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Transition-Metal-Catalyzed Immobilization of Organic Functional Groups onto Solid Supports through Vinylsilane Coupling Reactions

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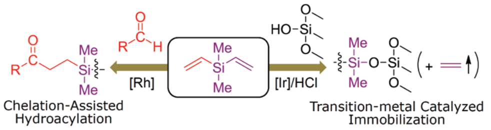
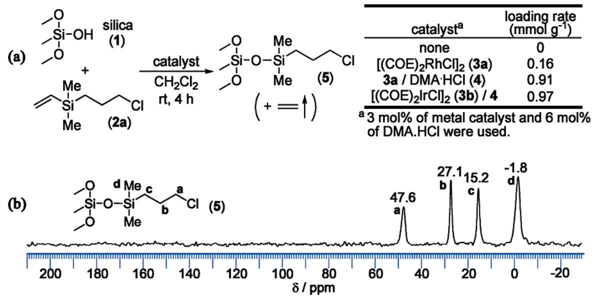
Surface modifications of inorganic solids, such as silica or glass, with organic functional groups have received considerable attention in materials science research.[1] Several protocols for surface modification of inorganic solids based on use of the postgrafting method have been devised.[2] However, alkoxysilanes[1b,2a−e] or chlorosilanes,[3] which are commonly used in this modification technique, are unstable substances that are sensitive to moisture, hard to transform into the desired functionalized silane precursors, and difficult to purify by employing chromatographic methods. Allylsilanes have recently been developed to overcome these difficulties.[4] However, allylsilane derivatives that possess carboxylic acid groups cannot be prepared because of their facile acid-promoted destruction by protodesilylation. We recently observed that vinylsilanes react with alcohols under very mild conditions in the presence of rhodium(I)/HCl catalysts to afford alkoxysilanes.[5] This observation stimulated an investigation probing applications of vinylsilanes in catalytic immobilization of organic substances onto hydroxyl-containing surfaces of solid supports. One driving force for this effort was the recognition that vinylsilanes can tolerate both a variety of functional groups (including carboxylic acids) and conditions used for chromatographic purification. In this communication, we describe the results of a study that has led to the development of a vinylsilane-based transition-metal/HCl-catalyzed immobilization method for covalent attachment of organic functional groups to silica or glass surfaces. In addition, we have found that divinylsilanes can be used for coupling of functional organic molecules to solid supports. In this method, one vinyl group of the divinylsilane is used for immobilization onto a solid surface and the other participates in a C−C bond-forming reaction [e.g., hydroacylation (eq 1)].



(1)

Vinylsilanes can be immobilized onto silica by reaction with surface hydroxyl groups that is promoted by catalysts (Figure 1a). For example, when silica[6] (**1**, 100 mg) was treated with 3-chloropropyldimethylvinylsilane (**2a,** 0.75 mmol, 5.8 equiv/OH in **1**) in the presence of $[(\mathrm{COE})_2\mathrm{RhCl}]_2$ (**3a**, 3 mol % Rh based on **2a**) and *N*,*N*-dimethylacetamide hydrochloride salt[7] (DMA·HCl, **4**, 6 mol %) at room temperature for 4 h and then washed with methylene chloride and methanol, surface-modified silica **5** was produced. The loading rate of 3-chloropropyldimethylsilyl groups on silica was determined to be 0.91 mmol g^{-1}.[8] Studies exploring the use of other transition-metal catalysts for the coupling process[9] showed that iridium(I) complex **3b** promotes coupling of **4** with an activity of 0.97 mmol g^{-1} (Figure 1a).[10] Inspection of the solid-state ^{13}C cross-polarization magic-angle-spinning (CP-MAS) NMR spectrum of **5** showed that the 3-chloropropyldimethylsilyl moiety was covalently incorporated into **1** (Figure 1b).[4a,11]



catalyst[a]	loading rate (mmol g^{-1})
none	0
$[(\mathrm{COE})_2\mathrm{RhCl}]_2$ (**3a**)	0.16
3a / DMA·HCl (**4**)	0.91
$[(\mathrm{COE})_2\mathrm{IrCl}]_2$ (**3b**) / **4**	0.97

[a] 3 mol% of metal catalyst and 6 mol% of DMA.HCl were used.

