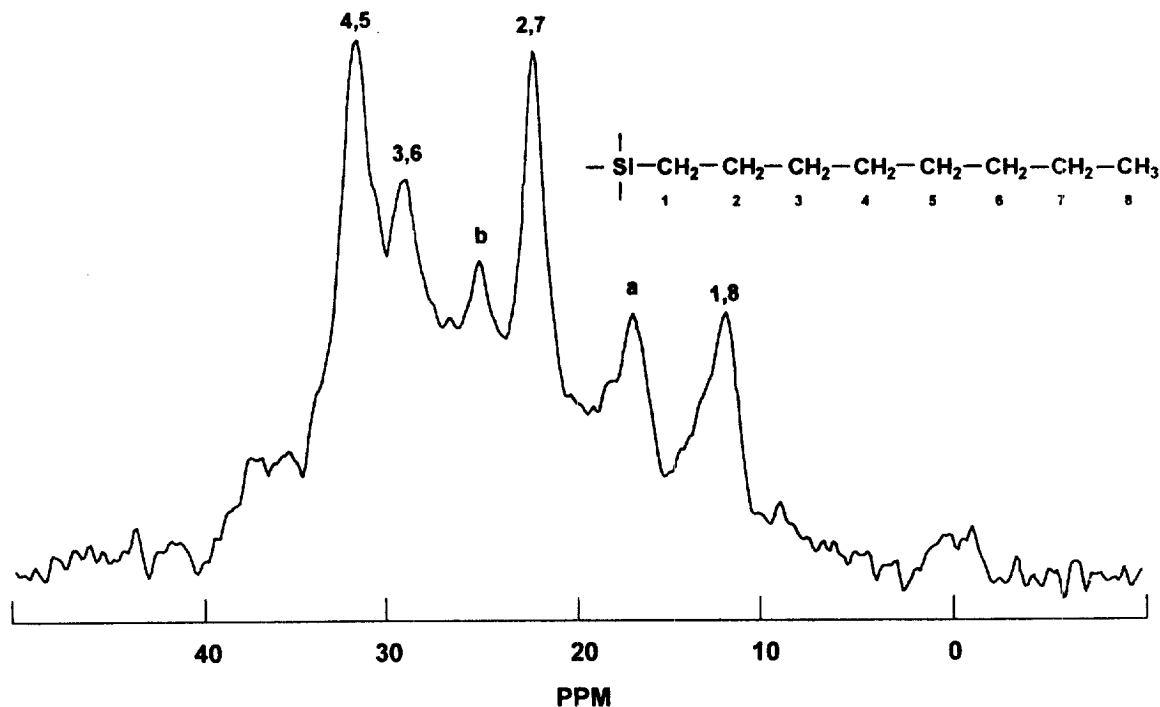It is important to determine if free radical addition

Fig. 2. ^{13}C CP-MAS NMR spectrum for the product of the reaction between silica hydride and 1-octene using free radical initiation by *tert.*-butyl peroxide.

is amenable to only a limited number of functional groups or if it has broad application to the bonding of as many or more types of organic moieties to the silica hydride surface as metal complex catalysis. The bonding of 1-octene represents a good first test since it is a medium-size moiety which would produce a typical reverse phase chromatographic material. In order to evaluate a larger hydrocarbon bonded group, the terminal olefin 1-triacontene ($C_{30}H_{60}$) was chosen. This is not necessarily an arbitrary choice since the C_{30} bonded phase has recently been shown to be a viable material for the separation of complex mixtures of polycyclic aromatic hydrocarbons (PAHs) and carotenoids [21]. Both DRIFT and ^{13}C CP-MAS spectra confirm the bonding the C_{30} moiety to the silica hydride surface. The essential features in the DRIFT spectrum are a decrease in the Si–H stretching frequency at 2250 cm^{-1} and the appearance of C–H aliphatic stretching bands in the range of 2800–3000 cm^{-1}. The ^{13}C CP-MAS (Fig. 3) spectrum shows the characteristic peak near 12 ppm representing the carbon attached
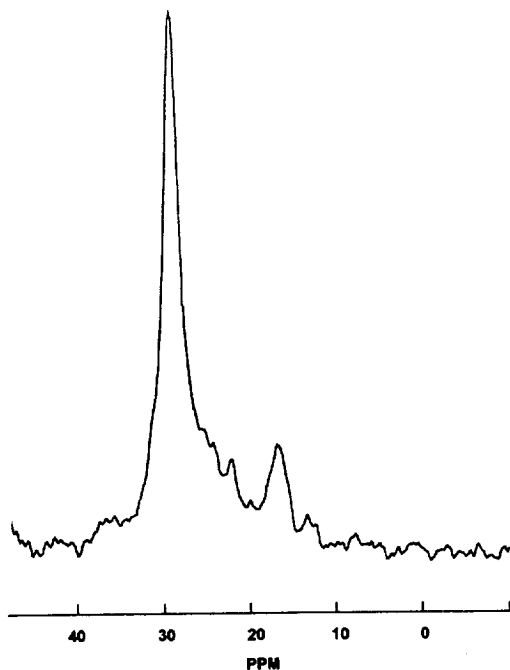

