

Letter

## [2-(3-Trimethoxysilylthio)ethyl]diphenylphosphine – a new agent for transition metal immobilization

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### Abstract

Reaction of vinyl diphenyl phosphine with (3-mercaptopropyl)trimethoxysilane was used to prepare [2-(3-trimethoxysilylpropylthio)ethyl]diphenyl phosphine (I) as a convenient functionalizing agent for inorganic supports. Rhodium complexes immobilized on silica modified with this agent are efficient catalysts for hydrosilylation of unsaturated compounds and thiophene by hydrodesulphurization.

**Keywords:** Alkoxy silylated phosphines; Rhodium; Immobilization

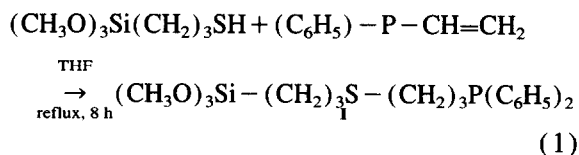
### 1. Introduction

Immobilization increases the efficiency, selectivity and life time of transition metal complexes and becomes thus one of promising branches of modern catalysis [1]. However, the progress in this field is conditioned by suitable supports. Of them, those showing most promise seem to be functionalized inorganic supports [2]. Their synthesis is usually achieved by modification of support surface with alkoxy silyl substituted ligands. These, after reaction with surface hydroxyl groups form the layer of ligands firmly bonded via siloxane bonds [2].

### 2. Results and discussion

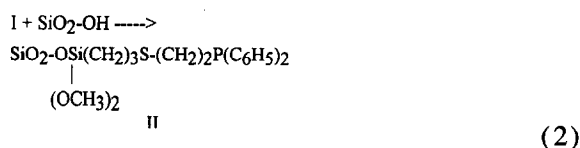
Unlike the so far used synthesis of alkoxy silyl substituted phosphines [3] by the elaborate sub-

stitution reaction of [ $\omega$ -halogenoalkyl]trialkoxysilane with alkali metal diphenyl phosphide, the present procedure is based on the addition of the S–H bond according to Eq. 1. The reaction proceeds smoothly in aprotic solvents without any catalyst, is complete in two hours under reflux, giving the product I in high yields.

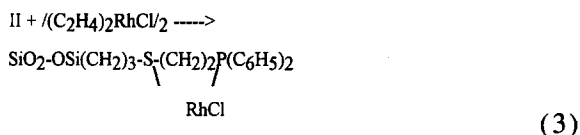


[2-(3-Trimethoxysilylpropylthio)ethyl]diphenyl phosphine (I) so obtained reacts efficiently with surface hydroxyl groups of inorganic supports according to Eq. 2

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and the phosphinated support **II** then coordinates firmly rhodium(I) complexes, as illustrated by Eq. 3.



The above procedure thus turned out to be an easy route to the alkoxy-silyl substituted phosphine with a long and flexible spacer, which otherwise can be obtained only with difficulty. By contrast to other similar phosphines, in the present case there is a thio group in the vicinity of the tertiary phosphorus atom. This circumstance (cf. Eq. 3) may lead to a partial bidentate bonding of the transition metal, resulting in some differences compared to the rhodium(I) complexes immobilized via (6-diphenylphosphino)hexyl)triethoxysilane [3] (Table 1).

Under otherwise identical conditions, the higher rhodium metal loading is obtained in the former case, and due to the stronger bonding to the support, the so immobilized complexes are practically inactive in the hydrogenation of 1-heptene. On the other hand, the significant difference

Table 1  
Preparation of phosphinated supports and immobilized rhodium complexes<sup>a</sup>

Support	SiO <sub>2</sub> , g	Ligand <sup>b</sup> , 1.1 mmol	Toluene, ml	Analysis %			
				C	P	Rh	S
1	10	CP	20	2.94	0.74	0.48	
2	2	CP	10	5.55	0.82	1.27	
3	10	SP	40	2.72	0.54	0.43	0.35
4	2	SP	10	8.82	1.08	1.89	1.35

<sup>a</sup> CP = [6-(triphenylphosphino)hexyl]triethoxysilane<sup>3</sup>, SP = title phosphine.

