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# Homogeneous catalytic hydrosilylation of the C=C double bond with platinum catalysts

## Rita Skoda-Földes, László Kollár and Bálint Heil

Institute of Organic Chemistry, University of Chemical Engineering, H-8200 Veszprém, P.O. Box 158 (Hungary)

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## Abstract

Hydrosilylation of vinyl- and vinylidene-type olefins (styrene (1a), 2-phenyl-propene (1b), methyl methacrylate (6)) has been carried out with either  $PtCl_2$  (dissolved in the substrate) or a platinum-phosphine catalyst prepared in situ. The activity and regioselectivity of the platinum-phosphine catalysts depend strongly on the phosphine structure and the metal/ligand ratio. Complexes involving chelating phosphines are inactive. Although mainly linear regioisomers are formed (2 and 7 respectively) in the reaction of 6, some 1,4-addition of the silane to the conjugated system also takes place to give a silyl ketene acetal derivative (8). A marked decrease in the reaction rate is observed if  $Ph_3SiH$  instead of  $Et_3SiH$  is used as the hydrosilylating agent.

## Introduction

Catalytic hydrosilylation of the C=C bond plays an important role in synthetic organic chemistry. Some of the silicon-containing derivatives are biologically active ("sila-drugs") [1], and others are valuable intermediates in organic syntheses. The significance of the reaction is further enhanced by the fact that homogeneous catalytic enantioselective hydrosilylation provides an important method of introducing chiral centers into prochiral olefins. Unfortunately the optical yields achieved so far are rather low even with the most active palladium complexes of chiral ligands [2,3,4].

In addition to the widely used chloroplatinic acid ( $H_2PtCl_6$ , "Speier's catalyst"), the  $PtCl_2(styrene)_2$  complex has recently been successfully employed in the hydrosilylation of unfunctionalized olefins. Pregosin and his coworkers were able to characterize the catalytic species in this system by spectroscopic methods [5].

We describe here results of a study of hydrosilylation of various olefins with  $PtCl_2$  and platinum-phosphine catalyst, with particular reference to the influence of

the substrate, the silane, the nature of the phosphine, and the metal/ligand ratio on the catalytic activity and regioselectivity.

# **Results and discussion**

In the hydrosilylation of styrene by  $Et_3SiH$  in the presence of  $PtCl_2$  (Scheme 1 and Table 1) not only saturated hydrosilylated products (2a, 3a) but also unsaturated (4a) and hydrogenated (5a) derivatives are formed. The reaction with

$$\frac{R^{1}}{R^{2}}C = CH_{2} + R_{3}^{3}SIH \xrightarrow{PtCl_{2}} \frac{R^{1}}{R^{2}}CH-CH_{2}-SIR_{3}^{3} + \frac{R^{1}}{R^{2}}C - \frac{SIR^{3}}{CH_{3}} + \frac{R^{1}}{R^{2}}C - CH_{3} + \frac{R^{1}}$$

Scheme 1

Ph<sub>3</sub>SiH is slower, but it is also regiospecific, giving only the linear regioisomer and the side products (4a, 5a) are formed in substantial and similar yields. This phenomenon has been observed previously [5] and may be due to a  $\beta$ -hydride-elimination from the silylated alkyl-intermediate, and dihydro-platinum complex thus produced is probably responsible for the formation of 5a. 2-Phenyl-propene is also hydrosilylated regioselectively by Et<sub>3</sub>SiH to give 2b, but with Ph<sub>3</sub>SiH there is practically no reaction.

A more detailed investigation was carried out with methyl methacrylate (6) as substrate (Scheme 2, Table 2) and various catalysts.  $PtCl_2$  itself is very efficient, and

the main product is again the linear hydrosilylated derivative (7). In some experiments, however, 1,4-addition of  $Et_3SiH$  also takes place resulting in a silyl ketene acetal derivative (8). When  $PtCl_2$  is replaced by the preformed  $PtCl_2(PhCN)_2$  complex or  $PtCl_2 + (-)-(S)$ -1-phenyl-ethylamine catalyst prepared in situ (run 2, 3)

Table 1	
Hydrosilylation of styrenes with a PtCl <sub>2</sub> catalyst <sup>a</sup>	