Fig. 3. ^{13}C CP-MAS NMR spectrum for the product of the reaction between silica hydride and 1-triacontene using free radical initiation by AIBN. (See Section 3 for peak identification).

directly to the silica surface, one large peak near 30 ppm that represents the bulk of the methylene groups on the alkyl chain and a few smaller peaks representing the methyl group and some methylenes near the two ends of the C_{30} moiety. Carbon analysis gives a surface coverage of 1.43 μmol m^{-2}. This is a reasonable bonding density for a long chain alkyl monomeric material and it is comparable to the best value (1.36 μmol m^{-2}) obtained by catalysis with hexachloroplatinic acid under similar reaction conditions.

While the spectral features in both the DRIFT and CP-MAS NMR spectra are consistent with bonding of the olefin to the surface hydride, both of the free radicals, AIBN and *tert.*-butyl peroxide, were tested under identical reaction conditions but in the absence of an olefin. In the DRIFT spectrum, there were no observable bands in the C–H stretching region and the Si–H peak at 2250 cm^{-1} did not decrease in intensity. A similar result was obtained for the ^{29}Si CP-MAS NMR. No new bands were detected in the spectrum and the Si–H peak at −85 ppm remained at approximately the same intensity. The ^{13}C CP-MAS spectrum displayed only the peaks for residual ethoxy groups as reported previously for Vydac silica hydride [6]. No new peaks attributable to the free radical initiator were evident for either AIBN or *tert.*-butyl peroxide. Only when the free radical initiator was used at a level at least ten times greater than for typical reaction conditions, was there a noticeable decrease in the Si–H peak in both the DRIFT and ^{29}Si CP-MAS NMR spectra.

A variety of terminal olefins have been bonded to silica hydride via metal complex catalysis [1], but one functional group, nitrile, as part of an alkene has never been successfully reacted via hydrosilation. The most likely cause for this failure is the strong affinity between the cyano moiety and platinum. The general observation when any nitrile containing terminal olefin is reacted with silica hydride is a noticeable darkening of the support material indicating reduction of the platinum in the complex to Pt(0). The presence of Pt on the surface is confirmed by ESCA and little or no carbon containing material is detected by elemental analysis, DRIFT and ^{13}C CP-MAS NMR. In contrast, when AIBN is used for the hydrosilation of 2-methyl-3-butenenitrile, the silica material is white after completion of the

reaction. Elemental analysis detects the presence of both carbon and nitrogen on the surface. The DRIFT spectrum shows strong C–H stretching in the 2800–3000 cm^{-1} region. Unfortunately, the cyano group cannot be positively identified since the C≡N stretching frequency overlaps with the Si–H stretching near 2250 cm^{-1}. In addition, it is not known what the relative intensities of these two absorbances are for the bonded organic nitrile and the silicon hydride. The experimental observation is that no new peak or shoulder on the existing SiH peak is detected in this region. However, confirmation of the bonding is obtained from the ^{13}C CP–MAS spectrum where a peak at 127 ppm is observed (in the expected chemical shift range for nitrile groups) and a peak around 12 ppm representing the carbon of the Si–C linkage at the surface.

