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Preliminary Communication

Mesitylene solvated platinum atoms as hydrosilylation catalysts *

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Abstract

Mesitylene solvated Pt atoms, obtained by reaction of Pt vapour and an excess of mesitylene, have been found to promote the catalytic hydrosilylation of dienes and acetylenes in high yields and selectivities.

The hydrosilylation of unsaturated substrates continues to receive a great deal of attention, largely focused on the development of very active and more selective new catalysts [1]. We report here that mesitylene solvated Pt atoms, obtained by reaction of Pt vapour and an excess of mesitylene, catalyze the hydrosilylation of alkynes and dienes affording vinyl and allyl silanes, respectively, with high regioselectivity. Lower amounts of homoallylic silane are also detected in the hydrosilylation of isoprene (Scheme 1).

In a typical experiment platinum vapour (200 mg), obtained by resistive heating of a tungsten filament surface coated with electrodeposited platinum [2], was condensed with mesitylene (70 ml) at liquid-nitrogen temperature in a glass metal atom reactor. The solid matrix obtained was warmed to *ca.* -40°C and the resulting brown solution filtered under dinitrogen in a Schlenk tube where it was handled at -20°C.

3 ml of the Pt/mesitylene solution, containing 0.02 mmol of platinum [3], were added to a mixture of degassed 1-hexyne (2 ml, 17.5 mmol) and triethoxysilane (0.8 ml, 4.3 mmol) at -20°C and the reaction mixture was stirred 1 h at room temperature in a 25 ml Pyrex Carius tube, fitted with a Corning Rotaflo Teflon tap. The mixture is a clear, termally stable solution, which can be kept even for several months without observing metal deposition. The silanes produced were isolated by fractional distillation under reduced pressure and their structure and isomeric composition determined by GC-MS and ^{1}H-NMR spectroscopy. The results obtained in the hydrosilylation of 1-hexyne, 2-hexyne and isoprene, using $HSiEt_3$, $HSi(OEt)_3$ and $HSiMeCl_2$ as hydrosilylation reagents, are summarized in Table 1.

The hydrosilylation of 1-hexyne can be carried out easily with different silanes, with very good conversion and high selectivity. With $HSiMeCl_2$ the reaction is almost complete after 0.5 h. The selectivity in the *β-trans* products is remarkable: two addition products are obtained, with 95% *β-trans*. *β-cis* Derivatives have not been observed and the *α*-addition product has been found in very small quantity (5%).

The hydrosilylation of 2-hexyne with $HSiMeCl_2$ can be conveniently performed at room temperature even though the reaction is slower than the analogous hydrosilylation of 1-hexyne, and the extent of selectivity in *β-trans* addition product is lower.

The mesitylene solvated Pt atoms also exhibit remarkable activity and selectivity in the hydrosilylation of isoprene; the reaction can be performed at temperatures ranging from 25 to 60°C, affording complete conversion to addition products in *ca.* 12–17 h. Among the possible reaction products deriving from a 1,4 (**I–III**) or 1,2 (**IV–VII**) addition (Scheme 2), compound **I** is in greatest amount (from 85% using $HSi(OEt)_3$ to 62% with $HSiMeCl_2$), with smaller amounts of 1,2-addition derivative (**IV**). No other products of 1,2-addition (**V–VII**), 1,4-addition (**II**, **III**) or of dihydrosilylated products have been detected.

A comparison of the results here reported with the literature data relative to the activity of other catalysts leads to the following conclusions:

(1) In the hydrosilylation of 1-hexyne the new catalysts have activity and selectivity as good as the best traditionally prepared Pt catalytic precursors such as the Karstedt catalyst [4] and *trans*-(di-μ-hydrido)bis(tricyclohexylphosphine)bis(silyl)diplatinum complex [5].

(2) In the hydrosilylation of isoprene a remarkable difference from traditional Pt catalytic systems is observed. The reaction takes easily place at room temperature affording, as main product, the 3-methyl-2-butenyl-silane (**IV**); some of the best traditional cata-

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* Dedicated to Professor G.P. Chiusoli on the occasion of his 70th birthday and in recognition of his important contributions to organometallic chemistry and its application to organic synthesis.

