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# Regio- and stereoselective hydrosilylation of immobilized terminal alkynes

Palle J. Pedersen, Jonas Henriksen, Charlotte H. Gotfredsen, Mads H. Clausen *

*Department of Chemistry, Technical University of Denmark, Building 201, DK-2800 Kgs. Lyngby, Denmark*

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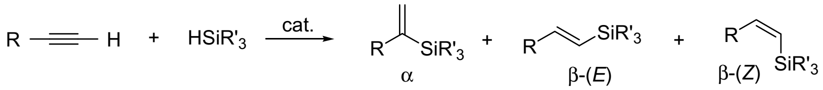
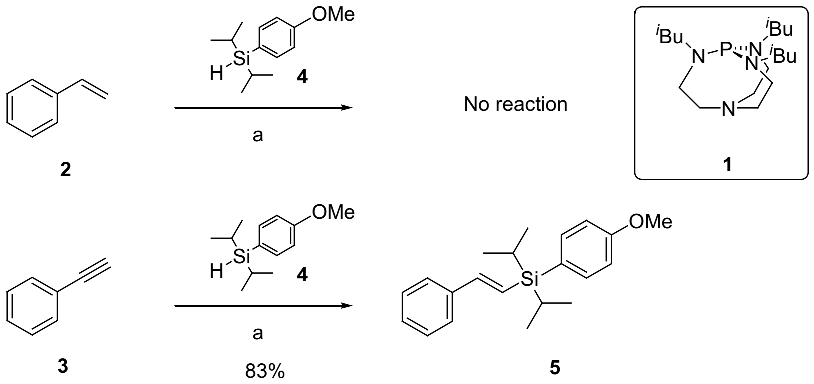
ABSTRACT

Regio- and stereoselective hydrosilylation of terminal alkynes on solid support using diisopropyl hydrosilanes yielding β-(*E*)-vinyl silanes with excellent selectivity is reported. The hydrosilylation is catalyzed by Pt(DVDS)/P($^{i}$BuNCH$_2$CH$_2$)$_3$N (DVDS = 1,3-divinyl-1,1,3,3-tetramethyl-disiloxane), in which the bulky proazaphosphatrane ligand plays a key role for the selectivity. The immobilized products are characterized with *gel phase* $^{13}$C NMR and $^{1}$H high resolution magic angle spinning NMR.

Solid supported organic synthesis is dependent on efficient reactions that are compatible with the supports and meets the special demands of immobilized reactants. With this in mind we have investigated the regio- and stereoselective hydrosilylation of terminal alkynes yielding β-(*E*)-vinyl silanes. The hydrosilylation reaction, discovered by Sommer et al. in 1947,[1] can be characterized as an addition of hydrosilanes to unsaturated carbon–carbon (or carbon-heteroatom) bonds such as alkenes and alkynes. The



**Scheme 1.**



**Scheme 2.** Reagents and conditions: (a) Pt(DVDS)/1 (1 mol %), THF, 23 h, 20 °C.

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* Corresponding author. Tel.: +45 45252131; fax: +45 45933968.
*E-mail address:* mhc@kemi.dtu.dk (M. H. Clausen).

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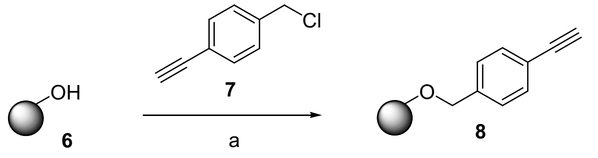
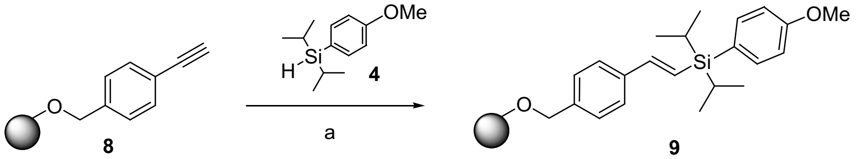


**Scheme 3.** Reagents and conditions: (a) KO$^t$Bu, Bu$_4$NI, THF, 40 h, 60 °C.

reaction can be catalyzed by various metal complexes, with the platinum compounds Pt(DVDS)$_2$ (Karstedt's catalyst)[2a] and $H_2PtCl_6 \cdot 6H_2O$ (Speier's catalyst)[2b] as the most prominent and popular.