Substrate	Silane	Reaction	Conversion <sup>b</sup>	Product distribution (%) <sup>c</sup>			
		time (h)	(%)	2	3	4	5
1a	Et <sub>3</sub> SiH	4	98	76	2	11	11
1a	Ph <sub>3</sub> SiH	96	98	37	_	31	32
1b	Et <sub>3</sub> SiH	96	4	100		_	_
1b	Ph <sub>3</sub> SiH	96	~	_	-	_	-

<sup>a</sup> Reaction conditions: Pt/substrate = 1/600; room. temp. (298 K); Ar atmosphere. <sup>b</sup> mol reacted substrate/mol initial substrate × 100. <sup>c</sup> mol product/mol reacted substrate × 100.

the acetal derivative (8) is no longer formed but otherwise the product distribution remains practically unchanged. No enantioselective induction by the latter catalyst was detected. When the phosphine used along with the  $PtCl_2(PhCN)_2$  complex was varied considerable variation in activity was observed. Addition of two equivalents of the monodentate tertiary phosphines greatly lowers the catalytic activity (run 14, 17), and in the case of the none-basic triarylphosphine  $Ph_3P$  no activity at all was detected (run 10, 11). The catalyst containing optically active monodentate phosphine (BzMePhP) did not bring about any optical induction (run 4). In the light of this information it is not surprising that complexes formed from chelating bidentate phosphines such as BDPP (run 18) are completely inactive even when the strong "trans-activating" ligand  $SnCl_3^-$  is present (run 19); in this run only a polymeric product was isolated from the reaction mixture.

Except for reaction catalysed by  $PtCl_2$ , the silyl ketene acetal derivative was only observed when  $Bu_3P$  or  $(cHex)_3P$  was the phosphine in the catalyst and when the substrate was present in excess (run 6, 7, 16) (Procedure B, see also Experimental). Its formation may be connected with the basicity of these phosphines, but it was not detected when  $CHCl_3$  was used as solvent (Procedure A, see Experimental) even when the substrate was present in excess.

The mechanism mentioned above for formation of the unsaturated (9) and the hydrogenated (10) derivatives may not only one operating. The possibility of another pathway has to be considered because 10 shall observed when no 9 could be detected.

Use of  $Ph_3SiH$  again resulted in slower reaction, but the chemo- and regioselectivity of the reaction was excellent. It is noteworthy that Pregosin and his coworkers did not observe any reaction of this silane with  $PtCl_2(styrene)_2$  as catalyst [6].

#### Experimental

#### Reagents

PtCl<sub>2</sub>, Ph<sub>3</sub>P and Bu<sub>3</sub>P were purchased from Fluka. Et<sub>3</sub>P and (cHex)<sub>3</sub>P were made by published methods [7,8]. PtCl<sub>2</sub>(PhCN)<sub>2</sub> was prepared from PtCl<sub>2</sub> in hot benzonitrile [9]. PtCl(SnCl<sub>3</sub>)(BDPP) (BDPP = (-)-(2S,4S)-2,4-bis(diphenylphosphino)-pentane) and (-)-(S)-BzMePhP were prepared as described previously [10,11]. (-)-(S)-1-phenylethylamine was purchased from Fluka ( $\alpha_{\rm D}^{20} = -39.2^{\circ}$ (neat)). Solvents were dried and distilled under argon. The substrates were freshly distilled before use.

The <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> with TMS as internal standard on a Tesla BS 487C spectrometer at 80 MHz, and <sup>13</sup>C NMR spectra at 20.1 MHz on a Varian CFT-20 spectrometer. Mass spectra were recorded with a JEOLCO MS 01 SG-2 spectrometer at 75 eV.

Optical rotations of the products were measured on neat samples with a Schmidt-Haensch LM visual polarimeter after vacuum distillation of the reaction mixture. GLC analyses were carried out on a Hewlett-Packard 5830A gas chromatograph fitted with a column coated with SP-2100.