Another functional group which has been bonded via Spier's catalyst is the diol moiety in the compound 7-octene-1,2-diol (7-OD) [6]. It was shown that while significant bonding was obtained, a small fraction of the starting olefin was attached to the silica surface via one of the hydroxy groups. Fig. 4 shows the ^{13}C CP-MAS NMR spectrum of 7-OD bonded to silica using AIBN as the free radical initiator. The spectrum shown in the figure is essentially the same as the one reported earlier for the

bonding of 7-OD by Spier's catalyst [6]. The two differences are a very low intensity of olefin peaks and somewhat broader peaks for the remainder of the spectrum. The barely detectable olefin peaks indicate that only a small fraction of 7-OD is bonded through the hydroxyl groups. A similar result, low intensity of olefin peaks, is obtained when 3-butene-1-ol is bonded by either AIBN or tert.-butyl peroxide. Therefore, it appears that free radical initiation may offer advantages over metal complex catalysis for bonding another type of organic moiety.

Finally a last example is the bonding of acetylene compounds. A relatively simple compound was chosen as the test molecule in this case, propiolic acid. Some difficulty bonding this compound was experienced when the reaction was attempted by metal complex catalysis. The process of bonding acetylene compounds to silica hydride surfaces will be the subject of a future report. Under similar reaction conditions to the those for other functional groups, the DRIFT and the ^{13}C CP-MAS NMR spectra are consistent with bonding.

The very broad peaks that appear below most of the sharper resonances assigned to carbon atoms of the bonded moiety as in the case of 1-octene (Fig. 2) and 7-OD (Fig. 4) are probably due to some polymerization of the olefin [13].
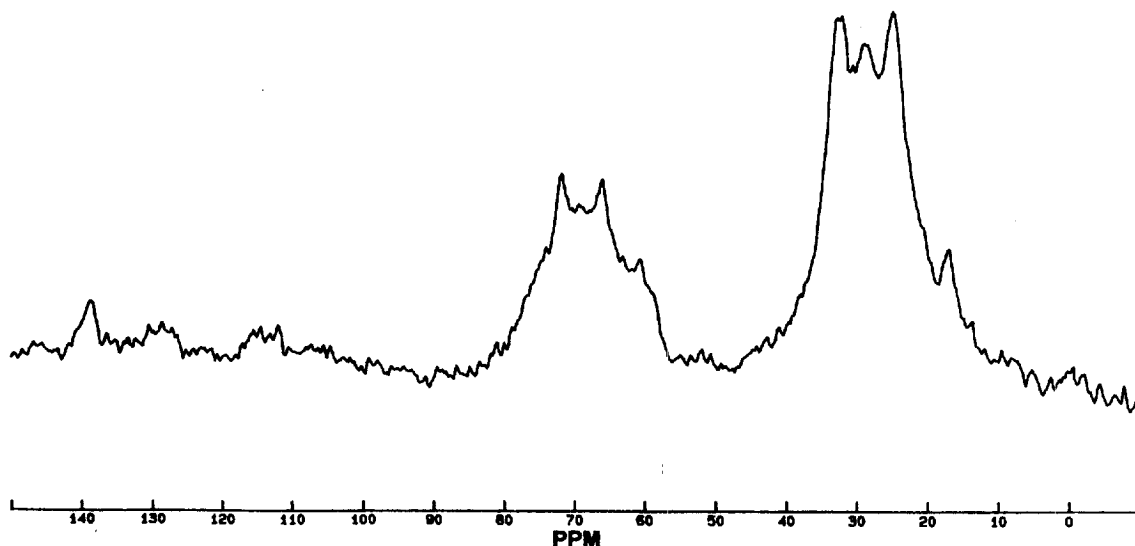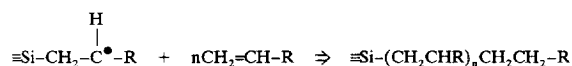

Fig. 4. ^{13}C CP-MAS NMR spectrum for the product of the reaction between silica hydride and 7-OD using free radical initiation by AIBN. (See Section 3 for peak identification).

$$\equiv Si-CH_2-\overset{\overset{\displaystyle H}{|}}{C^\bullet}-R \quad + \quad nCH_2=CH-R \quad \Rightarrow \quad \equiv Si-(CH_2CHR)_nCH_2CH_2-R$$

