Functionalization on Silica Gel with Allylsilanes. A New Method of Covalent Attachment of Organic Functional Groups on Silica Gel

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Binding of an organic functional group to a silica surface via a covalent bond is the most reliable method of modification and functionalization of the silica surface. The covalent bond used for the binding is mostly the Si–O–Si bond, where one of the silicon atoms is on the silica surface and the other comes from organosilicon compounds, and the Si–O–Si bond is formed by the reaction of an Si–OH group on the silica gel surface with organosilicon compounds containing a leaving group of high reactivity on the silicon atom. The organosilicon compounds most commonly used are those containing an alkoxy leaving group (R₂Si(OR)₃) or a halide (R₂SiX₄). Halides, acyloxy, and amino groups on the silicon atom (X = halide, OCOR', and NR₂ in R,SiX₄-n) have been also used for the Si–O–Si bond formation. Unfortunately, these functional groups are so reactive toward hydrolysis that the silicon compounds cannot be handled under hydrolytic conditions or cannot be purified by silica gel chromatography. Here we wish to report a new method of functionalizing a silica surface, which is realized by use of (allyl)organosilanes (Scheme 1). They are stable under regular hydrolytic conditions but undergo deallylation forming an Si–O–Si bond on the silica under certain conditions.

We chose 2-propenyl(3-chloropropyl)dimethylsilane (1) as an organo-functionalized allylsilane, which is stable enough to be purified by silica gel column chromatography at room temperature (40 °C or lower), and we examined its reactivity toward silica gel at higher temperature. It was found that the Si–O–Si bond formation on the silica surface takes place efficiently with the allylsilane 1 at the temperature of refluxing toluene. The results obtained for the reaction of allylsilane 1 with FSM-16 and amorphous silica are summarized in Table 1, which also contains the data obtained with alkoxysilane, methoxy(3-chloropropyl)dimethylsilane (2), for comparison. As a typical experimental procedure (entry 2), 1.0 g of FSM-16 was treated with 0.895 g (5.0 mmol, 1.0 equiv of SiOH on the silica gel) of allylsilane 1 in 30 mL of refluxing toluene for 15 h. Filtration and Soxhlet extraction with methanol for 24 h and with benzene for 48 h followed by drying at 120 °C for 15 h under 0.2 mmHg gave 1.14 g of the functionalized FSM-16. Introduction of the 3-chloropropyltrimethylsilyl group onto the silica gel was confirmed by ²⁹Si and ¹³C NMR spectra (vide infra), and its amount was determined to be 1.3 mmol per 1.0 g of the starting FSM-16 by elemental analysis of the chlorine atom. The use of a greater amount of the allylsilane 1 under otherwise the same conditions gave the silica gel containing a greater amount of the 3-chloropropyltrimethylsilyl group, 1.7 mmol per 1.0 g of the FSM-16 being obtained with 15 mmol of 1 (entry 4). It should be noted that the present method using the allylsilane 1 is more efficient than that using methoxysilane 2, which has been often used for the functionalization. With a smaller amount of the organosilicon compounds and in a shorter reaction time, a greater amount of the silyl group is introduced on the silica gel.

The Si–O–Si bond formation between the 3-chloropropyltrimethylsilyl group and the FSM-16 surface was demonstrated by ²⁹Si and ¹³C CP-MAS NMR spectra. Figure 1 contains the NMR spectra for allylsilane 1 (a and d), FSM-16 treated with allylsilane 1 (b and e), and FSM-16 treated with methoxysilane 2 (c and f). The resonance of ²⁹Si at 1.7 ppm observed for allylsilane 1 (a) was replaced by the resonance at 15.0 ppm by treatment with FSM-16 (b). This chemical shift is a typical value for trialkylsilyloxy groups on the silica surface and is essentially the same as that in the FSM-16 (c), which is obtained by a standard procedure for the modification of a silica surface with a 3-chloropropyltrimethylsilyl group using methoxysilane 2. Three ¹³C singlets at 23.11, 113.16, and 134.56 ppm which are assigned to the allyl carbons on the allylsilane 1 (d) disappeared by treatment with FSM-16 (e). The other four singlets remained on the FSM-16, indicating that the