Hydrosilylation of terminal alkynes could result in three isomeric vinyl silanes as illustrated in Scheme 1. Even though both the Karstedt and the Speier catalysts favor the formation of the β-(*E*)-vinyl silane isomer, the α-vinyl silane is produced to a significant degree (10–30%),[3] whereas β-(*Z*)-vinyl silanes usually do not appear above the trace level when these catalysts are applied. Recently, Denmark et al. and others[3a–c] demonstrated that addition of bulky phosphorus ligands improved the β-(*E*):α ratio significantly and by applying the commercially available triisobutyl proazaphosphatrane ligand **1**[4] Verkade and co-workers obtained the β-(*E*) isomer with over 97% selectivity and in good yields.[3b]



**Scheme 4.** Reagents and conditions: (a) Pt(DVDS)/1 (1 mol %), THF, 53 h, 60 °C.

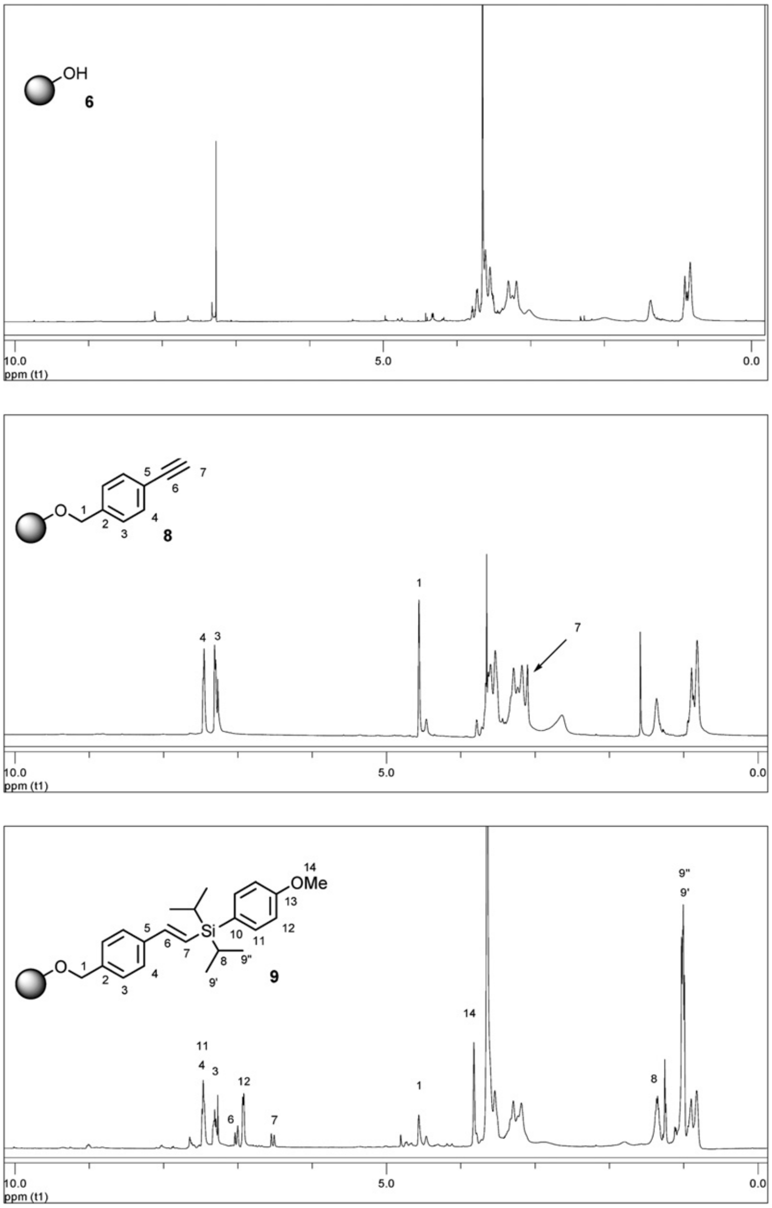


**Figure 1.** $^1H$ HR-MAS NMR (500 MHz, $CDCl_3$) spectra of resins **6**, **8** and **9**, including proton assignment.