<sup>b</sup> The given amount of support was treated with 0.25 mmol of Rh<sub>2</sub>Cl<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>4</sub>.

Table 2

Hydrosilylation of 1-heptene (10 mmol) with tris(trimethylsiloxy)silane (10 mmol) catalyzed by immobilized Rh complexes (10<sup>-3</sup> mmol) at 100°C

Catalyst	Conversion <sup>a</sup> %		
	0.5 h	1 h	2 h
1	74	77	81
2	73	83	83
3	76	82	82
4	76	80	86

<sup>a</sup> Determined by GLC.

Table 3

Relative rate constants  $k_{rel}$  of thiophene hydrodesulphurization and thiophene conversions  $X$

Catalyst	Rh, wt. %	$X^a$	$k_{rel}^b$
Shell 324	—	0.65	1
1	0.48	0.45	0.45
2	1.27	0.55	0.76
3	0.43	0.27	1.30
4	1.89	0.76	1.36

Temperature 320°C, total pressure 1.6 MPa, partial pressure of thiophene 0.6 kPa, 0.01 g of catalyst, hydrogen flow rate 1.5 mol/h, and thiophene flow rate 0.06 mmol/h.

<sup>a</sup> Conversion expressed as mole fraction.

<sup>b</sup>  $k_{rel}$  = ratio of the rate constants achieved with immobilized Rh catalyst and industrial Shell 324 [NiMo]Al<sub>2</sub>O<sub>3</sub> catalyst.

between these two complexes have not been observed on their application as hydrosilylation catalysts (Table 2).

Finally, obviously due to the presence of the thio group, the immobilized complexes proved to be efficient catalysts for the industrially important thiophene hydrodesulphurization. Furthermore, the fresh catalyst was even better than the commercial one [4] (Table 3). Summarizing, new immobilized rhodium(I) complexes are efficient catalysts for hydrosilylation of alkenes and hydrodesulphurization of thiophene. The above described synthesis thus does away with one of the factors which limit the synthesis and application of heterogenized complexes.

### 3. Experimental

[2-(3-Trimethoxysilylpropylthio)ethyl]diphenylphosphine was prepared by the reaction of

a stirred solution of 10 mmol of (3-mercaptopropyl)trimethoxysilane in 10 ml of dry tetrahydrofuran under reflux with 10 mmol of diphenylphosphine for 8 h. Then, the solvent was distilled off and the residues were removed by vacuum evaporation at 150°C. The product was mixed with hexane and stirred, and then dried in vacuo, giving 82% yield of the pure phosphine.  $^{31}\text{P-NMR}$  ( $\text{C}_6\text{D}_6$ );  $\delta = -16.2$  ppm. For  $\text{C}_{20}\text{H}_{29}\text{O}_3\text{PSSi}$  calculated (%) C = 58.80, H = 7.15, P = 7.58, S = 7.85; found (%) C = 58.96, H = 7.90, P = 7.90, S = 8.32.

The supports were functionalized in the following way: a known amount of silica was immersed into dry toluene and a toluene solution of the silane was then added with stirring. After shaking, the mixture was refluxed for 1 h. Half the volume of toluene was distilled off, the support was filtered off, washed thrice with toluene and dried under vacuum. The immobilization of rhodium(I) complexes on these supports was made by shaking their toluene solutions with the support, which was then filtered off, washed thrice with toluene and again dried in vacuo. The treatment conditions are presented in Table 1.

Hydrodesulphurization of thiophene was performed using the already reported procedure [5]. The catalyst bed was placed in a flow reactor. The reaction mixture containing thiophene and hydrogen was introduced at laboratory temperature, and then the temperature was increased by 3°C per min up to the reaction temperature 320°C. After establishment of steady conditions, the conversion of thiophene was determined chromatographically. The catalytic activity of the complexes in hydrosilylation [2] and hydrogenation [3] was determined as described earlier.

### Acknowledgements

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