Table 1. Loadings of (3-Chloropropyl)silanes 1 and 2 on Silicas

<table>
<thead>
<tr>
<th>entry</th>
<th>organosilane</th>
<th>time</th>
<th>loading</th>
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<tbody>
<tr>
<td></td>
<td>(mmol) silica gel</td>
<td>(h)</td>
<td>(mmol g⁻¹)</td>
</tr>
<tr>
<td>1</td>
<td>1 (3) FSM-16</td>
<td>15</td>
<td>1.1</td>
</tr>
<tr>
<td>2</td>
<td>1 (5) FSM-16</td>
<td>15</td>
<td>1.3</td>
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<tr>
<td>3</td>
<td>1 (10) FSM-16</td>
<td>15</td>
<td>1.6</td>
</tr>
<tr>
<td>4</td>
<td>1 (15) FSM-16</td>
<td>15</td>
<td>1.7</td>
</tr>
<tr>
<td>5</td>
<td>1 (10) FSM-16</td>
<td>0.5</td>
<td>1.1</td>
</tr>
<tr>
<td>6</td>
<td>1 (10) FSM-16</td>
<td>48</td>
<td>1.6</td>
</tr>
<tr>
<td>7</td>
<td>2 (3) FSM-16</td>
<td>15</td>
<td>0.8</td>
</tr>
<tr>
<td>8</td>
<td>2 (5) FSM-16</td>
<td>15</td>
<td>0.8</td>
</tr>
<tr>
<td>9</td>
<td>2 (10) FSM-16</td>
<td>15</td>
<td>1.2</td>
</tr>
<tr>
<td>10</td>
<td>2 (15) FSM-16</td>
<td>15</td>
<td>1.3</td>
</tr>
<tr>
<td>11</td>
<td>2 (10) FSM-16</td>
<td>0.5</td>
<td>0.6</td>
</tr>
<tr>
<td>12</td>
<td>2 (10) FSM-16</td>
<td>48</td>
<td>1.6</td>
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<td>0.3</td>
</tr>
<tr>
<td>14</td>
<td>2 (10) amorphous silica</td>
<td>15</td>
<td>0.5</td>
</tr>
</tbody>
</table>

* All reactions were carried out for 1.0 g of silica gel support in 30 mL of refluxing toluene. Obtained by elemental analysis of Cl.

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while the allyl group was lost from the allylsilane, the 3-chloropropyldimethylsilyl group was attached to the silica surface. 

29Si and 13C NMR spectra of 2-propenyl(3-chloropropyl)dimethyldisilane 1 in CDCl3 (a and d), 29Si and 13C CP-MAS NMR spectra of the reaction products of 1 with FSM-16 (b and e), and those of 2 with FSM-16 (c and f).

3-chloropropyl(dimethyl)silyl group was attached to the silica surface while the allyl group was lost from the allylsilane. It is worth noting that the allylsilane 1 is a better modifying reagent than methoxysilane 2 with respect to the chemical purity of the silica surface. With methoxysilane 2, which releases the methanol at the Si–O–Si bond formation, a considerable amount of methoxy group on the silica gel is observed at 49.3 ppm (f). In the reaction with allylsilane 1, the leaving molecule from the silicon atom is propene, which is not reactive toward silica gel and is readily removed from the reaction mixture. It is likely that the reaction proceeds, as the protodesilylation of allylic silanes, by way of a β-silyl cation intermediate which is formed by the protonation of the allyl group with silanol on the silica surface and undergoes nucleophilic attack by the silanol oxygen leaving propene.

The present method makes it possible to modify the silica gel surface with heavy organo-functional groups, which cannot be purified by distillation due to their nonvolatility. For example, the BINAP skeleton was attached to the FSM-16 surface by use of allylsilane 4, which was obtained by the amide bond formation of BINAP-carboxylic acid 3 with 2-propenyl(3-aminopropyl)dimethylsilane. The BINAP-allylsilane 4 (3.96 g, 4.7 mmol), which was purified by silica gel chromatography (hexane/ethyl acetate = 2/1), was treated with FSM-16 (0.91 g) in refluxing toluene for 15 h to give the FSM-16 5 containing 0.3 mmol/g of the BINAP unit (Scheme 2).

