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

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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

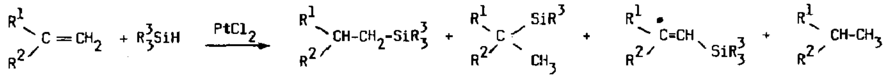
Catalytic hydrosilylation of the C=C bond plays an important role in synthetic organic chemistry. Some of the silicon-containing derivatives are biologically active ("sila-drugs") [1], and others are valuable intermediates in organic syntheses. The significance of the reaction is further enhanced by 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 succesfully 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



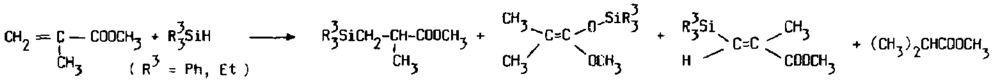
(1a R^1 = Ph, R^2 = H, R^3 = Ph, Et; (2) (3) (4) (5)

1b R^1 = Ph, R^2 = Me)

Scheme 1

Ph_3SiH 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 β-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_3SiH to give **2b**, but with Ph_3SiH 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



(6) (7) (8) (9) (10)

Scheme 2

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 $PtCl_2$ catalyst [a]

Substrate	Silane	Reaction time (h)	Conversion [b] (%)	Product distribution (%) [c]			
				2	3	4	5
1a	Et_3SiH	4	98	76	2	11	11
1a	Ph_3SiH	96	98	37	–	31	32
1b	Et_3SiH	96	4	100	–	–	–
1b	Ph_3SiH	96	–	–	–	–	–

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

$PtCl_2$, Ph_3P and Bu_3P were purchased from Fluka. Et_3P and $(cHex)_3P$ were made by published methods [7,8]. $PtCl_2(PhCN)_2$ was prepared from $PtCl_2$ in hot benzonitrile [9]. $PtCl(SnCl_3)(BDPP)$ (BDPP = (−)-(2*S*,4*S*)-2,4-bis(diphenylphosphino)-pentane) and (−)-(*S*)-BzMePhP were prepared as described previously [10,11]. (−)-(*S*)-1-phenylethylamine was purchased from Fluka (α_D^{20} = −39.2° (neat)). Solvents were dried and distilled under argon. The substrates were freshly distilled before use.

The ^1H NMR spectra were recorded in $CDCl_3$ with TMS as internal standard on a Tesla BS 487C spectrometer at 80 MHz, and ^{13}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) $CHCl_3$ under argon in a Schlenk tube, then

Table 2

Hydrosilylation of methyl methacrylate (**6**) with various platinum catalysts

Run	Silane	Catalyst	Conversion (%)	Reaction time (h)	Product distribution (%)				Proc.
					7	**8**	**9**	**10**	
1	Et_3SiH	$PtCl_2$ [a]	92	24	91	4	2	3	A [a]
2	Et_3SiH	$PtCl_2(PhCN)_2$	89	24	93	–	1	6	A
3	Et_3SiH	$PtCl_2$ + (–)-(*S*)-1-PhEtNH$_2$	97	24	94	–	1	5	A
4	Et_3SiH	$PtCl_2(PhCN)_2$ + (–)-(*S*)-BzMePhP	43	48	90	–	–	10	A
5	Et_3SiH	$PtCl_2(PhCN)_2 + Bu_3P$	25	24	86	–	–	14	A
6	Et_3SiH	$PtCl_2 + Bu_3P$	21	72	70	13	–	17	B
7	Et_3SiH	$PtCl_2(PhCN)_2 + Bu_3P$	41	72	61	15	–	24	B
8	Et_3SiH	$PtCl_2(PhCN)_2 + Ph_3P$	28	48	92	–	–	8	A
9	Et_3SiH	$PtCl_2(PhCN)_2 + Ph_3P$	84	72	99	–	–	1	B
10	Et_3SiH	$PtCl_2(PhCN)_2 + 2Ph_3P$	–	48	–	–	–	–	A
11	Et_3SiH	$PtCl_2(Ph_3P)_2$	–	48	–	–	–	–	A
12	Et_3SiH	$PtCl_2(PhCN)_2 + Et_3P$	56	24	94	–	–	6	A
13	Et_3SiH	$PtCl_2(PhCN)_2 + Et_3P$	30	24	100	–	–	–	B
14	Et_3SiH	$PtCl_2(PhCN)_2 + 2Et_3P$	6	72	93	–	–	7	A
15	Et_3SiH	$PtCl_2(PhCN)_2 + (cHex)_3P$	540	24	91	–	–	9	A
16	Et_3SiH	$PtCl_2(PhCN)_2 + (cHex)_3P$	52	24	85	6	5	4	B
17	Et_3SiH	$PtCl_2(PhCN)_2 + 2(cHex)_3P$	29	24	96	–	–	4	A
18	Et_3SiH	$PtCl_2BDPP$ [b]	–	96	–	–	–	–	A
19	Et_3SiH	$PtCl(SnCl_3)BDPP$ [b]	–	96	–	–	–	–	A
20	Ph_3SiH	$PtCl_2$	95	96	99	–	–	1	A

[a] Without $CHCl_3$. [b] BDPP = (–)-(2*S*,4*S*)-2,4-bis(diphenylphosphino)-pentane.

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 ^1H and ^{13}C NMR spectroscopy and mass spectrometry.

Characterization of the products

Methyl 2-methyl-3-triethylsilyl-propionate (7). ^1H NMR ($CDCl_3$): 0.43 (q, 6H, CH_2, $J = 7$ Hz); 0.83 (t, 9H, CH_3, $J = 7$ Hz); 1.12 (d, 3H, CH_3, $J = 7$ Hz); 2.45 (sx, 1H, CH, $J = 7.2$ Hz); 3.55 (s, 3H, OCH_3). ^{13}C-NMR($CDCl_3$): 6.63 ($\mathit{C}H_2CH_3$); 7.39($CH_2\mathit{C}H_3$); 16.75(Si$\mathit{C}H_2$CH); 20.98 ($CH_2CH\mathit{C}H_3$); 35.37 ($\mathit{C}HCH_3$); 51.39 ($O\mathit{C}H_3$); 178.01 ($\mathit{C}OO$). MS m/z/rel. intensity: 187/1000; 117/870; 89/400; 61/140; 59/130

1-Methoxy-2-methyl-1-triethylsiloxy-prop-1-ene (8). ^1H-NMR ($CDCl_3$): 0.45 (q, 6H, CH_2, $J = 7.5$ Hz); 0.95 (t, 9H, CH_3, $J = 7.5$ Hz); 1.55 (s, 6H, CH_3); 3.5 (s, 3H, OCH_3). ^{13}C-NMR ($CDCl_3$): 5.05 ($\mathit{C}H_2CH_3$); 6.59 ($CH_2\mathit{C}H_3$); 16.17 (=C-$\mathit{C}H_3$); 16.84 (=C-$\mathit{C}H_3$); 57.04 ($O\mathit{C}H_3$); 90,96 ($(CH_3)_2\mathit{C}=$); 150,01 (= $\mathit{C}(OCH_3)(OSiEt_3)$). 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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