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## Immobilization of biomolecules via ruthenium-catalyzed functionalization of the surface of silica with a vinylsilane <sup>☆</sup>

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## ABSTRACT

A new ruthenium complex catalyzed procedure for the efficient *O*-silylation of an SiO–H group on the silica surface of glass beads with controlled pores (CPG) using 1-trimethylsiloxy-3-dimethylvinylsilylpropane leading to Si–O–Si bond formation with the evolution of ethylene is described. The formed linker contains alkyl hydroxyl groups which can be reacted with a nucleoside phosphoramidite unit. The CPG support containing alkyl hydroxyl groups is successfully applied in automatic chemical synthesis of DNA fragments.

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Surfaces of silica or glass modified with organic functional groups have received considerable attention in materials science. They are widely applied in biopolymer synthesis as solid supports,<sup>1</sup> microarray surfaces,<sup>2</sup> and as chemical carriers.<sup>3</sup> Most silica surface modification methods are based on the reaction between Si–OH groups of the surface with alkoxy-, chloro-, or acyloxysilanes.<sup>4</sup> However, these unstable and reactive silylating reagents are sensitive to moisture, cannot be handled under hydrolytic conditions and cannot be purified by silica gel chromatography. To overcome these difficulties, allylsilanes have been applied recently as moisture-stable silylating reagents for silica surface functionalization.<sup>5,6</sup> Jun and Park have developed a new grafting methodology based on the iridium-catalyzed reaction of vinylsilanes with silica or glass surfaces.<sup>7</sup>

The silylative coupling of olefins with vinyl-substituted organosilicon compounds, which we have previously developed as a new, effective catalytic method for the activation of the =C–H bond of olefins and =C–Si bond of organosilicon compounds (generally occurring in the presence of complexes containing M–H and M–Si bonds),<sup>8,9</sup> has recently been found to be general and also exhibited by vinyl derivatives of other *p*-block elements (e.g. boron<sup>10</sup>

and germanium.<sup>11</sup>) This mode of catalytic reactivity has also been successfully extended to catalytic activation of other sp<sup>2</sup> carbons, i.e. =C<sub>aryl</sub>–H bonds<sup>12</sup> and sp-hybridized carbon–hydrogen bonds,<sup>13</sup> as well as by the O–H bonds of silanols,<sup>14</sup> alcohols<sup>15</sup> and boronic acids<sup>16</sup> (Scheme 1).

The mechanism of this general reaction, in which vinyl metalloid compounds (CH<sub>2</sub>=CHER<sub>n</sub>) act as metallating agents and hydrogen acceptors, has been proved to involve the insertion of the vinyl metalloid compound into the TM–H bond (where TM = Ru, Rh, Ir or Co), and β-metalloid transfer to the transition metal with elimination of ethylene and generation of a TM–E (E = Si, Ge, B) bond. In the next step, migratory insertion of a coupling substrate (alkene, alkyne) or oxidative addition of a compound containing an –OH group into the TM–E bond followed by β-hydride transfer to the metal (or reductive elimination) eliminates the metallated product.<sup>8</sup>

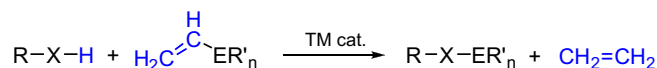
In view of our recent reports on the successful use of vinylsilanes, vinylboronates, and vinylgermanes as new hydrogen acceptors for the *O*-metallation of silanols,<sup>14a–c</sup> the aim of this work was to check the possibility of extending the role of vinylsilanes as silylating agents in the *O*-silylation of hydroxyl functional groups on the surface of silica. This has great potential in the hydrophobization strategy of inorganic (and organometallic) materials, and is more and more widely applied in the synthesis of biomolecules such as nucleic acids.

Herein, we report a new and complementary catalytic method of functionalizing a silica surface, which involves activation of

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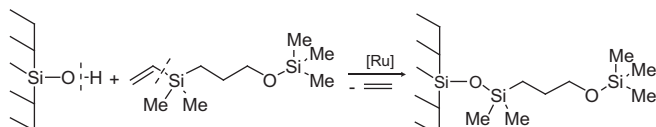


X = HC=CH, C≡C, O, or Ar

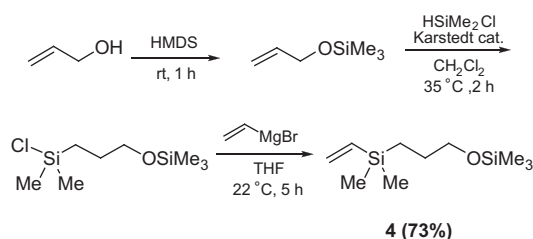
ER'<sub>n</sub> = SiR<sub>3</sub>, GeR<sub>3</sub>, BR<sub>2</sub>, Ar, R<sub>3</sub>C

R = R' = alkyl, aryl, siloxyl

**Scheme 1.** Catalytic metallation by deethenative coupling with vinyl metalloids and concomitant elimination of ethene.