To summarize, we found a new method for the modification of the silica gel surface by use of (allyl)organosilanes. In refluxing toluene, deallylation on the allylsilane takes place to form the Si–O–Si bond with the silicon on the silica gel. The present method will have broad applications in the surface-modifying technology on the silica gel as a reliable functionalization method. Immobilization of a catalyst on a silica surface is one of the examples.

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**Supporting Information Available:** Experimental procedures, spectroscopic and analytical data for the substrates and products (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

**References**


(5) Silica gel (Davisil), with a particle diameter range of 100–200 mesh and a surface area of 480 m2 g−1, was purchased from Aldrich.


(10) The generation of propene was confirmed by the detection of 1,2-dibromopropane, which is formed by treatment of the evolved gas with bromine.


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Supporting Data

General. All moisture sensitive manipulations were carried out under a nitrogen atmosphere. Nitrogen gas was dried by passage through P2O5. NMR spectra were recorded on a JEOL JNM LA500 spectrometer (500 MHz for 1H, 125 MHz for 13C, 100 MHz for 29Si, and 200 MHz for 31P). Solid-state CP-MAS NMR spectra (13C and 29Si) were recorded on a Bruker MSL-300WB spectrometer (75 MHz for 13C and 60 MHz for 29Si). Chemical shifts are reported in δ ppm referenced to an internal SiMe4 standard for 1H and 29Si NMR, and chloroform-d (δ 77.0) for 13C NMR and external 85% H3PO4 standard for 31P NMR.

Materials. Chlorodimethylsilane was purchased from Tokyo Chemical Industry. FSM-16 (a pore diameter, 2.8 nm; a surface area, 966 m² g⁻¹) was prepared according to the reported procedures1 and it was heated at 140 °C for 17 h under vacuum at 10⁻⁵ mmHg before use. Silica gel (Davisil), with a particle diameter range of 100-200 mesh and a surface area of 480 m²/g, was purchased from Aldrich. It was refluxed with conc. HCl for 6 h, filtered, washed with water, and dried at 140 °C for 17 h under vacuum at 10⁻⁵ mmHg. [IrCl(cod)]2 was prepared according to the reported procedures.2

Preparation of 2-Propenyl(3-chloropropyl)dimethylsilane (1). This compound was prepared according to the reported procedures.3,4 To a mixture of [IrCl(cod)]2 (7.6 mg, 0.010 mmol Ir), allyl chloride (9.8 mL, 120 mmol), and 1,5-cyclooctadiene (30 µL, 0.24 mmol) was added chlorodimethylsilane (13.0 mL, 120 mmol) at 35 °C, and the reaction mixture was stirred at 40 °C for 6 h. The mixture was distilled under reduced pressure to give 18.2 g (89% yield) of chloro(3-chloropropyl)dimethylsilane. 1H NMR (CDCl3) δ 0.44 (s, 6H), 0.95 (m, 2H), 1.89 (m, 2H), 3.55 (t, J = 6.7 Hz, 2H); 13C NMR (CDCl3) δ 1.37, 16.34, 26.54, 46.79; 29Si NMR (CDCl3) δ 31.20. To a solution of chloro(3-chloropropyl)dimethylsilane (8.82 g, 51.5 mmol) in Et2O (60 mL) was added allylmagnesium bromide (1 M, 62.0 mL, 62.0 mmol) at 0 °C, and the reaction mixture was stirred at room temperature for 3 h. The mixture was quenched with 5% hydrochloric acid and extracted with Et2O. The
organic layer was washed with saturated sodium bicarbonate solution and brine. After drying over MgSO₄, organic solvent was removed in vacuo and the residue was chromatographed on silica gel (hexane/ethyl acetate = 10/1) to give 8.50 g (93% yield) of 2-propenyl(3-chloropropyl)dimethylsilane (1). ¹H NMR (CDCl₃) δ 0.01 (s, 6H), 0.63 (m, 2H), 1.53 (dd, J = 8.2, 1.2, 1.0 Hz, 2H), 1.77 (m, 2H), 3.50 (t, J = 7.0 Hz, 2H), 4.84 (ddt, J = 10.2, 2.2, 1.0 Hz, 1H), 4.85 (ddt, J = 16.9, 2.1, 1.5 Hz, 1H), 5.77 (ddt, J = 16.9, 10.2, 8.2 Hz, 1H); ¹³C NMR (CDCl₃) δ −3.86, 12.59, 23.11, 27.71, 47.62, 113.16, 134.56; ²⁹Si NMR (CDCl₃) δ 1.70.