The relatively high bonding density reported above for the C_8 may be explained by the presence of some polymerized material. While it is difficult to predict the extent of such a reaction, the broad peaks in the spectrum indicate that this mechanism is possible. The broad peaks would be due to the multiple environments present as "n" varies as well as the more restricted motion of the polymeric species in comparison to the monomer. It also seems likely that the degree of polymerization is reduced as the size of the R group is increased. This can be seen by comparing Figs. 2 and 4 to Fig. 3. The chain lengths for the bonded groups in Figs. 2 and 4 are each octyl and the relative intensities and areas of the broad peaks are similar. However when the chain length is increased to C_{30} for the bonded material shown in Fig. 3, then the intensity of any broad peaks, particularly the one associated with the main peak at 30 ppm, is quite low and hence polymerization appears to be minimal. The degree of polymerization can be increased by increasing the relative amount of free radical initiator. Fig. 5 shows the ^{13}C CP-MAS NMR spectrum for the addition of 1-octene to silica hydride when the amount of free
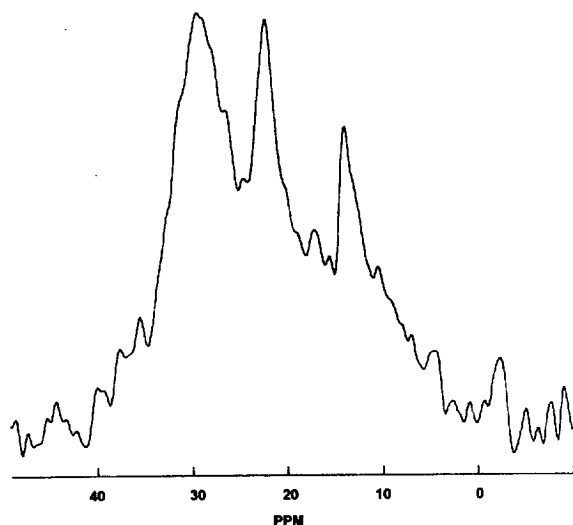

Fig. 5. ^{13}C CP-MAS NMR spectrum for the product of the reaction between silica hydride and 1-octene using excess free radical initiator (tert.-butyl peroxide). (See Fig. 2 for peak identification).

radical initiator is doubled. It can be seen that the intensity and area of the broad peaks has increased in relation to the sharper resonances which are presumably due to the monomeric bonded species. All of the factors reported above indicate that free radical initiation has resulted in the bonding of various organic groups to the silica hydride surface.

As a final test some chromatographic characterization of two materials bonded by free radical addition are compared to identical phases produced from metal complex hydrosilation. The first example involves separation of a standard reverse phase test mixture on the C_{30} bonded phase which is shown in Fig. 6A. The elution order is as expected in comparison to other alkyl bonded phases (C_8 and C_{18}). Both peak shape and efficiency are comparable to the values obtained on C_{18} columns carefully prepared by conventional organosilanization ($A_S \cong 1$ and $N/m \cong 35\ 000$ for the last eluting compound). A more stringent test of the chromatographic performance is demonstrated in the chromatogram shown in Fig. 6B. A mixture of tricyclic antidepressants is separated with both good efficiency and peak shape. These compounds are known to be extremely sensitive to the presence of residual silanols on the surface. Even conventionally synthesized phases that are end-capped can often result in broad tailing peaks which are indicative of a few very active Si–OH groups remaining on the surface. The hydride-based material has been shown to have relatively few silanols due to the efficiency of the silanization process in comparison to organosilanization [3]. This is an important potential advantage with respect to conventional phases since endcapping reagents are not 100% efficient due to their size which means some silanol sites are not accessible to these compounds. In addition, the hydrides seem to be relatively resistant to hydrolysis under normal operation. Columns which have been used for several thousand column volumes have been unpacked and subsequent spectroscopic analysis (DRIFT and ^{29}Si CP-MAS NMR) have shown spectral features essentially identical to the original material.