#### Hydrosilylation experiments

*Procedure A*: 9.4 mg (0.02 mmol) of  $PtCl_2(PhCN)_2$  and 5.2 mg (0.02 mmol) of  $Ph_3P$  were dissolved in 1 ml (12 mmol) CHCl<sub>3</sub> under argon in a Schlenk tube, then

sion PtCl $_{a}^{a}$ PtCl $_{a}^{a}$	Run	Silane	Catalyst	Conver-	Reaction	Product	Product distribution (%)	(%)		Proc.	
B <sub>1</sub> SIH         PtCl <sub>2</sub> 92         24           B <sub>1</sub> SIH         PtCl <sub>2</sub> (PhCN) <sub>2</sub> 99         24           B <sub>1</sub> SIH         PtCl <sub>2</sub> (PhCN) <sub>2</sub> 97         24           B <sub>1</sub> SIH         PtCl <sub>2</sub> (PhCN) <sub>2</sub> 89         24           B <sub>1</sub> SIH         PtCl <sub>2</sub> (PhCN) <sub>2</sub> 89         24           B <sub>1</sub> SIH         PtCl <sub>2</sub> (PhCN) <sub>2</sub> 80         24           B <sub>1</sub> SIH         PtCl <sub>2</sub> (PhCN) <sub>2</sub> 80         25           B <sub>1</sub> SIH         PtCl <sub>2</sub> (PhCN) <sub>2</sub> 80         26           B <sub>1</sub> SIH         PtCl <sub>2</sub> (PhCN) <sub>2</sub> 80         21         72           B <sub>1</sub> SIH         PtCl <sub>2</sub> (PhCN) <sub>2</sub> 80         21         72           B <sub>1</sub> SIH         PtCl <sub>2</sub> (PhCN) <sub>2</sub> 80         21         72           B <sub>1</sub> SIH         PtCl <sub>2</sub> (PhCN) <sub>2</sub> 81         41         72           B <sub>1</sub> SIH         PtCl <sub>2</sub> (PhCN) <sub>2</sub> 84         72         84           B <sub>1</sub> SIH         PtCl <sub>2</sub> (PhCN) <sub>2</sub> 84         72         84           B <sub>1</sub> SIH         PtCl <sub>2</sub> (PhCN) <sub>2</sub> 84         72         84           B <sub>1</sub> SIH         PtCl <sub>2</sub> (PhCN) <sub>2</sub> 84         72         84				sion (%)	time (h)	F	æ	6	10		
Ei,SIH         PrCl_2(PhCN)_2         89         24           Ei,SIH         PrCl_2(PhCN)_2 + (-)(S)-1-PhEtNH_2         97         24           Ei,SIH         PrCl_2(PhCN)_2 + (-)(S)-2         97         24           Ei,SIH         PrCl_2(PhCN)_2 + (-)(S)-2         97         24           Ei,SIH         PrCl_2(PhCN)_2 + Bu_3P         43         43         44           Ei,SIH         PrCl_2(PhCN)_2 + Bu_3P         25         24         48           Ei,SIH         PrCl_2(PhCN)_2 + Bu_3P         25         24         48           Ei,SIH         PrCl_2(PhCN)_2 + Ph_3P         25         24         48           Ei,SIH         PrCl_2(PhCN)_2 + Ph_3P         26         48         72           Ei,SIH         PrCl_2(PhCN)_2 + 2Ph_3P         26         24         72           Ei,SIH         PrCl_2(PhCN)_2 + Ei_3P         26         24         72           Ei,SIH         PrCl_2(PhCN)_2 + Ei_3P         56         24         26         24           Ei,SIH         PrCl_2(PhCN)_2 + 2Ei_3P         56         24         26         24           Ei,SIH         PrCl_2(PhCN)_2 + 2Ei_3P         56         24         24         24           Ei_3SH         PrC	1	Et <sub>1</sub> SiH	PtCl, "	92	24	61	4	5	9	A "	