**Table 1**
NMR data ($CDCl_3$) for the model compound **5** and the functionalized PEG resin **9**

| Atom[a] | $^1$H $\delta_H$ for **5** | HR-MAS $\delta_H$ for **9** | $^{13}$C $\delta_C$ for **5** | *Gel phase* $\delta_C$ for **9** |
|---|---|---|---|---|
| 1 | — | 4.57 (s) | — | [b] |
| 2 | 7.32–7.28 (m) | — | 128.3 | [c] |
| 3 | 7.37 (t, $J$ = 7.2 Hz) | 7.33–7.29 (m) | 128.7 | 128.0 |
| 4 | 7.53–7.48 (m) | 7.48–7.45 (m) | 126.6 | 126.5 |
| 5 | — | — | 138.5 | 138.3 |
| 6 | 7.06 (d, $J$ = 19.4 Hz) | 7.02 (d, $J \sim 19$ Hz) | 147.5 | 147.1 |
| 7 | 6.57 (d, $J$ = 19.4 Hz) | 6.53 (d, $J \sim 19$ Hz) | 122.7 | 122.6 |
| 8 | 1.38 (sept., $J$ = 7.4 Hz) | 1.36–1.34 (m) | 11.0 | 10.9 |
| 9′ | 1.05 (d, $J$ = 7.4 Hz) | 1.02 (d, $J$ = 7.1 Hz) | 18.0 | 17.9 |
| 9″ | 1.02 (d, $J$ = 7.4 Hz) | 1.00 (d, $J$ = 7.1 Hz) | 18.0 | 17.9 |
| 10 | — | — | 125.0 | 125.0 |
| 11 | 7.53–7.48 (m) | 7.48–7.45 (m) | 137.1 | 136.9 |
| 12 | 6.95 (d, $J$ = 8.6 Hz) | 6.93 (d, $J$ = 7.7 Hz) | 113.5 | 113.4 |
| 13 | — | — | 160.5 | 160.4 |
| 14 | 3.84 (s) | 3.82 (s) | 55.1 | 55.0 |

[a] See Figure 1 for atom numbering.
[b] Hidden by the signal for the polymer backbone at ~70 ppm.
[c] Not detectable.

Whereas the hydrosilylation of terminal alkenes on solid support is known,[5] on-bead hydrosilylation of terminal alkynes has hitherto not been reported in the literature. The regio- and stereoselective hydrosilylation of alkynes has features that make this reaction particularly interesting. Due to the double π-system, alkynes are more reactive than alkenes[3d,e] which enables hydrosilylation with bulky hydrosilanes. The range of applicable hydrosilanes is much larger for hydrosilylation of alkynes compared to alkenes, where hydrosilylation is restricted to small and non-bulky silanes. Additionally, the product vinyl silanes are interesting since they are reactive toward electrophiles, can partake in the Pd-catalyzed Hiyama cross coupling[6] and have also been successfully employed in ring-closing metathesis and cross-metathesis reactions.[7]

In order to demonstrate the reactivity difference between alkenes and alkynes, we subjected styrene and phenyl acetylene to hydrosilylation conditions with the bulky hydrosilane **4**[8] (Scheme 2) under the catalysis of Karstedt's catalyst and the triisobutyl proazaphosphatrane ligand **1**. We did not observe any product formation in the experiment with styrene, whereas phenyl acetylene was converted to the desired β-(*E*)-vinyl silane **5** in 83% yield with better than 98% selectivity.[9]

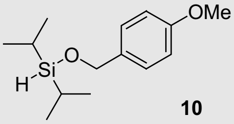
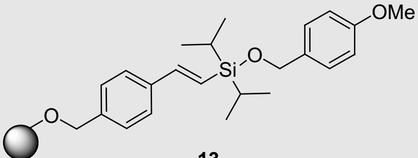
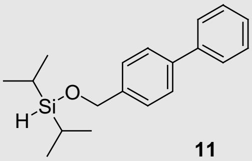
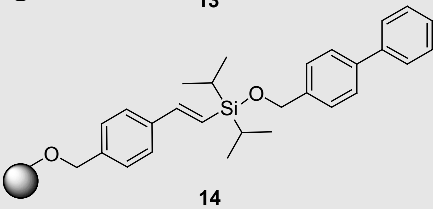
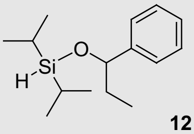
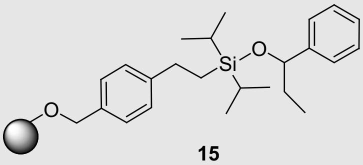
One of the challenges of working with solid phase synthesis is the analysis and characterization of the immobilized compounds. High resolution magic angle spinning NMR (HR-MAS NMR) has been shown to be a very powerful tool for structure elucidation of polymer-bound molecules.[10] $^1$H HR-MAS NMR and *gel phase* $^{13}$C NMR[11] are very valuable and robust techniques in the characterization of the immobilized molecules in the present study.