The second comparison involves the diol material made by bonding of 7-OD to the hydride intermediate. The data for the 7-OD columns synthesized by the two hydrosilation methods as well as for two other diol bonded phases is shown in Table 1 for a
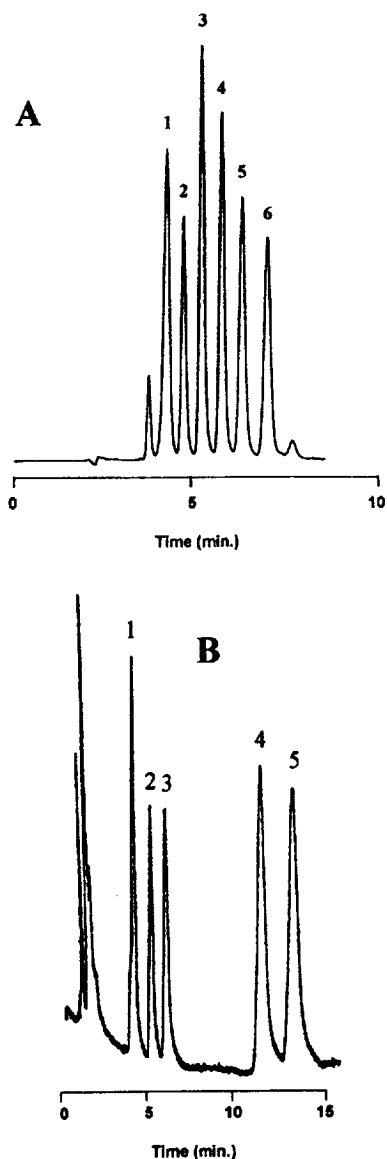
Fig. 6. Separations on the C_{30} column bonded by free radical initiation (AIBN). (A) Standard reverse phase test mixture. Mobile phase: methanol–water (65:35). Flow-rate = 0.5 ml/min. Solutes: 1 = benzene; 2 = toluene; 3 = ethylbenzene; 4 = isopropylbenzene; 5 = tert.-butylbenzene and 6 = anthracene. (B) Tricyclic antidepressants. Mobile phase: 12 mM phosphate buffer, pH 6.7–methanol–acetonitrile (10:45:45). Flow-rate = 1 ml/min. Solutes: 1 = doxepin; 2 = D,L propranol; 3 = clomipramine; 4 = nortriptyline; 5 = desipramine.

Table 1
Retention data of aromatic compounds on diol columns with n-heptane mobile phase

No.	Solutes	k'			
		1	2	3	4
1	Benzene	0.05	0.14	0.13	0.09
2	Chlorobenzene	0.04	0.15	0.12	
3	p-Dibromobenzene	0.06	0.15	0.12	
4	1-Methylnaphthalene	0.07	0.22	0.12	
5	2-Methylnaphthalene	0.07	0.22	0.12	
6	Naphthalene	0.09	0.23	0.11	0.24
7	Nitrobenzene	0.56	1.34	0.30	
8	Anthracene	0.19	0.40	0.15	
9	Benzo[k]fluoranthene	0.50	0.59	0.32	
10	Biphenyl	0.10	0.24	0.11	0.24
11	Fluoranthene	0.27	0.34	0.20	0.67
12	Fluorene	0.12	0.32	0.12	0.33
13	Phenanthrene	0.20	0.39	0.15	0.47
14	Chrysene	0.41	0.76	0.27	
15	Perylene	0.58	0.66	0.37	

Column 1 = Diol column by free radical addition – from the laboratory.
Column 2 = AGE column from the laboratory (AGE-diol via allyl glycidyl ether).
Column 3 = 7-OD column from the laboratory (7-OD-diol via 7-octene-1,2-diol).
Column 4 = Diol cartridge, Lichrosorb 100 from Merck – data from Ref. [29].

series of aromatic compounds measured under normal-phase operation. Where retention is significant the general order of elution is commercial diol > AGE laboratory diol > diol by free radical > diol by Pt. Retention on the commercial diol is greatest because it is synthesized from allyl glycidyl ether and contains residual silanols on the surface so it is the most polar. The laboratory AGE also comes from allyl glycidyl ether but the surface contains mainly hydrides rather than silanols so it is not as polar as the commercial diol. The 7-OD is a less polar moiety than AGE which results in lower retention than the either of the phases synthesized from allyl glycidyl ether. There is greater retention for the free radical 7-OD than the Pt 7-OD because of greater bonding density (6.0% C vs. 3.6% C). A similar conclusion can be drawn among the three hydride-based columns for a series of phenols run (Table 2) in the normal-phase mode.