Figure 1. (a) Catalytic immobilization of **2a** onto silica (**1**) using various catalyst mixtures. (b) ^{13}C CP-MAS NMR spectrum of **5** formed by **3b/4**.

This methodology can be employed in a simple inorganic−organic coupling strategy that relies on the use of divinylsilanes as linker species. In this process, one vinyl group of the divinylsilane is used for C−C bond formation with the functional organic substance and the other vinyl group participates in immobilization to the surface. Among the many possible types of C−C bond-forming reactions that occur via C−H bond activation,[12] chelation-assisted hydroacylation was chosen for this application.[13] Reaction of benzaldehyde (**6a**) with dimethyldivinylsilane (**2b**) in the presence of a mixture of $(\mathrm{Ph_3P})_3\mathrm{RhCl}$ (**3c**), 2-amino-3-picoline (**7**), and p-$\mathrm{CF_3-C_6H_4-CO_2H}$ (**8**) produced 3-(dimethyl(vinyl)silyl)phenylpropan-1-one (**9a**) in a high 92% yield (Table 1, entry 1). Since the divinylsilane is much more reactive in the coupling reaction than a monovinylsilane, **9a** was readily obtained without the intervention of the side reaction involving double hydroacylation.[14] This reaction was performed using various functionalized aldehydes **6**, each of which gave the corresponding functionalized vinylsilane **9** in high yield (Table 1).

Further investigations demonstrated that the functionalized vinylsilanes **9** can be catalytically grafted to **1**. Specifically, reactions of **9** in the presence of **3b** and **4** led to formation of organic functional group-immobilized silicas **10** with high loading efficiencies (0.58−1.04 mmol g^{-1}). Even the boronate-impregnated vinylsilane **9c** participated in this process (entry 3). Also, vinylsilane **9e** containing the stable carboxylic group could be prepared using this protocol through the reaction of 4-formylbenzoic acid (**6e**) with **2b** (entry 5). NHS-ester-functionalized silica **10l** was also readily generated by esterification of **9e** with *N*-hydroxysuccinimide followed by immobilization of the resulting **9l** on **1** in the presence of **3b** and **4**. The loading rate of NHS groups in **10l** was found to be 0.70 mmol g^{-1} (Scheme 1). Furthermore, the resulting **10l** can serve as a useful handle for the introduction of primary-amine-based organic substances. For example, reaction of **10l** with the dansyl-group-functionalized amine **11** at room temperature gave the fluorescent, dansyl-group-immobilized silica **12** with a loading

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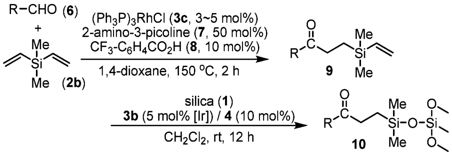
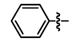
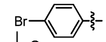
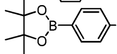
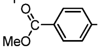
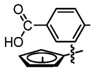
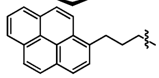
of 0.65 mmol g^{-1}. Vinylsilanes containing *n*-alkyl groups with different chain lengths (**9h**−**k**) were also immobilized onto **1** with high loading efficiencies (0.74−0.94 mmol g^{-1}; entries 8−11).

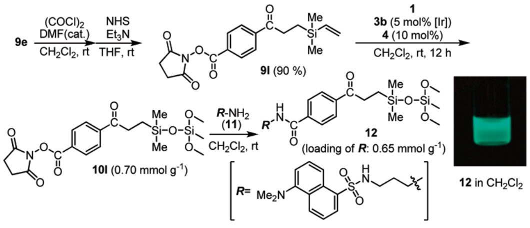
Table 1. Immobilization of the R Group of Aldehyde **6** onto Silica (**1**) Using Dimethyldivinylsilane (**2b**) as a Covalent Bonding Mediator