Preparation of Methoxy(3-chloropropyl)dimethylsilane (2). This compound was prepared according to the reported procedures. To a solution of chloro(3-chloropropyl)dimethylsilane (5.00 mL, 30.5 mmol) in methanol (3.0 mL, 76.3 mmol) and Et₂O (150 mL) was added triethylamine (6.00 mL, 42.7 mmol) at 0 °C, and the reaction mixture was refluxed for 5 h. After filtration of insoluble salt, the solvent was removed in vacuo. The residue was distilled by bulb-to-bulb distillation under reduced pressure to give 4.90 g (96% yield) of methoxy(3-chloropropyl)dimethylsilane (2). ¹H NMR (CDCl₃) δ 0.12 (s, 6H), 0.72 (m, 2H), 1.82 (m, 2H), 3.44 (s, 3H), 3.52 (t, J = 6.9 Hz, 2H); ¹³C NMR (CDCl₃) δ −3.31, 13.17, 26.57, 46.92, 49.50; ²⁹Si NMR (CDCl₃) δ 18.28.

Preparation of (R)-4-[2,2'-(Diphenylphosphino)-1,1'-binaphth-6-yl]butanoic acid (3). Prepared from (R)-binaphthol according to the reported procedures: ¹H NMR (CDCl₃) δ 1.94 (quint, J = 7.4 Hz, 2H), 2.32 (t, J = 7.5 Hz, 2H), 2.70 (t, J = 7.5 Hz, 2H), 6.68 (d, J = 8.7 Hz, 1H), 6.71 (d, J = 9.0 Hz, 1H), 6.85 (d, J = 8.6 Hz, 1H), 6.91 (dt, J = 7.6, 1.0 Hz, 1H), 7.03-7.18 (m, 20H), 7.33 (t, J = 7.5 Hz, 1H), 7.42 (dd, J = 8.5, 1.5 Hz, 1H), 7.42 (dd, J = 8.5, 1.8 Hz, 1H), 7.58 (s, 1H), 7.81 (d, J = 8.7 Hz, 1H), 7.81 (d, J = 7.9 Hz, 1H), 7.87 (d, J = 8.6 Hz, 1H); ³¹P NMR (CDCl₃) δ −14.93 (d, Jₚ₋ₚ = 12 Hz), −14.80 (d, Jₚ₋ₚ = 12 Hz).