Ei_5SH         PCG_2 (PhCN)_2 + (-)-(5)-1-PhEtNH_2         97         24           Ei_5SH         PCG_2 (PhCN)_2 + (-)-(5)-         43         48           Ei_5SH         PCG_2 (PhCN)_2 + Bu_3 P         23         48           Ei_5SH         PCG_2 (PhCN)_2 + Bu_3 P         25         24           Ei_5SH         PCG_2 (PhCN)_2 + Bu_3 P         23         48           Ei_5SH         PCG_2 (PhCN)_2 + Bu_3 P         23         24           Ei_5SH         PCG_2 (PhCN)_2 + 2Ph_3 P         28         48         72           Ei_5SH         PCG_2 (PhCN)_2 + Er_3 P         26         24         72           Ei_5SH         PCG_2 (PCN)_2 + Er_3 P         6         72         48           Ei_5SH         PCG_2 (PCN)_2 + Er_3 P         6         72         48           Ei_5SH         PCG_2 (PCN)_2 + Er_3 P         6         72         48           Ei_5SH         PCG_2 (PCN)_2 + Er_3 P         6         72         48           Ei_5SH         PCG_2 (PCN)	7	Et, SiH	PtCl,(PhCN),	89	24	93	I	1	6	۲	
Ei_3SH         PCC <sub>2</sub> (PhCN) <sub>2</sub> + (-)(S)-           BzMePh         BzMePh         24           BzMePh         PCC <sub>2</sub> (PhCN) <sub>2</sub> + Bu <sub>3</sub> P         25         24           Et <sub>3</sub> SH         PCC <sub>2</sub> (PhCN) <sub>2</sub> + Bu <sub>3</sub> P         21         72           Et <sub>3</sub> SH         PCC <sub>2</sub> (PhCN) <sub>2</sub> + Bu <sub>3</sub> P         21         72           Et <sub>3</sub> SH         PCC <sub>2</sub> (PhCN) <sub>2</sub> + Bu <sub>3</sub> P         21         72           Et <sub>3</sub> SH         PCC <sub>2</sub> (PhCN) <sub>2</sub> + Ph <sub>3</sub> P         21         72           Et <sub>3</sub> SH         PCC <sub>2</sub> (PhCN) <sub>2</sub> + Ph <sub>3</sub> P         23         48           Et <sub>3</sub> SH         PCC <sub>2</sub> (PhCN) <sub>2</sub> + Ph <sub>3</sub> P         24         72           Et <sub>3</sub> SH         PCC <sub>2</sub> (PhCN) <sub>2</sub> + Et <sub>3</sub> P         26         24           Et <sub>3</sub> SH         PCC <sub>2</sub> (PhCN) <sub>2</sub> + Et <sub>3</sub> P         56         24           Et <sub>3</sub> SH         PCC <sub>2</sub> (PhCN) <sub>2</sub> + Et <sub>3</sub> P         56         24           Et <sub>3</sub> SH         PCC <sub>2</sub> (PhCN) <sub>2</sub> + Et <sub>3</sub> P         56         24           Et <sub>3</sub> SH         PCC <sub>2</sub> (PhCN) <sub>2</sub> + Et <sub>3</sub> P         56         24           Et <sub>3</sub> SH         PCC <sub>2</sub> (PhCN) <sub>2</sub> + Et <sub>3</sub> P         56         24           Et <sub>3</sub> SH         PCC <sub>2</sub> (PhCN) <sub>2</sub> + Et <sub>3</sub> P         50         24           Et <sub>3</sub> SH         PCC <sub>2</sub> (PhCN) <sub>2</sub> + 2(cHex) <sub>3</sub> P         50	e	Et <sub>3</sub> SiH		67	24	94	ł	1	5	۲	