entry	R−⌇	isolated yield of **9** (%)	loading rate[a] (mmol g^{-1})
1	 (**6a**)	92 (**9a**)	0.90 (**10a**)
2	 (**6b**)	70 (**9b**)	1.04 (**10b**)
3	 (**6c**)	63 (**9c**)	0.64 (**10c**)
4	 (**6d**)	81 (**9d**)	0.88 (**10d**)
5	 (**6e**)	63 (**9e**)[b]	0.80 (**10e**)
6	 (**6f**)	75 (**9f**)[c]	0.58 (**10f**)
7	 (**6g**)	68 (**9g**)	0.73 (**10g**)
8	 n=1 (**6h**)	65 (**9h**)	0.94 (**10h**)
9	n=4 (**6i**)	77 (**9i**)	0.94 (**10i**)
10	n=7 (**6j**)	78 (**9j**)	0.87 (**10j**)
11	n=15 (**6k**)	77 (**9k**)	0.74 (**10k**)

[a] Determined by the C value from elemental analysis. [b] At 160 °C for 6 h. [c] At 130 °C for 12 h.

Scheme 1



The new grafting immobilization protocol was applied to the modification of the surface of glass microscope slides. After treatment with piranha solution (7:3 mixture of H_2SO_4 and 34.6% H_2O_2) for 30 min to generate a large amount of surface hydroxyl groups, the slides were reacted with *n*-alkyl-group-impregnated vinylsilanes **9h**−**j** in the presence of **3b** and **4**. In each case, the glass surface became significantly hydrophobic in comparison with the surface prior to immobilization of the alkyl group, as estimated from contact angle measurements (7° for the bare surface and 71−94° for the immobilized ones; Figure 2). Studies showed that the contact angle increased as the length of the alkyl chain increased.

In conclusion, the effort described above has led to the development of a novel and efficient grafting methodology based on transition-metal-catalyzed reactions of vinylsilanes that enables the introduction of functional organic molecules onto silica or glass surfaces. Dimethyldivinylsilane can be used in this procedure as a linker to covalently bond organic molecules to hydroxyl surfaces of solid supports.

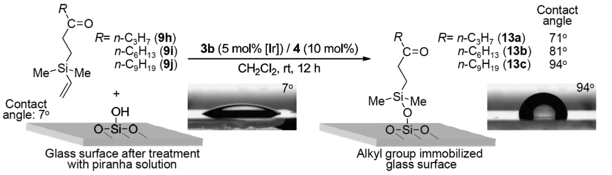


Figure 2. Surface modification of glass slides with vinylsilanes containing various alkyl chains and the results of contact angle measurements (for details, see the Supporting Information.)

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Supporting Information Available: Experimental procedures and spectroscopic and analytical data for **9a**−**l** and **10a**−**l**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) Silica (**1**) was purchased in the form of mesoporous silica balls (10 μm; 11 nm pore diameter; 300 m^2/g) from Kromasil. The hydroxyl group content of the surface of **1** was determined to be 1.3 mmol g^{-1} by reaction with HMDS (see ref 1a).

(7) DMA•HCl salt (**4**) was used instead of HCl dissolved in 1,4-dioxane. Also see: James, B. R.; Morris, R. H.; Kvintovics, P. *Can. J. Chem.* **1986**, *64*, 897.

(8) The loading rate of 3-chloropropyldimethylsilyl groups was determined on the basis of carbon composition using elementary analysis.

(9) Ru, Pt, and Pd catalysts did not show any catalytic activity in this reaction (for details of the catalysts used, see the Supporting Information).

(10) ICP-MS analysis of the resulting **5** showed that the Ir catalyst used was almost removed in the washing step (for details, see the Supporting Information).

(11) ^{29}Si solid-state NMR spectra of **1** and **5** were also recorded (see the Supporting Information).

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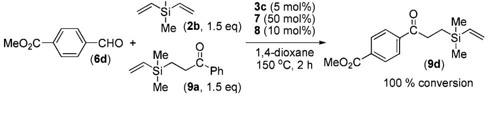
(14) When the competitive reaction of **6d** with **2b** and **9a** was carried out in the presence of the corresponding catalyst mixture at 150 °C for 2 h, only **9d** was obtained, leaving **9a** unreacted:



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