

## Platinum Complex-catalysed Dehydrogenative Monosilylation of Alkenes with Disilanes

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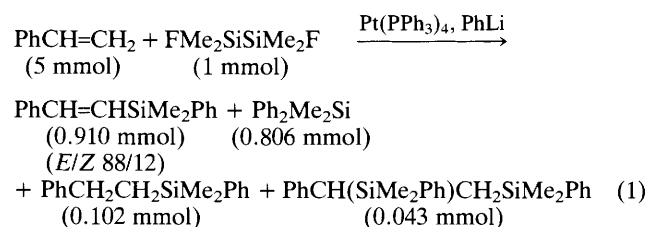
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Alkenes react with disilanes in the presence of platinum phosphine complex catalysts to give alk-1-enylsilanes.

The use of disilanes for the synthesis of silicon chemicals is increasingly important.<sup>1</sup> In a previous paper, we reported the first successful double silylation of alkenes; ethylene and norbornene underwent addition reaction with disilanes to give 1,2-bis(silyl)ethane derivatives.<sup>2</sup> In attempts to extend the scope of the reaction, we have come across the unexpected formation of alkenylsilanes. Alkenylsilane formation has been well documented<sup>3</sup> in the reaction of hydrosilanes with alkenes, but has never been reported in the reaction of a disilane with an alkene. We report herein this new type of dehydrogenative monosilylation of alkenes.

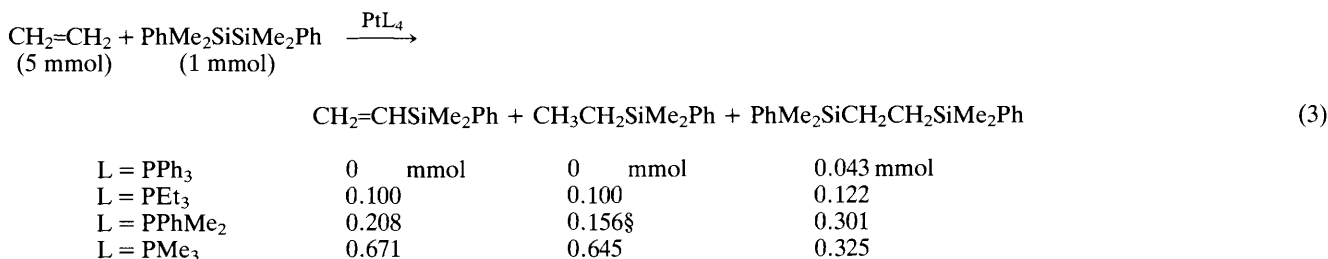
A solution of styrene (5 mmol), 1,2-difluoro-1,1,2,2-tetramethyldisilane (1 mmol), and Pt(PPh<sub>3</sub>)<sub>4</sub> (0.04 mmol) in benzene (3 ml) was heated in a Hastelloy C autoclave at 150 °C for 22 h. GC and GC-MS analyses of the resulting solution and the gas phase over the solution suggested the formation of β-(fluorodimethylsilyl)styrenes and fluorodimethylsilane as the major products. Upon phenylation of the reaction mixture with phenyl-lithium, these products were converted into β-(phenyldimethylsilyl)styrenes (0.910 mmol, *E/Z* 88/12) and

diphenyldimethylsilane (0.806 mmol), respectively [equation (1)].<sup>†</sup>



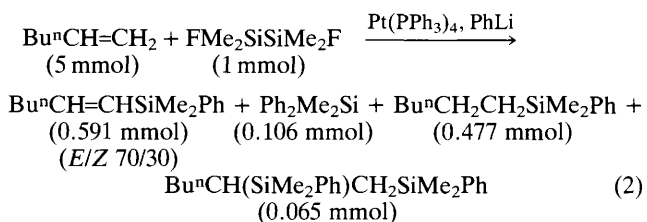
In the phenylated solution, 2-(phenyldimethylsilyl)ethylbenzene and 1,2-bis(phenyldimethylsilyl)ethylbenzene were also detected but these were only minor products. Note that the yield of β-(phenyldimethylsilyl)styrenes was nearly the same as the combined yield of diphenyldimethylsilane and

<sup>†</sup> The phenylation products were identified by comparison of the GC retention times and MS fragmentations with those of authentic samples prepared by different methods.



2-(phenyldimethylsilyl)ethylbenzene. This is rationalized by the following sequence of events having taken place; one of the  $\beta$ -hydrogens of styrene has been displaced by one of the silicon atoms in the disilane. The other silicon atom combines with the hydrogen atom coming from styrene to form hydrosilane which partly undergoes hydrosilylation with styrene.

Hex-1-ene reacted similarly, as shown in equation (2), although in contrast with the styrene reaction, the initially formed fluorodimethylsilane seemed to have been largely consumed in hydrosilylation of the substrate.‡



As previously proposed, the double silylation of ethylene is considered to proceed *via* the oxidative addition of a disilane, insertion of ethylene into one of the resulting silicon-platinum bonds, and reductive elimination of the silyl( $\beta$ -silylethyl)platinum intermediate. In line with this proposal, the present results may be explained in terms of  $\beta$ -hydride elimination of the silyl( $\beta$ -silylethyl)platinum intermediate. The reaction course ( $\beta$ -hydride elimination/reductive elimination) may be associated with the steric and electronic nature of the silyl and  $\beta$ -silylethyl groups attached to the platinum centre. We have separately reported that treatment of *cis*-(PhMe<sub>2</sub>Si)<sub>2</sub>-Pt(PPh<sub>2</sub>Me)<sub>2</sub> with styrene afforded  $\beta$ -(phenyldimethylsilyl)styrene. On the other hand, similar treatment with ethylene resulted in selective formation of 1,2-bis(phenyldimethylsilyl)ethane.<sup>4</sup>

‡ When a mixture of styrene (1 mmol) and hex-1-ene (1 mmol) in benzene was treated with chlorodimethylsilane (1 mmol) in the presence of Pt(PPh<sub>3</sub>)<sub>4</sub> at 90 °C for 16 h, hexylchlorodimethylsilane was formed in 41% yield, while styrene remained unchanged.

§ A small amount of HSiMe<sub>2</sub>Ph was detected.

Reinvestigation of the reactivity of ethylene has revealed that the auxiliary phosphine ligand also affects the reaction course. As reported previously, Pt(PPh<sub>3</sub>)<sub>4</sub> is a selective catalyst for the double silylation of ethylene with various disilanes; vinylsilanes are not formed at all. However, use of the more electron donating and less sterically demanding phosphine as the ligand in the reaction with 1,2-diphenyl-1,1,2,2-tetramethyldisilane under the same reaction conditions not only enhanced the catalytic activity, but promoted the dehydrogenative monosilylation leading to the formation of the vinylsilane, equation (3). These observations strongly support that the silyl( $\beta$ -silylethyl)platinum complex is a common intermediate involved in both double silylation and dehydrogenative monosilylation of alkenes.

In summary, this communication provides the first examples of dehydrogenative monosilylation of alkenes with disilanes to give alkenylsilanes which have been known to be a useful class of compounds in organic synthesis.<sup>5</sup> We are exploring more efficient catalysis, extended to other alkene substrates.

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