BzMePh         BzMePh         43         48 $B_{13}SH$ $PCC_2(PhCN)_2 + Bu_3P$ 23         24 $B_{13}SH$ $PCC_2(PhCN)_2 + Bu_3P$ 21         72 $B_{13}SH$ $PCC_2(PhCN)_2 + Bu_3P$ 21         72 $B_{13}SH$ $PCC_2(PhCN)_2 + Ph_3P$ 21         72 $B_{13}SH$ $PCC_2(PhCN)_2 + Ph_3P$ 28         48 $B_{13}SH$ $PCC_2(PhCN)_2 + Ph_3P$ 28         48 $B_{13}SH$ $PCC_2(PhCN)_2 + Ph_3P$ 28         48 $B_{13}SH$ $PCC_2(PhCN)_2 + 2Ph_3P$ 28         48 $B_{13}SH$ $PCC_2(PhCN)_2 + Et_3P$ 24         72 $B_{13}SH$ $PCC_2(PhCN)_2 + Et_3P$ 56         24 $B_{13}SH$ $PCC_2(PhCN)_2 + Et_3P$ 540         24 $B_{13}SH$ $PCC_2(PhCN)_2 + (Etex)_3P$ 540         24	4	Et <sub>3</sub> SiH	-								
Et_3SH         PCG_2(PhCN)_2 + Bu_3 P         25         24           Et_3SH         PCG_2 + Bu_3 P         21         72           Et_3SH         PCG_2 + Bu_3 P         21         72           Et_3SH         PCG_2 (PhCN)_2 + Ph_3 P         21         72           Et_3SH         PCG_2 (PhCN)_2 + Ph_3 P         21         72           Et_3SH         PCG_2 (PhCN)_2 + Ph_3 P         28         48           Et_3SH         PCG_2 (PhCN)_2 + Ph_3 P         28         48           Et_3SH         PCG_2 (PhCN)_2 + 2Ph_3 P         28         48           Et_3SH         PCG_2 (PhCN)_2 + 2Ph_3 P         28         48           Et_3SH         PCG_2 (PhCN)_2 + 2Ph_3 P         28         48           Et_3SH         PCG_2 (PhCN)_2 + Et_3 P         56         24           Et_3SH         PCG_2 (PCN)_2 + 2(cHex)_3 P         540         24           Et_3SH         PCG_2 (PCN)_2 + 2(cHex)_3 P         52         24           Et_3SH         PCG_2 (PCN)_2 + 2(cHex)_		I		43	48	90	I	I	10	۲	
Ei_5SH         PCG_2 + Bu_3P         21         72           Ei_5SH         PCG_2(PhCN)_2 + Ph_3P         21         72           Ei_5SH         PCG_2(PhCN)_2 + Ph_3P         41         72           Ei_5SH         PCG_2(PhCN)_2 + Ph_3P         28         48           Ei_5SH         PCG_2(PhCN)_2 + Ph_3P         28         48           Ei_5SH         PCG_2(PhCN)_2 + Ph_3P         28         48           Ei_5SH         PCG_2(PhCN)_2 + 2Ph_3P         28         48           Ei_5SH         PCG_2(PhCN)_2 + 2Ph_3P         28         48           Ei_5SH         PCG_2(PhCN)_2 + 2Ph_3P         54         72           Ei_5SH         PCG_2(PhCN)_2 + Ei_3P         56         24         48           Ei_5SH         PCG_2(PhCN)_2 + Ei_3P         56         24         56         24         56         24         56         24         56         24         54 </td <td>S</td> <td><b>Et</b><sub>3</sub>SiH</td> <td><math>PtCl_2(PhCN)_2 + Bu_3P</math></td> <td>25</td> <td>24</td> <td>86</td> <td>I</td> <td>I</td> <td>14</td> <td>×</td> <td></td>	S	<b>Et</b> <sub>3</sub> SiH	$PtCl_2(PhCN)_2 + Bu_3P$	25	24	86	I	I	14	×	
Ei_5SH         PtCl_2(PhCN)_2 + Bh_3 P         41         72           Ei_5SH         PtCl_2(PhCN)_2 + Ph_3 P         41         72           Ei_5SH         PtCl_2(PhCN)_2 + Ph_3 P         84         72           Ei_5SH         PtCl_2(PhCN)_2 + Ph_3 P         84         72           Ei_5SH         PtCl_2(PhCN)_2 + Ph_3 P         84         72           Ei_5SH         PtCl_2(PhCN)_2 + 2Ph_3 P         84         72           Ei_5SH         PtCl_2(PhCN)_2 + 2Ph_3 P         6         72           Ei_5SH         PtCl_2(PhCN)_2 + Ei_3 P         56         24         48           Ei_5SH         PtCl_2(PhCN)_2 + Ei_3 P         56         24         48         72           Ei_5SH         PtCl_2(PhCN)_2 + Ei_3 P         56         24         72         48         72           Ei_5SH         PtCl_2(PhCN)_2 + 2(cHex)_3 P         56         24         54         24	9	Et,SiH	PtCl, + Bu, P	21	72	70	13	ı	17	B	