**Scheme 2.** Silica surface modification using a vinylsilane.

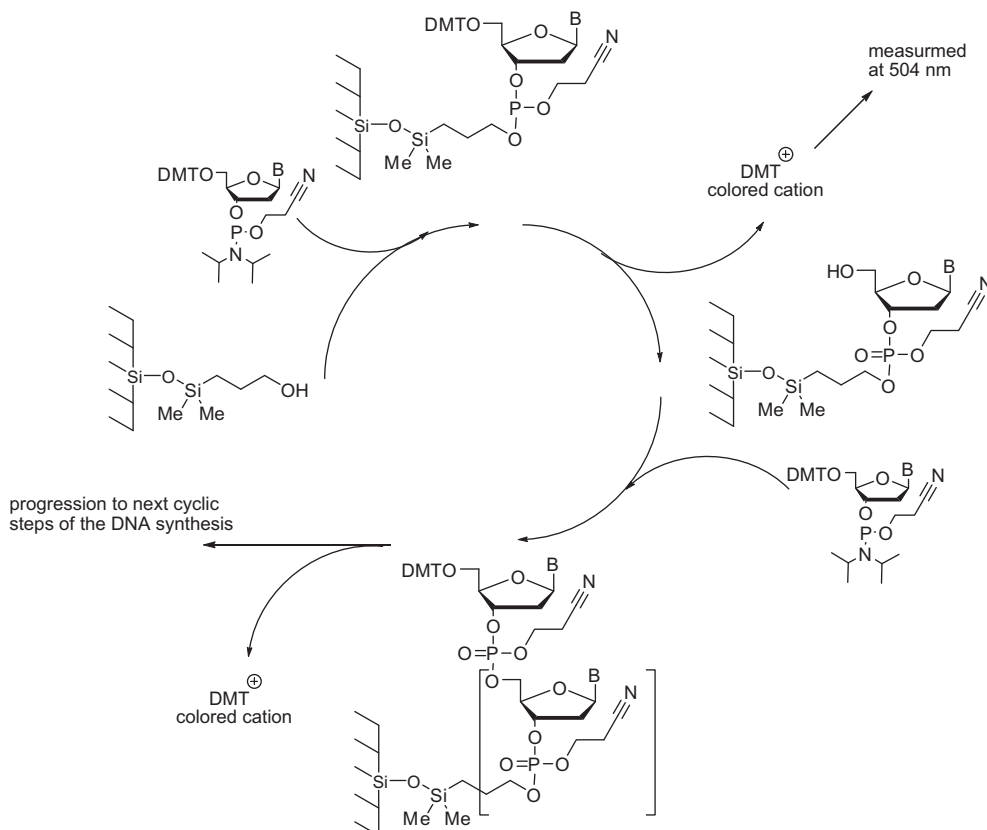


**Scheme 3.** Synthesis of 1-trimethylsiloxy-3-dimethylvinylsilylpropane.

the O–H bond on the surface by a moisture-unstable vinylsilane occurring in the presence of a ruthenium hydride catalyst via elimination of ethylene (Scheme 2). The prepared functionalized support with alkyl hydroxyl groups in the presence of ruthenium complexes **1–3** was used in automated chemical synthesis of nucleic acids. The obtained nucleic acid was subsequently able to hybridize with a complementary fluorescent probe. The nucleic acid chain grows freely on a functionalized support if: (i) it has enough space for growing the chain, and (ii) the linker connecting it with the support is stable under the synthetic conditions.

We chose 1-trimethylsiloxy-3-dimethylvinylsilylpropane **4** as an organo-functionalized vinylsilane, because the formed link is expected to be stable under the conditions of nucleic acid synthesis, and provides sufficient distance between the hydroxyl groups and the surface that enhances space for the growing chain. Compound **4** was prepared from commercially available allyl alcohol by using a sequential procedure: alcohol silylation – Pt-catalyzed hydrosilylation – Grignard substitution, in high overall yield (73%), as outlined in Scheme 3.<sup>17</sup>

Ruthenium(II) and ruthenium(0) complexes, i.e. [(RuHCl(CO)(PCy<sub>3</sub>)<sub>2</sub>)] **1**, [Ru<sub>3</sub>(CO)<sub>12</sub>] **2** and [Ru(COD)(COT)] **3**, which are known to be active in *O*-silylations of silanols with vinylsilanes<sup>14a</sup> and vinylgermanes<sup>14b</sup> were tested for the *O*-silylation of the hydroxyl groups of the silica surface with 1-trimethylsiloxy-3-dimethylvinylsilylpropane **4**. All the reactions were conducted following the original procedure for the synthesis of unsymmetrical siloxanes<sup>14a</sup> in the presence of 2 mol % of the catalyst with 2–4 equiv of the olefin in a Schlenk bomb flask fitted with a plug valve in toluene (110 °C). The effectiveness of the catalytic method was shown by functionalizing glass beads with controlled pores (CPG) and applying them in chemical syntheses of nucleic acids. The silyl ether



**Scheme 4.** Method for testing the solid CPG with a phosphoramidite unit in the chain extension reaction.

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