Preparation of 2-Propenyl(3-aminopropyl)dimethylsilane. Prepared from 2-propenyl(3-chloropropyl)dimethylsilane (1) according to the procedure for amination of 3-chloropropyl group. ²⁹Si NMR (CDCl₃) δ −1.71.
Preparation of N-[3-((2-Propenyl)dimethylsilyl)propyl]- (R)-4-[2,2′-(diphenylphosphino)-1,1′-binaphth-6-yl]butanamide (4). To a mixture of (R)-4-[2,2′-(diphenylphosphino)-1,1′-binaphth-6-yl]butanoic acid (3) (3.7 g, 5.2 mmol), 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (1.5 g, 7.8 mmol), and 1-hydroxybenzotriazole (1.4 g, 10.3 mmol) in 200 mL of DMF was added 2-propenyl(3-aminopropyl)dimethylsilane (1.1 g, 6.7 mmol), and the mixture was stirred at room temperature for 26 h. The mixture was quenched with hydrochloric acid and extracted with diethyl ether. The organic layer was washed with H₂O and saturated sodium bicarbonate solution. After drying over MgSO₄, organic solvent was removed in vacuo and the residue was chromatographed on silica gel (hexane/ethyl acetate = 2/1) to give 3.6 g (83% yield) of the title compound 4. ¹H NMR (CDCl₃) δ –0.02 (s, 6H), 0.50 (m, 2H), 1.47 (m, 2H), 1.50 (dt, J = 8.2, 1.2 Hz, 2H), 1.97 (quint d, J = 7.2, 2.6 Hz, 2H), 2.12 (t, J = 7.4 Hz, 2H), 2.70 (t, J = 7.4 Hz, 2H), 3.22 (dd, J = 13.2, 7.1 Hz, 2H), 4.80 (ddt, J = 10.2, 2.2, 1.0 Hz, 1H), 4.82 (ddt, J = 16.9, 2.2, 1.4 Hz, 1H), 5.36 (br s, 1H), 5.74 (ddt, J = 16.9, 10.2, 8.2 Hz, 1H), 6.73 (s, 2H), 6.85 (d, J = 8.5 Hz, 1H), 6.92 (dd, J = 8.5, 6.8, 1.2 Hz, 1H), 7.04-7.20 (m, 20H), 7.35 (ddd, J = 8.2, 6.7, 1.2 Hz, 1H), 7.42 (ddd, J = 8.5, 2.5, 2.2 Hz, 2H), 7.59 (s,1H), 7.82 (t, J = 9.2 Hz, 2H), 7.88 (d, J = 8.4 Hz, 1H); ²⁹Si NMR (CDCl₃) δ 1.67; ³¹P NMR (CDCl₃) δ –15.12 (d, J_P-P = 10 Hz), –14.97 (d, J_P-P = 10 Hz). Anal. Calcd for C₅₆H₅₅NOP₂Si: C, 79.31; H, 6.54. Found: C, 79.05; H, 6.64.

Loading of 3-Chloropropylsilanes on Silica Gels. The reaction conditions and results are summarized in Table 1. A typical procedure is given for the reaction of 2-propenyl(3-chloropropyl)dimethylsilane (1) (5 mmol) with FSM-16 (entry 2): To a suspension of dry FSM-16 (1.0 g) in 30 mL of toluene was added 2-propenyl(3-chloropropyl)dimethylsilane (1) (0.89 g, 5.0 mmol, 1.0 eq to SiOH), and the mixture was refluxed for 15 h. The modified FSM-16 was filtered, extracted in a Soxhlet apparatus with methanol for 24 h and then with benzene for 48 h. The allylsilane 1 (0.60 g, 3.4 mmol) was recovered by evaporation of the solvent from the filtrates and extracts. The modified FSM-16 was dried at 120 °C under reduced pressure (0.2 mmHg) for 15 h. Elemental analysis: Found: C, 8.08; H, 1.62; Cl, 3.89.

Loading of BINAP-Allylsilane on FSM-16. A procedure similar to that described above for treatment of FSM-16 with 1 was carried out with N-[3-((2-propenyl)dimethylsilyl)propyl]- (R)-4-[2,2′-(diphenylphosphino)-1,1′-binaphth-6-yl]-butanamide (4): To a suspension of dry FSM-16 (906 mg) in 30 mL of toluene was added 4 (3.96 g, 4.7 mmol, 1.0 eq to SiOH), and the mixture was refluxed for 15 h. The BINAP-modified FSM-16 5 was filtered, extracted in a Soxhlet apparatus with methanol for 24 h and then with benzene for 48 h, and dried at 120 °C under reduced
pressure (0.2 mmHg) for 15 h. Elemental analysis: Found: C, 14.65; H, 1.71; N, 0.31. From the filtrates and extracts 3.44 g (4.1 mmol) of 4 was recovered.

References