Et_3SH         PCG_2(PhCN)_2 + Ph_3P         28         48           Et_3SH         PCG_2(PhCN)_2 + Ph_3P         28         48           Et_3SH         PCG_2(PhCN)_2 + 2Ph_3P         28         48           Et_3SH         PCG_2(PhCN)_2 + 2Ph_3P         28         48           Et_3SH         PCG_2(PhCN)_2 + 2Ph_3P         28         72           Et_3SH         PCG_2(PhCN)_2 + Et_3P         56         24           Et_3SH         PCG_2(PhCN)_2 + Et_3P         56         24           Et_3SH         PCG_2(PhCN)_2 + Et_3P         56         24           Et_3SH         PCG_2(PhCN)_2 + 2Et_3P         56         24           Et_3SH         PCG_2(PhCN)_2 + 2Et_3P         56         24           Et_3SH         PCG_2(PhCN)_2 + 2Et_3P         6         72           Et_3SH         PCG_2(PCN)_2 + 2Et_3P         540         24           Et_3SH         PCG_2(PCN)_2 + 2(CHex)_3P         52         24           Et_3SH         PCG_2(PCN)_2 + 2(CHex)_3	7	Et, SiH		41	72	61	15	ı	24	B	
Ei_3SH         PCI_2(PhCN)_2 + Ph_3P         84         72           Et_3SH         PCI_2(PhCN)_2 + 2Ph_3P         84         72           Et_3SH         PCI_2(PhCN)_2 + 2Ph_3P         84         72           Et_3SH         PCI_2(PhCN)_2 + 2Ph_3P         6         72           Et_3SH         PCI_2(PhCN)_2 + Et_3P         56         24           Et_3SH         PCI_2(PhCN)_2 + Et_3P         56         24           Et_3SH         PCI_2(PhCN)_2 + Et_3P         56         24           Et_3SH         PCI_2(PhCN)_2 + Et_3P         56         24         72           Et_3SH         PCI_2(PhCN)_2 + Et_3P         6         72         8         72         8         72         8         72         8         1	œ	Et, SiH	$PtCl_2(PhCN)_2 + Ph_3P$	28	48	92	I	I	œ	¥	
$E_{1_3}SH$ $PCG_2(PhCN)_2 + 2Ph_3P$ -         48 $E_{1_3}SH$ $PCG_2(Ph_3P)_2$ -         48 $E_{1_3}SH$ $PCG_2(Ph_3P)_2$ -         48 $E_{1_3}SH$ $PCG_2(PhCN)_2 + Et_3P$ 56         24 $E_{1_3}SH$ $PCG_2(PhCN)_2 + (cHex)_3P$ 540         24 $E_{1_3}SH$ $PCG_2(PhCN)_2 + (cHex)_3P$ 540         24         72 $E_{1_3}SH$ $PCG_2(PhCN)_2 + (cHex)_3P$ 540         24         24         1 $E_{1_3}SH$ $PCG_2(PhCN)_2 + 2(cHex)_3P$ 52         24         24         24 $E_{1_3}SH$ $PCG_2(PhCN)_2 + 2(cHex)_3P$ 29         24         24 $E_{1_3}SH$ $PCG_2(PhCN)_2 + 2(cHex)_3P$ 29         24         24 $PG_3SH$ $PCG_2(PhCN)_2 + 2(cHex)_3P$ 29         24         24 $PG_3SH$ $PCG_3(PhOP)_2 $	6	Et <sub>s</sub> SiH	PtCl <sub>2</sub> (PhCN) <sub>2</sub> + Ph <sub>3</sub> P	84	72	66	ı	I	1	B	