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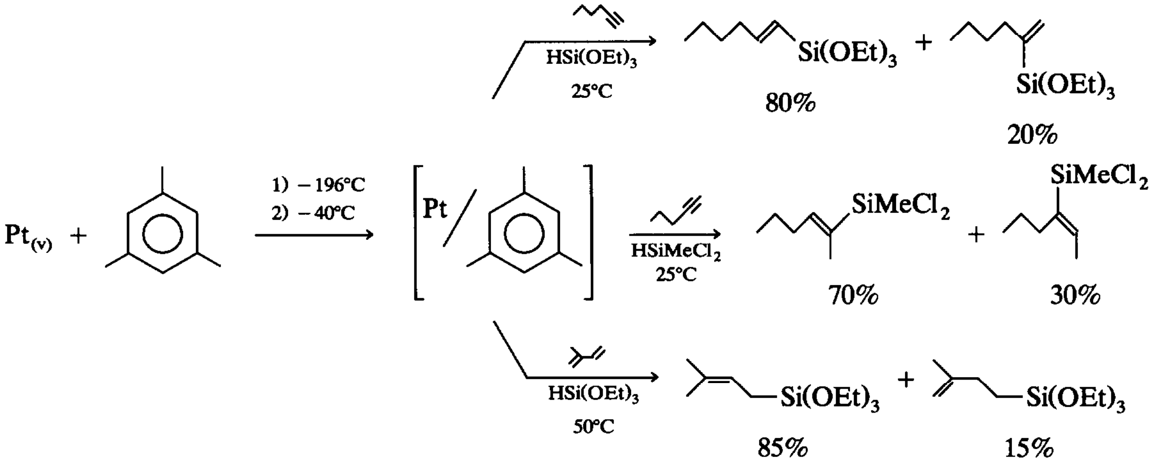
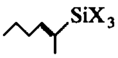
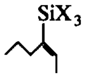
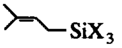
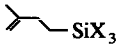
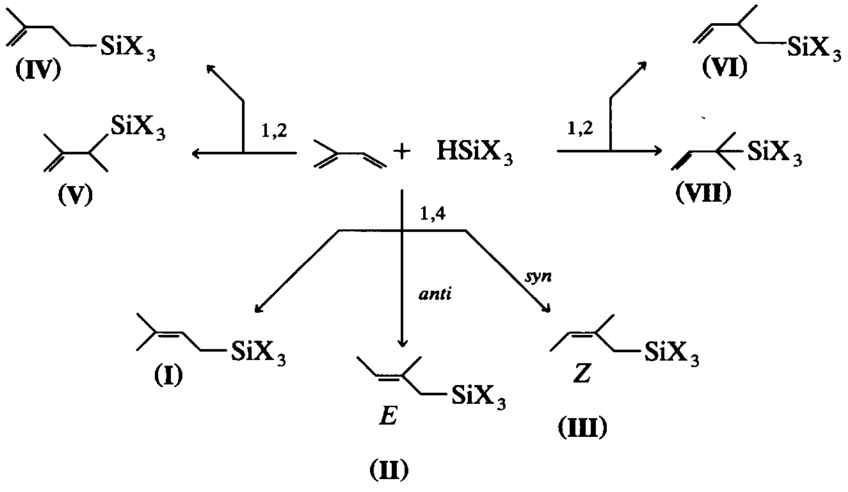


Scheme 1.

TABLE 1. Hydrosilylation of alkynes and isoprene catalyzed by [Pt/mesitylene]

Entry	Substrate	Silane [a]	T (°C)	t (h)	Conv. [b] (%)	Products distribution (%)	
							
1		$HSiEt_3$	80	1	89	86	14
2		$HSi(OEt)_3$	25	1	90	80	20
3		$HSiMeCl_2$	25	0.5	88	95	5
							
4		$HSiMeCl_2$	25	5	90	70	30
							
5		$HSi(OEt)_3$	50	12	100	85	15
6		$HSiMeCl_2$	25	17	100	62	38

[a] Silane 4.3 mmol; unsaturated substrate = 17. 4 mmol; platinum/silane (mg atom/mmol) = $5 \cdot 10^{-3}$. [b] Conversion of silane, as determined by gas chromatography.



Scheme 2.

lysts, such as the Speier catalyst ($H_2PtCl_6/{}^iPrOH$), require higher temperatures and longer reaction times. Contradictory results have been reported concerning the selectivity of this catalyst: it might afford mixtures of (*Z*) and (*E*) 1,4-addition products [6], or as elsewhere reported, only 2-methylbutenylsilane (**II**, **III**) [7]. [$Pt(PPh_3)_4$] affords a 1:1 mixture of the 1,2 addition product **IV** and the 1,4-bis(silyl)-2-methyl-butane as the double silylation product [8].

Preliminary low temperature NMR studies of the Pt/mesitylene solution show no signals in the metal hydride region, making a C–H activation of mesytilene with formation of a Pt–H species unlikely. The time-of-flight mass spectrum shows several signals ranging from 335 to 1140 mass units, some of which can be tentatively assigned to $Pt_2(mes)$, $Pt_2(mes)_3$, $Pt_3(mes)_3$ and $Pt_4(mes)_3$ (mes = mesytilene). Additional characterization studies are presently in progress.

The results here reported are a further example [9] of the usefulness of the metal vapour technique for the preparation of catalytic precursors which give better yields and selectivities than conventional catalytic systems for the same reaction.

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