In this Letter we used the polyethylene glycol (PEG) based solid support VersaBeads$^{TM}$ VO 2000 (**6**), which is a modified superpermeable organic combinatorial chemistry (SPOCC) resin.[12] For ease of comparison to the model system, we decided to functionalize the resin with 4-ethynyl benzyl chloride (**7**)[13] (Scheme 3), and estimated from $^1$H HR-MAS NMR and *gel phase* $^{13}$C NMR that the alkylation occurred cleanly with high conversion.

Hydrosilylation of the alkyne functionalized PEG resin **8** with hydrosilane **4** (Scheme 4) under the reaction conditions applied in the hydrosilylation of phenyl acetylene[14] was highly successful, as estimated from $^1$H HR-MAS NMR and *gel phase* $^{13}$C NMR. No alkyne signals were detected in the NMR spectra, indicating a high conversion, and additionally the reaction proceeded in a regio- and stereoselective manner, yielding solely the desired β-(*E*)-vinyl silane **9**. The narrow line widths and high resolution in the $^1$H HR-MAS NMR spectrum (Fig. 1) demonstrate the power of this tool in the structure elucidation of immobilized molecules. By taking advantage of the NMR data obtained for the β-(*E*)-vinyl silane **5**, it is possible to detect and identify each proton in the spectrum via its chemical shift and, even more impressive, also the coupling pattern for some protons (Fig. 1). A comparison of the $^1$H and $^{13}$C NMR data for **5** and **9** is presented in Table 1.

In order to investigate the scope of our method, a variety of different diisopropylsilyl ethers **10**–**12** were synthesized under standard silylation conditions[15] in yields ranging from 76% to 88%. The reactivity of silyl ethers **10**–**12** in hydrosilylations was verified by successful reactions with phenyl acetylene before they were

**Table 2**
On-bead hydrosilylation of the terminal alkyne **8** with various diisopropylsilyl ethers catalyzed by Pt(DVDS)/**1** yielding β-(*E*)-vinyl silanes[17]

| Entry | Hydrosilane | β-(*E*)-vinyl silane |
|---|---|---|
| 1 |  **10** |  **13** |
| 2 |  **11** |  **14** |
| 3[a] |  **12** |  **15** |

[a] The vinyl silane was not isolated, but treated immediately with 2,4,5-triisopropylbenzenesulfonylhydrazine, yielding the corresponding saturated silane **15**.

applied in solid-phase hydrosilylations (see Supplementary data). The regio- and stereoselective hydrosilylations yielded exclusively the β-(*E*)-vinyl silanes for all the tested diisopropyl silyl ethers **10**–**12** in Table 2, and NMR data confirmed an excellent conversion in all cases, since no alkyne signals could be detected after completion of the reactions. In the experiment with silane **12**, the resulting vinyl silane was further reduced in a one-pot procedure by treatment with the di-imide generated by thermal decomposition of 2,4,5-triisopropylbenzenesulfonylhydrazine.[16] This tandem protocol yielded the corresponding saturated silane **15**.

In conclusion, we have developed a regio- and stereoselective hydrosilylation of immobilized terminal alkynes on solid support. The sterically hindered diisopropyl hydrosilanes afforded β-(*E*)-vinyl silanes with excellent selectivity using the Pt(DVDS)/**1** catalytic system. The resin-bound compounds were characterized by $^{1}$H HR-MAS NMR and *gel phase* $^{13}$C NMR, illustrating the power and applicability of these tools in solid phase synthesis. We believe this method will prove valuable not only to future applications of vinyl silanes in solid-phase synthesis but also as a means of immobilizing alcohols under selective reaction conditions.

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## Supplementary data

Supplementary data (experimental procedures, characterization data and copies of NMR spectra) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.08.043.

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17. Detailed experimental procedures, characterization data and copies of NMR spectra are available in the Supplementary data.