$E_{1_3}SH$ $PCI_2(Ph_3P)_2$ -         48 $E_{1_3}SH$ $PCI_2(PhCN)_2 + Et_3P$ 56         24 $E_{1_3}SH$ $PCI_2(PhCN)_2 + Et_3P$ 56         24 $E_{1_3}SH$ $PCI_2(PhCN)_2 + Et_3P$ 56         24 $E_{1_3}SH$ $PCI_2(PhCN)_2 + Et_3P$ 30         24 $E_{1_3}SH$ $PCI_2(PhCN)_2 + Et_3P$ 6         72 $E_{1_3}SH$ $PCI_2(PhCN)_2 + (cHex)_3P$ 540         24 $E_{1_3}SH$ $PCI_2(PhCN)_2 + (cHex)_3P$ 540         24 $E_{1_3}SH$ $PCI_2(PhCN)_2 + (cHex)_3P$ 52         24 $E_{1_3}SH$ $PCI_2(PhCN)_2 + 2(cHex)_3P$ 29         24 $PL_3$ $PCI_2(PhCN)_2 + 2(cHex)_3P$ 29         24 $PL_3$ $PCI_3$ $PCI_3$ 29         24 $PL_3$ $PCI_3$ $PCI_3$ </td <td>10</td> <td>Et,SiH</td> <td><math>PtCl_2(PhCN)_2 + 2Ph_3P</math></td> <td></td> <td>48</td> <td>I</td> <td>I</td> <td>I</td> <td>ı</td> <td>۲</td> <td></td>	10	Et,SiH	$PtCl_2(PhCN)_2 + 2Ph_3P$		48	I	I	I	ı	۲	
$E_{1_3}SH$ $PtCl_2(PhCN)_2 + Et_3P$ 56         24         1 $E_{1_3}SH$ $PtCl_2(PhCN)_2 + Et_3P$ 56         24         1 $E_{1_3}SH$ $PtCl_2(PhCN)_2 + Et_3P$ 6         72 $E_{1_3}SH$ $PtCl_2(PhCN)_2 + Et_3P$ 6         72 $E_{1_3}SH$ $PtCl_2(PhCN)_2 + (cHex)_3P$ 540         24 $E_{1_3}SH$ $PtCl_2(PhCN)_2 + (cHex)_3P$ 540         24 $E_{1_3}SH$ $PtCl_2(PhCN)_2 + (cHex)_3P$ 52         24 $E_{1_3}SH$ $PtCl_2(PhCN)_2 + 2(cHex)_3P$ 52         24 $E_{1_3}SH$ $PtCl_2(PhCN)_2 + 2(cHex)_3P$ 52         24 $E_{1_3}SH$ $PtCl_2(PhCN)_2 + 2(cHex)_3P$ 29         24 $Pt_3SH$ $PtCl_2(PhCN)_2 + 2(cHex)_3P$ 29         24 $Pt_3SH$ $PtCl_3(BDPP^b$ -         96         96 $Ph_5H$ $PtCl_3$ 95         96         96	11	Et SiH	PtCl <sub>2</sub> (Ph <sub>3</sub> P) <sub>2</sub>	I	48	I	1	ı	I	4	
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Et_3SH         PtCl_2(PhCN)_2 + 2Et_3P         6         72           Et_3SiH         PtCl_2(PhCN)_2 + (cHex)_3P         540         24           Et_3SiH         PtCl_2(PhCN)_2 + (cHex)_3P         540         24           Et_3SiH         PtCl_2(PhCN)_2 + (cHex)_3P         52         24           Et_3SiH         PtCl_2(PhCN)_2 + 2(cHex)_3P         52         24           Et_3SiH         PtCl_2(PhCN)_2 + 2(cHex)_3P         29         24           Et_3SiH         PtCl_2(PhCN)_2 + 2(cHex)_3P         29         24           Et_3SiH         PtCl_2(BDPP)         -         96           Ph_3SiH         PtCl_3         95         96	13	Et, SiH		30	24	100	ł	ł	I	ß	
Et_3SiHPtCl_2(PhCN)_2 + (cHex)_3 P54024Et_3SiHPtCl_2(PhCN)_2 + (cHex)_3 P5224Et_3SiHPtCl_2(PhCN)_2 + 2(cHex)_3 P2924Et_3SiHPtCl_2(BDPP b-96Et_3SiHPtCl_3(BDPP b-96Et_3SiHPtCl_3(SDPP b-96Ph_3SiHPtCl_6 Cl_3(SDPP b-96Ph_3SiHPtCl, 09596	14	Et <sub>s</sub> SiH	+	6	72	66	I	I	7	¥	
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Et <sub>3</sub> SiH PtCl <sub>2</sub> (PhCN) <sub>2</sub> +2(cHex) <sub>3</sub> P 29 24 Et <sub>3</sub> SiH PtCl <sub>2</sub> BDPP <sup>b</sup> – 96 Et <sub>3</sub> SiH PtCl(SnCl <sub>3</sub> )BDPP <sup>b</sup> – 96 Ph <sub>3</sub> SiH PtCl <sub>3</sub> 95 96	16	Et, SiH		52	24	85	9	5	4	B	
Et <sub>i</sub> SiH PtCl <sub>2</sub> BDPP <sup>6</sup> – 96 Et <sub>1</sub> SiH PtCl(SnCl <sub>3</sub> )BDPP <sup>6</sup> – 96 Ph <sub>2</sub> SiH PtCl, 95 96	17	Et SiH	$PtCl_2(PhCN)_2 + 2(cHex)_3P$	29	24	96	Ι	I	4	¥	
Et <sub>3</sub> SiH PtCl(SnCl <sub>3</sub> )BDPP <sup>b</sup> – 96 Ph <sub>3</sub> SiH PtCl, 95 96	18	Et, SiH	PtCl, BDPP <sup>b</sup>	ł	96	I	1	ı	I	¥	
Ph,SiH PrCl, 95 96	19	Et, SiH	PtCl(SnCl <sub>3</sub> )BDPP <sup>b</sup>	I	96	ł	I	ı	ı	۲	
	20	Ph_SiH	PtCl <sub>2</sub>	95	96	66	1 -	I	1	A	