At present there is no evidence that the polymerization which has been observed spectroscopically has any chromatographic effect. The surface

Table 2

Retention of phenols with heptane–chloroform (50:50, v/v) mobile phase

No.	Solutes	k'		
		1	2	3
1	4-Bromophenol	1.59	1.70	1.35
2	3-Chlorophenol	1.54	1.58	1.32
3	4-Chlorophenol	1.50	1.66	1.25
4	4-Fluorophenol	1.48	1.74	1.17
5	Naphthol-2	1.44	1.58	1.11
6	3-Nitrophenol	2.48	2.95	2.24
7	4-Nitrophenol	3.02	4.07	2.84
8	Phenol	1.18	1.29	0.91
9	4-Phenylphenol	1.19	1.41	0.96

Column 1 = Diol column from the laboratory (7-OD-diol via 7-octene-1,2-diol free radical addition).
Column 2 = AGE column from the laboratory (AGE-diol via allyl glycidyl ether).
Column 3 = 7-OD column from the laboratory (7-OD-diol via 7-octene-1,2-diol metal complex catalysis).

area and pore size of the silicas modified by free radical addition are identical to those made by metal complex catalysis, i.e., close to the values obtained for the starting silica material. Some examples of efficiencies for solutes on two types of columns prepared by both methods are shown in Table 3. It appears that the two methods produced chromatographically similar stationary phases. It should also

Table 3

Comparison of efficiencies (N/m) of columns made by metal complex and free radical methods

Solute	C_{30}^a	
	Pt catalysis	Free radical initiation
N,N-Diethylaniline	31 000	31 000
Benzene	23 000	26 000
Toluene	24 000	26 000
Ethylbenzene	25 000	26 000
Isopropylbenzene	26 000	28 000
t-Butylbenzene	28 000	31 000
Anthracene	38 000	33 000
	Diol[b]	
3-Chlorophenol	14 000	15 000
4-Bromophenol	17 000	16 000
4-Phenylphenol	18 000	16 000
3-Nitrophenol	16 000	15 000

[a] Mobile phase, methanol–water (65:35), flow-rate = 0.5 ml/min.
[b] Mobile phase, heptane–chloroform (50:50), flow-rate = 1 ml/min.

be noted that no effects of the residual ethoxy groups are observed. The long term stability of these columns is excellent under the chromatographic conditions reported in this study. Material removed from these types of columns have resulted in carbon analyses, DRIFT spectra and ^{13}C CP-MAS NMR spectra which are similar to the starting bonded phases.

In conclusion, the silanization/hydrosilation method for bonded phase synthesis offers a versatile route for producing materials with a highly stable Si–C linkage at the surface without the use of organometallic reagents. The latter are limited in the types of functional groups which can be utilized and the reaction conditions are much more stringent than the hydride intermediate approach described here. Several other studies have demonstrated the advantages of this synthetic method for the bonding of calixarenes [26] and chiral moieties [27] on porous silica and substituted polyacrylamides on fused-silica capillary walls [28]. The hydride surface has relatively few silanols so that endcapping may not be necessary for even some challenging separations involving basic compounds. It now appears that free radical initiation for hydrosilation of a silica hydride surface is a viable alternative to metal complex catalysis. A variety of functional groups can be bonded to the silica surface. In some cases (nitriles and hydroxy containing moieties) the free radical method appears to offer advantages over the traditional Spier's catalysis approach. The unknown factor is what effect polymerization may have on the nature of the bonded material. It certainly appears that some degree of polymerization is observed in all cases but is obviously less as the bonded moiety is larger. Preliminary chromatographic evaluations indicate that the free radical bonded materials behave similarly to those produced by the metal complex hydrosilation method. Additional studies are underway to determine if the extent of polymerization can be reduced further and to assess whether there are any measurable chromatographic effects for bonded phases which possess some polymerized material.

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