<sup>*a*</sup> Without CHCl<sub>3</sub>. <sup>*b*</sup> BDPP = (-)-(2*S*,4*S*)-2,4-bis(diphenylphosphino)-pentane.

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Hydrosilylation of methyl methacrylate (6) with various platinum catalysts

Table 2

0.6 ml (5.7 mmol) of methyl methacrylate and 1 ml (6.2 mmol) of  $Et_3SiH$  were added to the yellow homogeneous solution.

*Procedure B*: 4.7 mg (0.01 mmol)  $PtCl_2(PhCN)_2$  and 2.6 mg (0.01 mmol)  $Ph_3P$  was dissolved in 2 ml (18.7 mmol) methyl methacrylate under argon in a Schlenk tube. The solution was stirred for 0.5 h and 0.5 ml (3.1 mmol) of  $Et_3SiH$  then added.

The reaction was monitored by GLC. At the end of the reaction the mixture was fractionally distilled to give samples for further characterization by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and mass spectrometry.

#### Characterization of the products

Methyl 2-methyl-3-triethylsilyl-propionate (7). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 0.43 (q, 6H, CH<sub>2</sub>, J = 7 Hz); 0.83 (t, 9H, CH<sub>3</sub>, J = 7 Hz); 1.12 (d, 3H, CH<sub>3</sub>, J = 7 Hz); 2.45 (sx, 1H, CH, J = 7.2 Hz); 3.55 (s, 3H, OCH<sub>3</sub>). <sup>13</sup>C-NMR(CDCl<sub>3</sub>): 6.63 (CH<sub>2</sub>CH<sub>3</sub>); 7.39(CH<sub>2</sub>CH<sub>3</sub>); 16.75(SiCH<sub>2</sub>CH); 20.98 (CH<sub>2</sub>CHCH<sub>3</sub>); 35.37 (CHCH<sub>3</sub>); 51.39 (OCH<sub>3</sub>); 178.01 (COO). MS m/z/rel. intensity: 187/1000; 117/870; 89/400; 61/140; 59/130

*I-Methoxy-2-methyl-1-triethylsiloxy-prop-1-ene* (8). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 0.45 (q, 6H, CH<sub>2</sub>, J = 7.5 Hz); 0.95 (t, 9H, CH<sub>3</sub>, J = 7.5 Hz); 1.55 (s, 6H, CH<sub>3</sub>); 3.5 (s, 3H, OCH<sub>3</sub>). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 5.05 (CH<sub>2</sub>CH<sub>3</sub>); 6.59 (CH<sub>2</sub>CH<sub>3</sub>); 16.17 (=C-CH<sub>3</sub>); 16.84 (=C-CH<sub>3</sub>); 57.04 (OCH<sub>3</sub>); 90,96 ((CH<sub>3</sub>)<sub>2</sub>C=); 150,01 (= C(OCH<sub>3</sub>)(OSiEt<sub>3</sub>)). MS m/z/rel.intensity: 216/170; 117/460; 87/1000; 70/910; 59/450

Methyl 2-methyl-3-triethylsilyl-acrylate (9). MS m/z/rel. intensity: 185/780; 157/1000; 129/250; 59/240.

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